

AN ABSTRACT OF THE THESIS OF

Caroline R. Bruno for the degree of Master of Science in Crop and Soil Science
presented on February 20, 2003.

Title: Paleoclimatic Changes Revealed by Soil Carbonate, and Stable Carbon and
Oxygen Isotopes, Eastern Korinthia, Greece

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Abstract Approved: _____

 Jay S. Noller

Soil carbonate is used to interpret paleoenvironmental conditions in the Eastern Korinthia, Greece, with the use of stable carbon and oxygen isotopes. The Eastern Korinthia consists of a series of marine terraces ranging in age from ~600 to 70.2 ka. The lateral stratigraphic context of the marine terraces allows the author to examine climatic change over geologic time and shows a positive shift in $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ signatures from light ($\delta^{13}\text{C} -10.10\text{\textperthousand}$, $\delta^{18}\text{O} -5.79\text{\textperthousand}$) to more positive values ($\delta^{13}\text{C} -3.10\text{\textperthousand}$, $\delta^{18}\text{O} -3.20\text{\textperthousand}$) from the oldest (VI) to youngest (I) terrace.

Vertical stratigraphy of the Loutro Elenis profile, at the base of the Oneion Range, shows parallel trends toward increasingly more positive $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values from the base ($\delta^{13}\text{C} -8.16\text{\textperthousand}$, $\delta^{18}\text{O} -5.37\text{\textperthousand}$) to the top ($\delta^{13}\text{C} -3.56\text{\textperthousand}$, $\delta^{18}\text{O} -4.19$) of the section. Paleosols within the Loutro Elenis profile and other soil profiles throughout the Korinthia demonstrate a cyclic $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ pattern that is attributed to enrichment of heavy isotopes towards the soil surface as a result of invasion of atmospheric CO₂ and evaporation. The overall shift to more positive $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ in the terrace sequence and the Loutro Elenis profile is attributed to increases in atmospheric CO₂ invasion, mean annual temperatures and evaporation.

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Paleoclimatic Changes Revealed by Soil Carbonate, and Stable Carbon and Oxygen
Isotopes

Eastern Korinthia, Greece

by

Caroline R. Bruno

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented February 20, 2003
Commencement June 2003

Master of Science thesis of Caroline R. Bruno
presented on February 20, 2003.

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ACKNOWLEDGEMENTS

Thanks to my friend Andrea Redman and her family for friendship, kindness, and providing me with a home away from home. Thanks to Jim Essman for his assistance with figures, editing, and putting up with me when I'm a grump.

Thanks to Dr. Jay Noller for introducing me to the field of soil science and the opportunity to work with the Eastern Korinthia Archaeological Survey. I have many fond memories of the Korinthia and will enjoy telling stories for years to come. Also, thank you for picking such a wonderful university for me to attend. I will never forget calling my parents from Korinth and letting them know the change of plans! Jay, I appreciate your guidance, patience and understanding. Thank you.

Thanks to my supportive family, especially my parents, Lois and Pat Bruno. Thank you for your words of encouragement, advice and love. All of these things have made me the person I am today.

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Paleoclimatic Changes Revealed by Soil Carbonate, and Stable Carbon and Oxygen Isotopes, Eastern Korinthia, Greece

1.0 Introduction

Studies of stable isotope stratigraphy led to significant advances in our understanding of paleoenvironmental change throughout the Quaternary (Wright, 2000). In terrestrial settings, such an approach has yielded important records from carbonate accumulations in soil (Cerling 1984; Amundson et al. 1989; Cerling and Quade 1993). Carbon and oxygen isotopes, in particular, reveal much about the bioclimate during soil development (Cerling et al., 1977; Cerling, 1984; Amundson et al., 1989; Cerling and Quade, 1993; Levin, 2002). Carbon isotopic ratio ($\delta^{13}\text{C}$) in soil is strongly influenced by the composition of soil CO_2 and the photosynthetic pathway utilized by plants, typically described as either C_3 or C_4 paths (Cerling, 1984; Ehleringer, 1989; Cerling et al., 1991). The proportion of C_3 and C_4 vegetation in any area is a function of climate, with temperate biomes supporting C_3 plants and arid regions populated by C_4 plants (Cerling, 1984; Ehleringer, 1989; Cerling and Quade, 1993). The oxygen isotope ratio ($\delta^{18}\text{O}$) of soil reflects meteoric water, soil water chemistry, evaporation and temperature (Cerling, 1984; Ehleringer, 1989; Amundson, 1989). In semi-arid to arid regions, analyses of carbon and oxygen stable isotopes in carbonate, a recalcitrant carbon-bearing mineral phase, has led to important interpretations of climatic conditions during soil formation (Cerling, 1984; Levin, 2002). The isotopic composition of pedogenic carbonate is resistant to alteration and has strong potential for closed-system behavior (Cerling, 1984).

This project investigates the origin and paleoenvironment of the formation of pedogenic carbonate in central Greece using oxygen and carbon stable isotopes. Previous studies, such as Griffiths et al. (2002), use stable isotopes of calcareous sediments to determine hydrological changes over the past 126 ka in Central Greece and show that the region has experienced a long-term downward trend in moisture availability beginning ~ 126 ka with several periods of climatic oscillations. This study focuses on the climatic conditions in the Eastern Korinthia from ~600 to 70.2 ka.

1.1 Study Location

The Isthmia region of the Eastern Korinthia is underlain by a series of uplifted marine terraces ranging in age from ~600 to 70.2 ka (Vita-Finzi and King, 1985; Dia et al., 1997). Ages of the marine terraces are used in combination with soil carbonate and the stable isotopes of carbon and oxygen to reveal changes in paleoclimate with time. Central Greece is an ideal location to study soil inorganic carbon (SIC) because the State Factors (Jenny, 1941) are well constrained. Calcic soils developed in calcareous deposits are widespread in Greece, as in much of the Mediterranean region (Pope and van Andel, 1984; van Andel, 1998; Soil Survey, 2000) (Fig. 1). Hence, results of this study should encourage further efforts to use calcic soils as paleoenvironmental proxies in the region.

1.2 Bioclimate

As with the rest of the globe, bioclimatic change in Greece has been significant over the past 500 ka (Adams and Faure, 1998; Archibald, 1999;

Wool
Diamond
25% Cotton Fiber



Figure 1: Map of the Eastern Mediterranean. Arrow indicates location of field area.

Griffiths et al., 2002). Central Greece experienced an overall downward trend in moisture availability, with oscillations in climatic conditions, as documented by Griffiths et al. (2002) beginning ~126 ka. As the shift to a more arid environment commenced at the end of the Pleistocene, vegetation adapted to changing conditions or, as pollen records show, many species of plants went extinct (Archibald, 1999). Plant species that remained had sclerophyllous physiologies well adapted to insufficient water supply during hot, dry summers (Archibald, 1999). The recent transition from full glacial to modern interglacial conditions should be illustrative of the range in past bioclimatic changes that oscillated across southern Europe for the past 500 ka. During the last glacial maximum, ca. 18,000 years ago, the Eastern Korinthia, along with most of southern Europe, was a temperate, short grass montane steppe (Adams and Faure, 1998). Transition from the montane steppe to a forested environment developed during the waning of the glacial 8,000 years ago to a cool, temperate, mixed conifer-broadleafed forest (Adams and Faure, 1998).

Soils of the Eastern Korinthia are currently under xeric moisture and mesic temperature regimes (J. Noller, unpublished data) like much of the Mediterranean. This climate promotes plant communities with dominantly C₃ physiology. Mean annual air temperature in the Eastern Korinthia is 18°C with a high of 45°C in August and a low of -2°C in February. Mean annual precipitation is 48 cm (J. Noller, unpublished data). Presently, much of the Mediterranean, including the Eastern Korinthia, is vegetated by a fragmented or open forests containing a

mixture of evergreen sclerophyllous C₃ shrubs such as *Cerastes* spp. and *Ceanothus* spp., and deciduous shrubs such as *Quercus coccifer*, *Olea* spp. and *Prunus spinosa* (Atalay, 1997; Adams and Faure, 1998; Archibald, 1999; Griffiths et al., 2002). The sclerophyllous shrubs range in height from 1- 3 m and have adaptations for high light intensity, and nitrogen or water deficiency (Archibald, 1999). Common herbaceous species include *Potentilla* spp., *Thymus* spp. and *Mentha* spp. that occupy rocky areas in central Greece (Griffiths et al., 2002).

1.3 Relief, Parent Material and Time

The Eastern Korinthia lies at the eastern end of the Korinth Basin, a fault-bounded graben created by extensional tectonics along E-W to NW-trending faults (Vita-Finzi and King, 1985; Keraudren and Sorel, 1988; Noller et al., 1997). Crustal extension is due to subduction of the African plate beneath Europe along the Hellenic trench and likely initiated in the Late Miocene or early Pliocene (Vita-Finzi and King, 1985; Dia et al., 1997). Tectonics imparted on the landscape the E-W trending Oneion Range, fronted by a series of back-tilted marine terraces and alluvial fans, in which uplift rates and ages of the landforms in question are well constrained compared to other regions of the eastern Mediterranean.

The stratigraphic contexts of soils in the Eastern Korinthia, Greece, provide an ideal setting to study the systematics of carbon and oxygen stable isotopes as proxy records of paleoenvironmental conditions over an extended period of geologic time (from ~600 ka through the present) for open and closed systems (Pirazzoli et al., 1994; Dia et al., 1997). Normal faulting and extension in central

Greece has resulted in major uplift in the Saronic and the Aegean seas resulting in shoreline regression and formation of marine terraces (Vita-Finzi and King, 1985; Dia et al., 1997). The marine terraces are capped by alluvial fan sediments shed from the limestone bedrock of the Oneion Range. Soils have developed in the alluvial parent material on the marine terraces.

Six marine terraces are documented and dated in the Isthmus field area (Fig. 2) (Vita-Finzi & King, 1985; Collier, 1990; Collier et al., 1992; Dia et al., 1997). Radiocarbon dating of mollusks in deposits of the youngest marine terrace yielded late Pleistocene ages (Vita-Finzi & King, 1985). U-series dating of coralline algae yields the most complete numerical age estimates of the terrace sequence (Dia et al., 1997). Correlation of the terraces to marine $\delta^{18}\text{O}$ stages ages (Keraudren & Sorel, 1987; Armijo et al., 1996) further corroborates these age assignments. On the basis of these multiple, independent studies the terraces which are 7 to 65 m above mean sea level range in age from 70.2 -385.5 ka (Table 1). This discussion will focus on terraces 40 - >100 m above present sea level, representing ages <200 to ~600 ka. These ages indicate that young terraces in the Isthmia region have a minimum uplift of 0.2-0.3 mm/yr, whereas terraces greater than 100 ka have uplift rates from 6.5 – 7.0 mm/yr.

The foot of the Oneion range is characterized by a colluvial-alluvial fan apron deposited over the past 400-700 ka. These deposits are shed off the 200-700 m near-vertical escarpment in the footwall of the Korinth fault and are incised seasonally (Fig. 3). Colluvial-alluvial deposits at the base of the Oneion range,

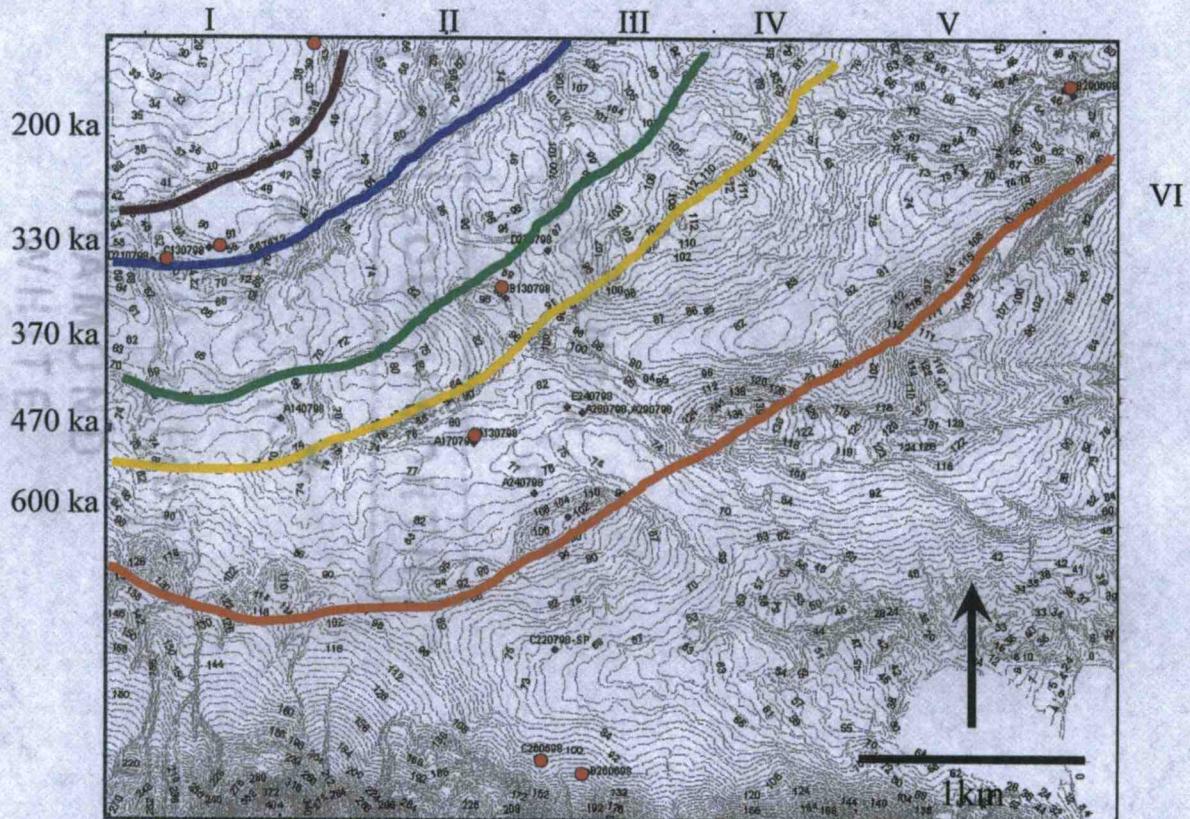


Figure 2: Terraces I-VI, associated ages, and sample locations. Lines represent backscarsps, for example, the purple line represents the backscarp of Terrace I. Red dots are sample locations. Contours are meters ALS.

Location	Profile	Elevation (m)	Age (ka)	Sample	$\delta^{18}\text{O}_{\text{PC}}$	$\delta^{13}\text{C}_{\text{PC}}$	Depth (cm)	Horizon	n	std ^{18}O	std ^{13}C
<i>Terrace I</i>	A090798-2	40	<200	210	-3.69	-3.57	1		2	0.5589	0.1164
				211	-3.10	-3.20	30				
<i>Terrace II</i>	C130798	56	200	226	-3.87	-5.93	5	A			
				227	-4.15	-6.73	33	A ₂			
				228	-3.72	-5.73	57	Bw			
				229	-4.26	-6.68	96	Bkj			
				230	-4.47	-7.24		Bkj ₂			
				231	-4.23	-8.67	178	Bkj ₃			
			D210798	243	-4.59	-5.22	32	Ap			
				244	-5.05	-6.17	54	A			
				245	-4.68	-6.44	84	Bk	2	0.1099	0.1746
				246	-4.64	-6.82	114	Bk _{2a}			
				263			144	Bk _{2b}			
				264			174	Bk ₃			
<i>Terrace IV</i>	B130798	98	370	220	-4.41	-7.83	32	Ap			
				221	-4.30	-8.00	62	Bk			
				222	-4.79	-7.60	92	Bk			
				223			131	K3			
				224			185	Btkj			

Table 1: Data corresponding to soil profiles on Terraces I, III, IV, V and VI. All samples listed are <2mm fraction of the soil matrix. $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values vs. PDB.

Location	Profile	Elevation (m)	Age	Sample	$\delta^{18}\text{O}_{\text{PC}}$	$\delta^{13}\text{C}_{\text{PC}}$	Depth (cm)	Horizon	n	std ^{18}O	std ^{13}C
<i>Terrace V</i>	A170798	78	470	236	-3.24	-7.39	42	Ap/B			
				237	-3.92	-8.06	80	Btkj			
				238	-3.63	-11.00	120	Btkj ₂			
				239	-3.80	-7.90	157	Btk	2	0.4495	0.0822
				240			197	Btb			
				241			228	Cox			
				242			242	Btgb			
	A230698	50	470	73	-4.25	-7.25	26	Ap ₂			
				74	-3.99	-7.51	56	Ap ₃			
				75	-4.43	-8.03	74	Bkj			
				76	-4.04	-8.69	94	Bkj ₂			
				77			117	2Bt			
				78			141	2Bt ₂			
				79			200	2Btkj ₃			
<i>Terrace VI</i>	B260698	108	<600	114	-5.63	-3.71	22	Bt	3	1.0016	0.2942
				116	-5.14	-6.85	98	Bt ₂			
				117	-5.85	-9.03	182	Ck			
				118	-5.32	-7.32	216+	2Btk			
				119	-4.95	-9.19	14	Ap	2	0.0684	0.5507
	C260698	100	<600	120	-4.47	-5.36	35	2A	2	0.0885	0.4437
				121	-4.66	-8.97	67	2Btkj			
				122	-4.49	-9.60	114	2Btkj ₂			
				123	-5.79	-10.10	178	2Btkj ₃			
				124			216	2Btkj ₄			
				125			238+	2Btkj ₅			

Table 1: continued. $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values vs. PDB.

*mean $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values are reported for those samples analyzed multiple times.

* (n) = the number of samples analyzed

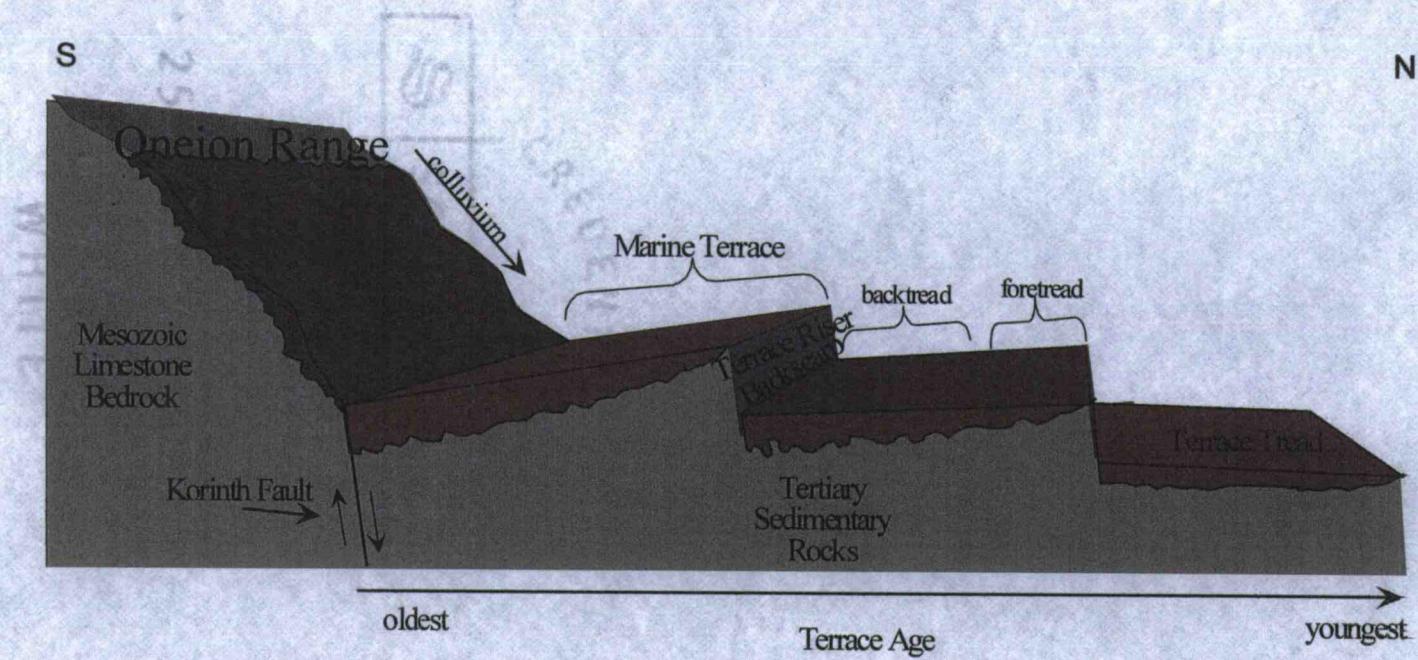


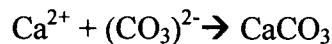
Figure 3: A schematic drawing of several marine terraces, key geomorphic positions, and the Oneion Range in the Eastern Korinthia. Terrace age decreases moving south to north.

such as the Loutro Elenis profile, exhibit several episodes of soil formation and burial.

2.0 Pedogenic Carbonate

2.1 Formation Processes

Inorganic processes have long been recognized to be solely responsible for the formation of pedogenic carbonate (Jenny, 1941; Birkeland, 1999). Earlier studies suggest soil carbonate precipitates from soil water during periods of low biological activity (Schlesinger et al., 1989). In the classic sense, carbonate precipitation in soil involves the following series of chemical reactions:



These reactions favor precipitation of carbonate under the conditions of 1) warm temperatures, 2) alkaline pH, 3) increased agitation, and 4) decreased soil moisture, e.g. evaporation (Prothero and Schwab, 1996; Newman et al., 1997; Lal and Kimble, 1999). Formation of pedogenic carbonate, in some cases, is limited by the availability of Ca^{2+} , which can be derived from mineral weathering, eolian, and/or pluvial sources (Birkeland, 1999). Dissolution or loss of soil carbonate occurs when soil moisture and soil CO_2 (g) concentrations increase or when pH decreases (Lal and Kimble, 1999). Freezing of soil solution may be an alternate means of soil

carbonate formation based on high atmospheric component of soil CO₂ in soil carbonates formed in the Holocene (Cerling, 1984).

The specific conditions, noted above, which promote carbonate precipitation, occur during interglacial periods (Reheis, 1987). Reheis (1987) documents carbonate accumulation during dry interglacial periods and illuvial clay accumulation on nodules during glacials or wet periods in deposits of Rock Creek and lower Clark's Fork, MT. Carbonate nodules develop a soil carbonate (white) and clay (red) stratigraphy which records a series of climatic oscillations between interglacial and glacial periods (Reheis, 1987).

Mounting evidence shows that microbial processes relating to the formation of soil carbonate are overlooked (Monger et al., 1991; Newman et al., 1997; Stocks-Fisher et al., 1999). Microorganisms are acknowledged for their role in carbonate formation in marine environments (Castanier et al., 1999), but their role is rarely addressed or accepted in CaCO₃ production in relation to terrestrial environments (Schlesinger et al., 1989).

In semi-arid and arid environments soil microbial activity results in calcite precipitation (Philips et al., 1987; Monger et al., 1991; Newman et al., 1997; Stocks-Fisher et al., 1999). Three lines of evidence indicate the precipitation of pedogenic carbonate by microbial activity: 1) fossilized microorganisms and their precipitates are revealed by scanning electron microscope and thin section analysis (Philips et al., 1987; Monger et al., 1991; Newman et al., 1997); 2) bacteria have the ability to precipitate calcite in culture studies (Monger et al., 1991; Stocks-

Fisher et al., 1999); and 3) soils inoculated with microorganisms precipitate calcium carbonate, whereas sterile soils do not (Monger et al. 1991).

Microbial carbonate in soil has varied origins and forms. Calcified filaments, resembling those of fungal hyphae, are present in calcic and petrocalcic horizons (Monger et al., 1991; Newman et al., 1997). Filaments have a tubular structure, suggesting that precipitation occurs on the exterior surfaces of the hyphae and organic decomposition of the core hyphae follows (Monger et al., 1991). Circle-shaped calcite forms in laminar zones of Bk horizons in New Mexico, USA, are identified as mycorrhizal precipitates (Monger et al., 1991). These laminar zones are similar to stromatolites and often form above the petrocalcic horizon or as carbonate crusts on parent material and may reflect biomineralization (Pentecost and Riding, 1986; Reams, 1990; Monger et al., 1991). This contrasts with the long-held view that these layers are the result of lateral flow of carbonate-precipitating soil water (Birkland, 1999).

Microbial precipitation of carbonate is estimated to occur at significantly faster rates than inorganic precipitation modes (Table 2) (Harden et al., 1985; Scott et al., 1991; Castanier et al., 1999). Microorganisms have the ability to precipitate 68% more CaCO_3 than inorganically precipitated CaCO_3 in water when allotted equal amounts of Ca (Stocks-Fischer et al., 1999). The amount of biologically precipitated calcium carbonate in marine settings is greater than originally assumed, and presages additional findings supporting the role of microorganisms in

Environmental Setting	Rate of CaCO₃ formation (g/m²/yr)	Accumulation thickness per year
<i>Ocean</i> (Castanier et al. 1999)	10	4μ
<i>Reef</i> (Castanier et al. 1999)	500	.2mm
<i>Paralic^a</i> (Castanier et al. 1999)	5000	2mm
Terrestrial		
<i>La Sal Mountains, UT</i> (Harden et al., 1985)	1.4×10^{-7} ---- 2.6×10^{-7}	-----
<i>Lake Bonneville</i> (Scotts et al., 1991)	5.0×10^{-7}	-----

Table 1: Rate of CaCO₃ precipitationin various aquatic and terrestrial environments.

a: brackish water; lagoonal

precipitating soil carbonate (Schlesinger et al., 1989; Stocks-Fischer et al., 1999; Sumner, 2001).

2.2 Stable Isotopes and Pedogenic Carbonate

Analyses of mineralized carbon and oxygen by stable isotope chemistry allow for paleoenvironmental interpretations as well as quantitative estimates of the carbon (as a carbonate mineral phase) stored in soils (Cerling and Quade, 1993; Nordt et al., 1997; Lal and Kimble, 1999). Carbonate minerals, principally calcite (CaCO_3) and dolomite ($\text{Ca}_x\text{Mg}_y\text{CO}_3$), have traditionally been considered the primary mineralized, inorganic host of carbon in soils (Jenny, 1941; Gile et al., 1969). Although likely derived by some measure from organic processes, this discussion of carbonate in soil will treat it all in its present inorganic form. Soil inorganic carbon (SIC) resides in pools of lithogenic or pedogenic origin (Rabenhorst et al., 1984; Eswaran et al., 1995). Lithogenic inorganic carbon (LIC) consists of carbonate formed by geological processes, such as the deposition of calcareous mud in a lake environment or reef formation by coralline algae (Mermut et al., 2000; Sumner, 2001; Griffiths et al., 2002). LIC originating in marine limestone is enriched in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($\delta^{13}\text{C} = -1.46$ to -1.29 , $\delta^{18}\text{O} = -2.42\text{\textperthousand}$ to $-1.62\text{\textperthousand}$), whereas that in freshwater limestone is less enriched in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($\delta^{13}\text{C} = -9.26\text{\textperthousand}$ to $-8.32\text{\textperthousand}$, $\delta^{18}\text{O} = -6.55\text{\textperthousand}$ to $-5.07\text{\textperthousand}$) (Salamons and Mook, 1976; Rabenhorst et al., 1984; Talbot, 1990). Isotopic signatures of pedogenic inorganic carbon (PIC) are influenced by soil water, groundwater, and rainfall chemistry, evaporation, transpiration, leaching, temperature, microbial activity, parent

material, composition of carbon dioxide, and diagenetic effects (Rabenhorst, 1984; Cerling, 1984; West et al., 1988; Amundson, 1989; Cerling and Quade, 1993). These factors must be considered when interpreting trends in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the pedogenic environment.

Microorganisms influence stable isotope signatures of calcium carbonate precipitated in marine environments (Newman et al., 1997; Sumner, 2001), and they might well do the same in the subaerial environment of soil. Lighter mass isotopes, such as ^{12}C , tend to react faster than heavier mass isotopes, such as ^{13}C , in biological process (Amundson, 1989; Kendall and Caldwell, 1998). Therefore, microorganisms preferentially remove ^{12}C from their surrounding environments and become enriched in ^{12}C relative to the heavier ^{13}C (Kendall and Caldwell, 1998; Sumner, 2001). In turn, the area surrounding the microorganism becomes enriched in ^{13}C compared to ^{12}C (Sumner, 2001). An example of preferential removal of ^{12}C occurs in some types of microbial mats or stromatilites found in marine environments. Sumner (2001) states that carbonate minerals which precipitate in a microbial mat record a heavier $\delta^{13}\text{C}$ signature compared to carbonate minerals which precipitate from surrounding waters. It is expected that microorganisms influence isotopic signatures of carbonate in the terrestrial environment of soils.

3.0 Materials and Methods

Sample locations were selected based on the accessibility of road cuts, building foundations and cut banks. Soil profiles were selected, sampled and

described according to the Soil Survey Manual (Soil Survey Staff, 1993). Stages of soil carbonate development follow those of Machette (!985). Samples were analyzed for bulk density, total C,N, S and P, total carbonate, and C and O isotopes. Samples were collected in 1998 by Amy Steffen, Tom Tartaron, and Jay Noller, and in 2000 and 2001 by Caroline Bruno and members of the Eastern Korinthia Aracheaological Survey (EKAS).

Bulk density was determined by the paraffin clod method (Blake and Hartge, 1986). Peds were weighed, dipped in paraffin and reweighed. In some instances, peds were not completely covered with paraffin and a hot spatula was dipped in paraffin and then hot wax was delicately placed on peds for full coverage. Peds were weighed while suspended in air and while immersed in water to determine bulk density. A quartz crystal was used for calibration.

Carbon, sulfur, and nitrogen were analyzed by the Central Analytical Lab (CAL), Oregon State University, with a Leco CNS-2000 Macro Analyzer. Total phosphorous was analyzed with an Alpkem RFA 300, also at CAL.

Total carbonate was determined by a procedure described by Ashworth (1997). An internal standard, pure CaCO₃, and a blank functioned as controls with each analysis run. The blank determined mass loss by evaporation. Total carbonate percentage is determined by the loss in weight of the sample, as a result of CO₂(g) evolution. The amount of CO₂ lost is converted to CaCO₃ based on formula weights assuming pure calcite in the soil mineral phase. Randomly selected samples were weighed on a timed schedule as dolomite requires 10-20

minutes longer for complete dissolution compared with calcite (Singer and Janitzky, 1986). All samples yielded quick, complete dissolution indicating the presence of dolomite is a negligible phase in soils of this study. This procedure is a modified form of those performed by Raad (1978) and Goh et al. (1993).

Pedogenic carbon ($^{13}\text{C}_{\text{PC}}$) and oxygen ($^{18}\text{O}_{\text{PC}}$) stable isotopic analyses were performed by Bill Rugh in the laboratory of Professor Alan Mix of Oregon State University. Soil samples for isotope analyses were selected based on terrace position, completely sampled profiles, and sample size. Soil matrix samples for stable isotope analyses were crushed and passed through 2 mm sieves. Soil horizons with carbonate development such as Btk or Bkm horizons contained small nodules of soil carbonate and carbonate powder that passed through the 2 mm sieves. Samples from such horizons represent concentrated forms of soil carbonate. Visible organic material was removed from samples. Marine and freshwater limestones were powdered for analyses using a grinding tool. Analyses were completed on a Finnegan/Mat-251 mass spectrometer and are reported in standard parts per million notation relative to Pee Dee Belemnite (PDB) (Kendall and Caldwell, 1998).

Two samples from the upper 30 cm of the soil were analyzed from Terrace I, one profile from terrace IV, and two profiles were analyzed from Terraces II, V and VI. Samples of pedogenic carbonate from bulk soil (n=82) and parent material (n=10) were analyzed from 17 soil profiles (Tables 1, 3, 4, 5).

Paleosols	Sample	$\delta^{18}\text{O}_{\text{PC}}$	$\delta^{13}\text{C}_{\text{PC}}$	Total CO ₃	Munsell	Depth (cm)	Horizon	Stage	Age (ka)
modern soil	148	-4.19	-3.56	6%	10YR 2/2	30	A		
	149	-4.77	-6.33	12%	10YR 3/6	40	A ₂		
	150	-4.18	-4.40	16%	7.5YR3/4	66	Bw		5
	152	-4.21	-2.48		7.5YR3/4	94	Btkj	I	
1	155	-5.55	-10.08	14%	7.5YR 5/6	112	2Btk	I	
	156	-5.26	-6.97	17%	7.5YR 4/6	190	2Btkj	I ⁺	10-15
2	162	-5.56	-9.10	16%	7.5 YR 4/6	344	3Btk ₁	I	
	163	-5.67	-9.23	24%		374	3Btk ₂	II	40-55
3	166	-5.20	-7.16	22%	5YR 7/4	385	4Btkb ₁	III	
	168	-5.60	-7.57	33%		445	4Btkb ₂	III	140-205
4	169	-6.55	-8.06	14%	5 YR 5/5	543	5Btkjb ₁	I	
	170	-6.70	-9.48			571	5Btkjb ₂	I	
	171	-6.87	-11.3	14%		599	5Btkjb ₃	I	145-215
	172	-5.37	-8.16	9%		627	5Btkjb ₄	I	

Table 3: The Loutro Elenis Profile: isotopic composition, total carbonate, bulk density, soil morphology, carbonate accumulation stage and approximate age based on ages developed by Machette (1985). $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ vs. PDB

Profile	sample	$\delta^{18}\text{O}_{\text{PC}}$	$\delta^{13}\text{C}_{\text{PC}}$	depth (cm)	n	std ^{18}O	std ^{13}C
<i>A240698</i>	81	-3.39	-5.78	13			
	82	-3.28	-5.71	29	3	0.8631	1.2581
	84	-3.54	-5.94	124			
<i>B240698</i>	86	-3.93	-3.89	-			
	87	-2.53	-3.31	50			
	88	-3.11	-4.02	84			
	89	-3.23	-4.26	89			
<i>C240698</i>	94	-3.45	-5.66	28			
	95	-4.03	-6.54	83			
<i>C250698</i>	99	-4.94	-4.05	105			
	100	-5.31	-4.33	137			
	101	-5.48	-4.29	206			
<i>A260698-1</i>	102	-5.37	-3.77	8			
	103	-5.45	-4.43	54			
	104	-5.60	-3.01	56			
<i>A260698-2</i>	107	-5.21	-4.93	24			
	108	-5.37	-5.03	54			
	110	-5.43	-3.94	113			
	112	-5.28	-6.17	-			
	113	-5.24	-4.98	-			
<i>A270698</i>	126	-4.61	-4.04	16			
	127	-5.36	-4.86	22			
	128	-5.22	-5.57	64	3	0.3147	0.2203
<i>B290698-1</i>	142	-5.43	-2.50	18			
	143	-5.74	-1.46	33	3	0.1234	0.2559
<i>A010798</i>	164	-5.22	-3.09	23			
	165	-5.26	-2.97	63			
	174	-5.51	-4.50	85			
	175	-4.76	-6.61	147			
	176	-5.36	-8.21	238			

Table 4: Data corresponding to soil profiles in the Eastern Korinthia. $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ vs. PDB

*mean $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values are reported for those sample analyzed multiple times

*(n)=number of samples analyzed

Parent Material	Sample #	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
Cairn soil			
	bc00ld	-2.89	-2.64
	bc0011	-2.59	-3.10
Marine Limestone			
	2D	-1.66	-1.45
	2D	-1.62	-1.42
		-1.64	-1.44
		0.03	0.03
	2E	-2.24	-1.35
	2E	-2.29	-1.29
		-2.27	-1.32
		0.03	0.05
	RILL	-2.42	-1.50
		-2.11	-1.42
		-2.27	-1.46
		0.22	0.06
			mean
			std
Travertine			
	KFR	-5.21	-8.96
	KFR	-5.33	-9.12
		-5.27	-9.04
		0.08	0.11
	KFRW	-5.07	-8.32
	KFRW	-5.17	-8.38
		-5.12	-8.35
		0.07	0.05
	KFW	-5.73	-9.11
	KFZ	-6.55	-9.20
	KFZ	-6.51	-9.26
		-6.53	-9.23
		0.03	0.04
			mean
			std
Marl			
	Marl	-5.64	-8.87

Table 5: This table shows $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures for potential soil parent material in the Eastern Korinthia. Several of these samples were analyzed multiple times and the average of these numbers were plotted. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ vs PDB.

4.0 Results

4.1 Loutro Elenis Soil Chronosequence

Long-term trends in sedimentation, pedogenesis, and $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ are revealed in a 18-m-deep sequence of soils and colluvial-alluvial deposits at Loutro Elenis (Fig. 4). The Loutro Elenis soil chronosequence, a pre-incisive chronosequence (Birkeland, 1999), formed at the base of the eastern Oneion Range along the Korinth fault. This profile contains records of at least five episodes of soil formation, including four paleosols. Each paleosol is morphologically distinct; all show similar genetic properties of argillic and calcic horizon development. It is likely that the individual paleosols represent periods of landscape stability that are recorded elsewhere in Greece (van Andel, 1998). New paleosols started to form after major erosional events which buried older paleosols. None of the paleosols contain an obvious A horizon, which could be due to loss of organic matter during burial. The upper boundaries (tops) of paleosols tend to be clear and wavy, possibly due to sheet erosion (Table 3). Profiles tend to become increasingly redder with age (Table 3). Horizons are gravelly to cobbly and often include boulders in the base of one or more horizons. Peds are confined by coarse fragments and commonly incorporate gravel.

Most paleosols in the Loutro Elenis profile (with the exception of paleosol 4) show an increase in total carbonate with depth as shown in Table 3. With this increase in total carbonate, bulk density also tends to increase. PIC content increases as the soil matures from zero percent PIC to a Stage IV, fully cemented,

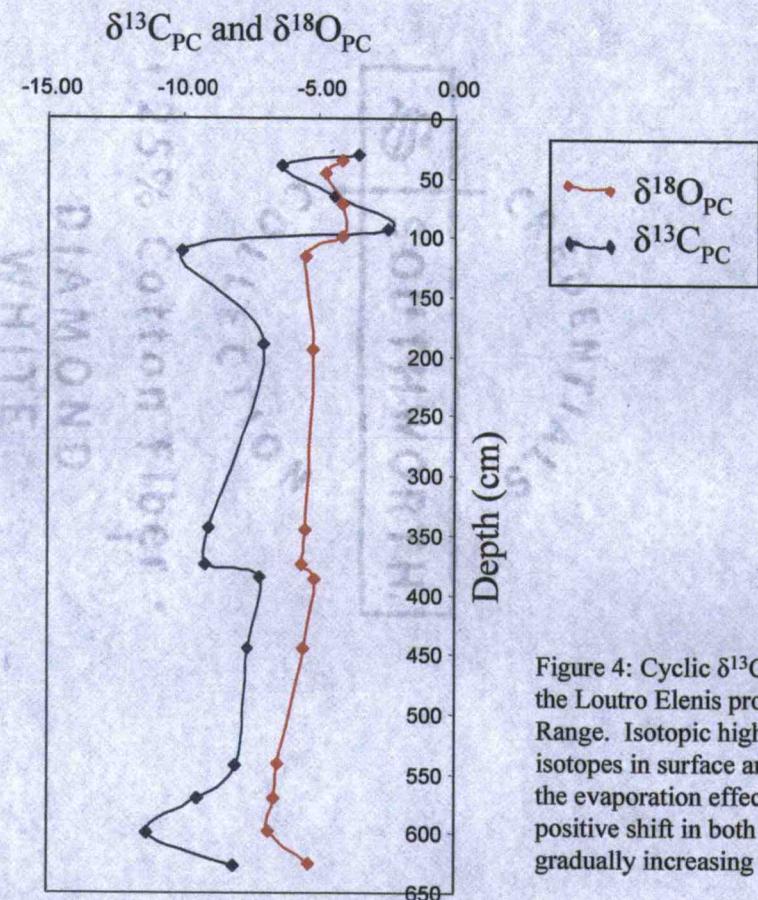


Figure 4: Cyclic $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ trends vs depth in the Loutro Elenis profile at the base of the Oneion Range. Isotopic highs represent enrichment of heavy isotopes in surface and near-surface soils as a result of the evaporation effect. The overall trend shows a positive shift in both $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ indicating a gradually increasing mean annual temperature.

petrocalcic K horizon (van Andel, 1998; Birkeland, 1999). Stages are based on percentages of CaCO_3 in each horizon as well as carbonate morphology. For example, Stage I of carbonate morphology consists of approximately 4% PIC with thin coatings and some filaments. Stage V, however, is a continuous, massive medium that has a laminar to platy structure and contains over 90% CaCO_3 . Paleosols 2, 3, 4 and 5 show advanced stages of calcium carbonate development (Table 3). A positive correlation between carbonate accumulation stage and formation rate has been established (Machette, 1985). On the basis of these morphologies and correlation with carbonate stages in limestone rocks of North America (Machette, 1985; Reheis et al., 1992), the paleosols are each assigned estimated exposure ages (Table 3).

Cyclic stable isotope patterns are observed in the Loutro Elenis profile. Down profile within each paleosol, $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values trend from heavy at the top of the solum to lighter mid-solum and then gradually heavier toward the base of the solum. This pattern clearly repeats itself five times in the Loutro Elenis profile (Fig. 4).

4.2 Marine Terrace Soil Chronosequence

The Isthmian soil chronosequence, a post-incisive chronosequence (Birkeland, 1999), consists of profiles studied on the marine-terrace series (Fig. 2). Surface soils from Terrace I tend to be loamy sands with some sand grains coated with clay. Terrace II exhibits organic rich surface soils with beginning stages (I to II) of subsoil pedogenic carbonate development. Clay accumulations are not

prevalent in Terrace II soils. No samples were collected from Terrace III. Terrace IV soils have deep A horizons. These soils contain significant amounts of carbonate nodules with subsurface soils exhibiting Stage II to III carbonate development. Clay films are present in subsurface soils of terrace IV. Terrace V soils have deeply plowed A horizons. Clay content is notable in subsurface soils on Terrace V. Lower A horizons contain Stage I', while subsurface soils have stage I and III carbonate development. Soils on Terrace VI are developed on alluvial fans and are likely younger than the 600 ka terrace. These soils do not have A horizons. Clay development is notable in the uppermost subsurface soils and stages of carbonate accumulation range from I' to II. Soils developed on Terrace VI have at least two different parent materials. Clay and carbonate accumulation increase from Terrace I to Terrace VI. Overall trends in the Loutro Elenis profile and the terrace sequence are shown in Figures 5 and 6. The mean $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values of each terrace were plotted (Fig. 7).

Soil matrix samples ranging from soft, unconsolidated surface soils to hard sub-angular blocky subsurface horizons were collected and analyzed from Terraces I-VI with the exception of Terrace III (Table 1). These samples represent a series of isotopic signatures from stages in time based on soil formation on individually uplifted marine terraces.

Stable carbon values in the pedogenic carbonate range from -11.30 to

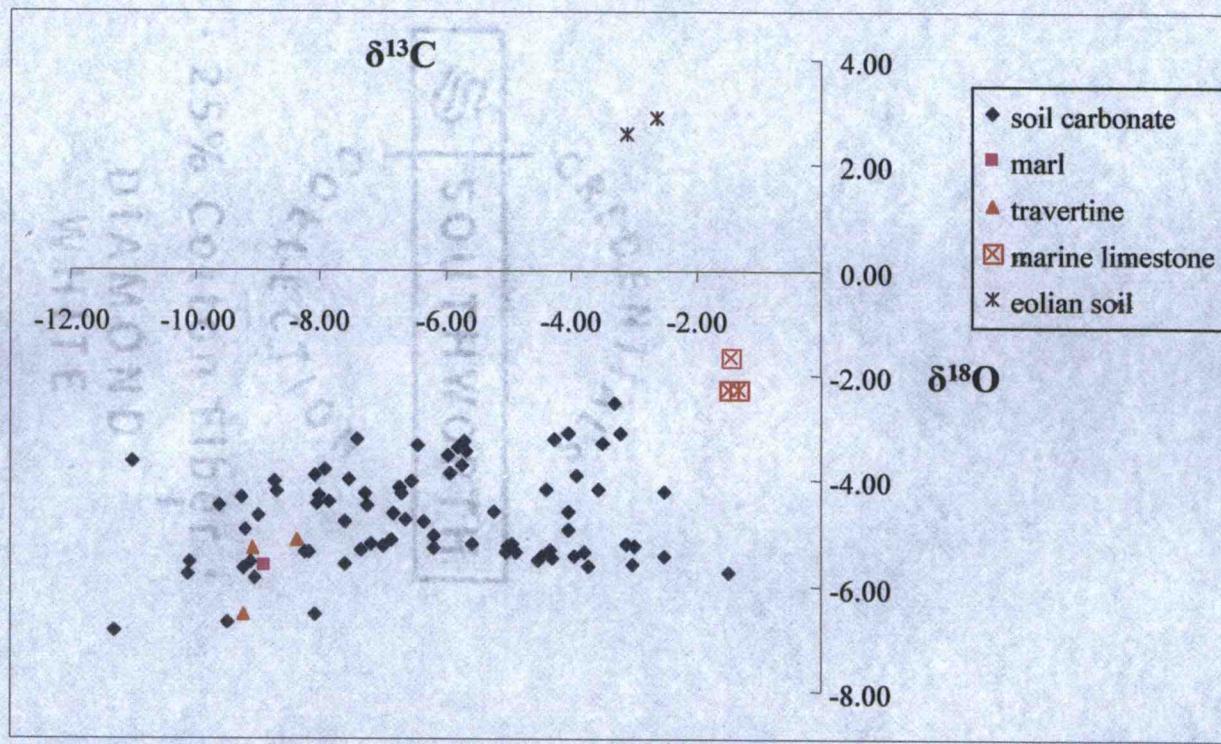


Figure 5: Soil carbonate and potential parent material stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values reported vs. PDB.

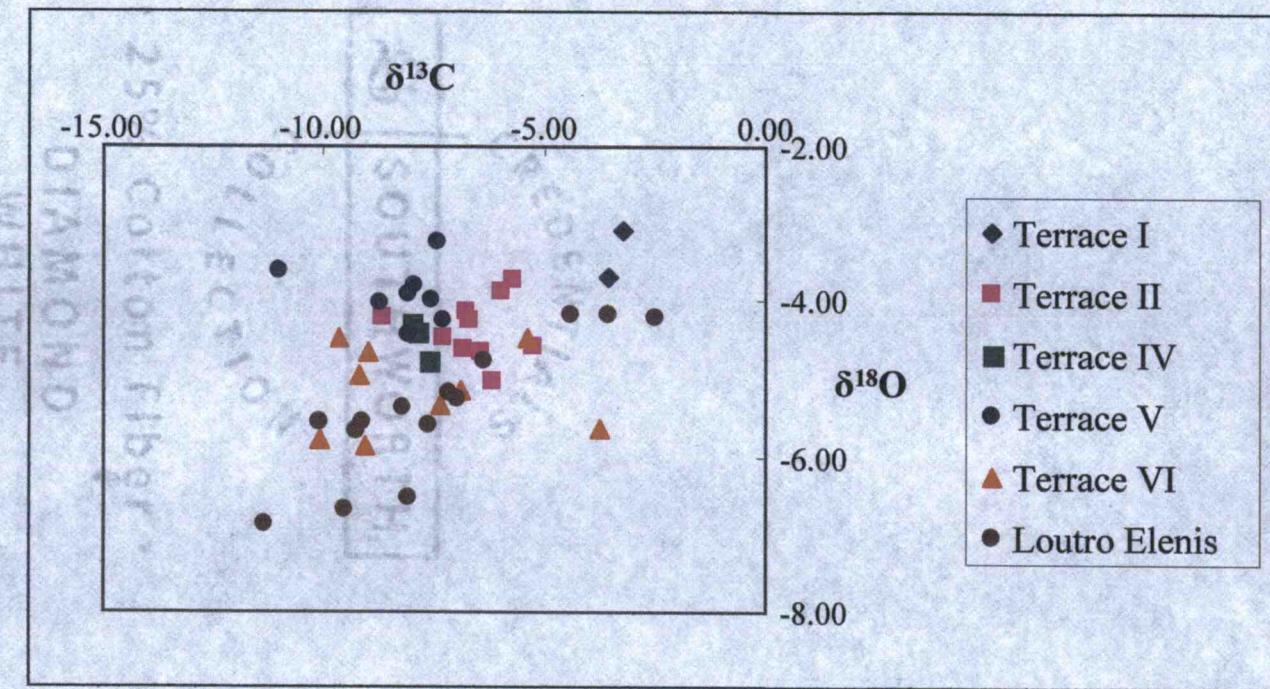


Figure 6: Terraces in the Eastern Korinthia and the Loutro Elenis profile show a positive trend in $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values. $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values reported vs. PDB.

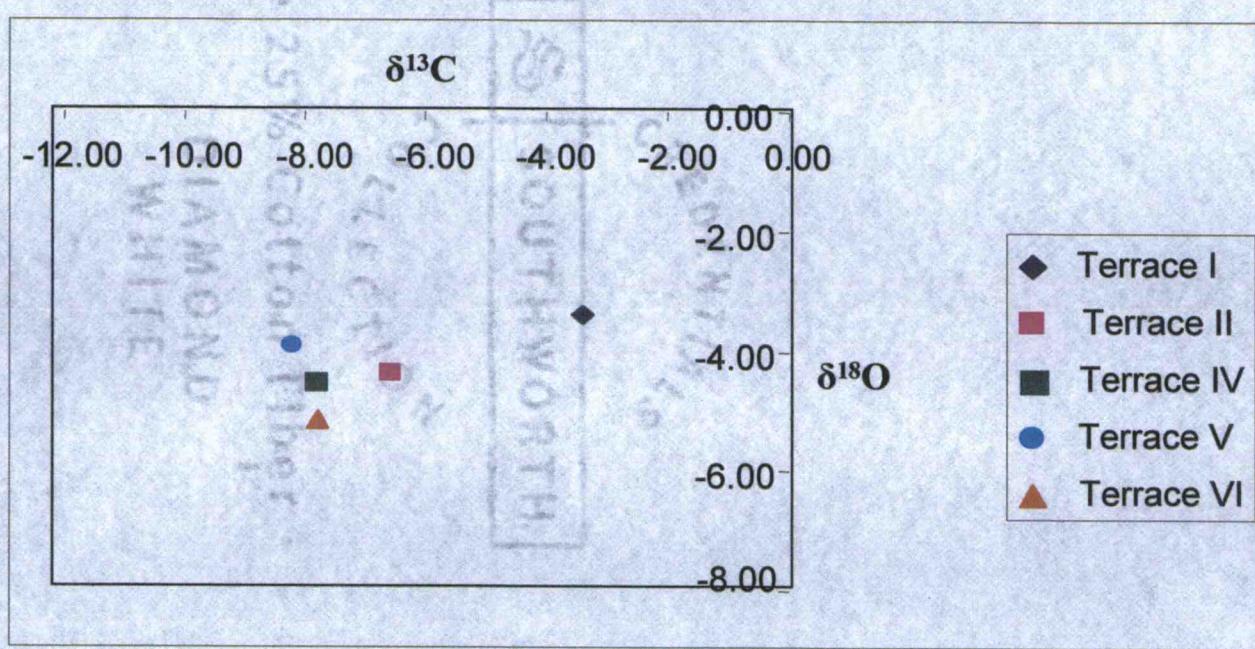


Figure 7: Mean $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values for Terrace I-VI. Isotope values oscillate from terraces VI-IV. $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values increase from terrace IV to terrace I. $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values reported vs. PDB.

-1.40‰ and corresponding $\delta^{18}\text{O}$ values range from -6.87 to -2.53‰ (Table 1,4). Mean values for all pedogenic carbonate samples are -6.17 and -4.67‰ for $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$, which corresponds to soil carbonate values in semi-arid to arid environments (Quade and Cerling, 1990; Kelly and Yonker, 1993; Nordt et al., 1996). Trends in oxygen and carbon isotopic compositions of the pedogenic carbonate correspond; both $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values show a positive shift from the oldest to youngest terrace (Schlesinger et al., 1989) (Figs. 6,7). Carbon values are more broadly variable than those for oxygen. Several additional profiles (C130798, D210798 and A270698) show enrichment of heavy $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ isotopes in surface and near-surface soils (Fig. 8). Profiles C130798 and D210798 are samples from Terrace III and profile A270698 is located in a river cutbank. Profiles C130798 and D210798 show patterns similar to the Loutro Elenis profile (Fig. 8).

4.3 Parent Material Sources

Parent material sources for the studied soils include freshwater calcareous rocks, marine limestone, and eolian material. Freshwater carbonates were sampled from spring and ancient lacustrine deposits, whereas marine limestones were sampled from quarried rock. Eolian material was sampled from large cairns along the Eastern Corinthian coast.

Parent material was analyzed to identify potential end member isotope values. Freshwater calcareous rocks ($\delta^{13}\text{C} = -9.26\text{‰}$ to -8.32‰ , $\delta^{18}\text{O} = -6.55\text{‰}$ to -5.07‰) have lighter $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values than the marine limestones ($\delta^{13}\text{C} = -1.46$ to -1.29 , $\delta^{18}\text{O} = -2.42\text{‰}$ to -1.62‰) (Fig. 5, Table 5) (Salamons and Mook, 1976;

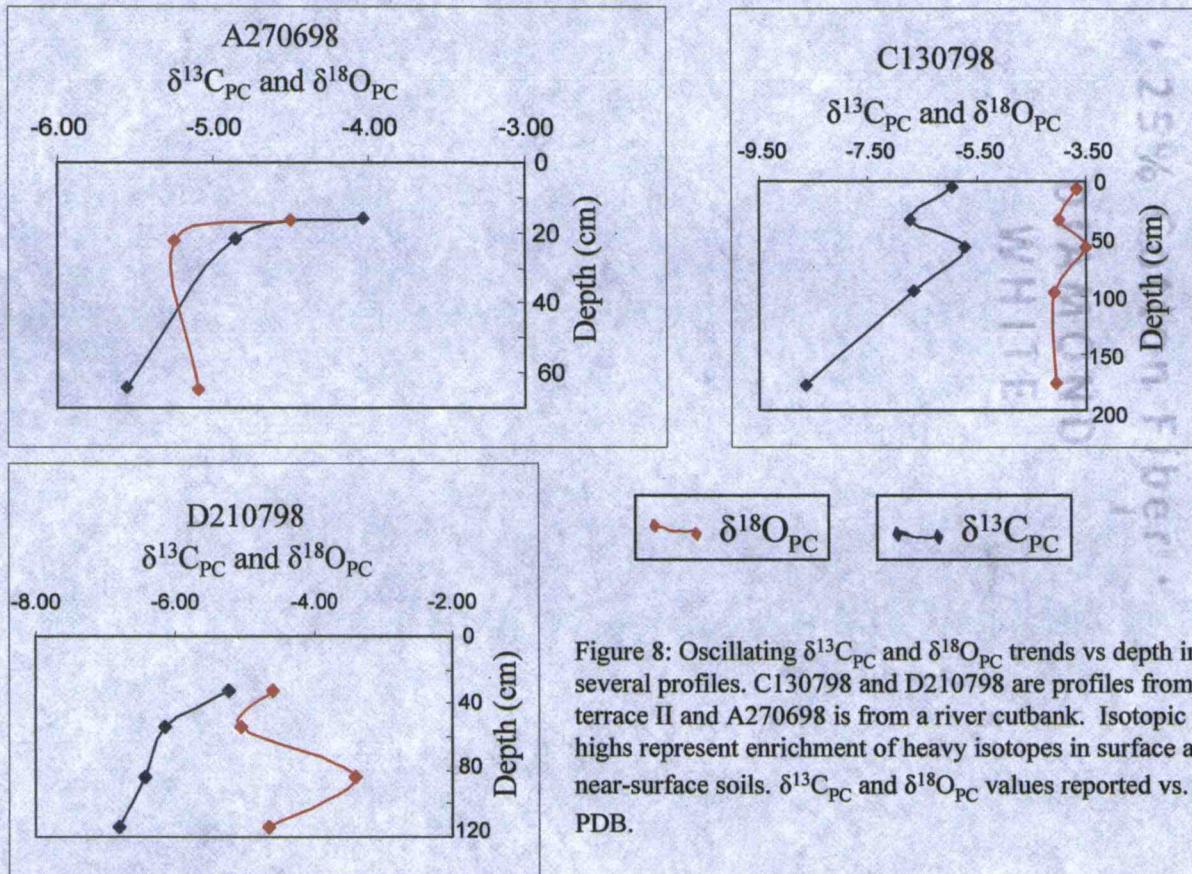


Figure 8: Oscillating $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ trends vs depth in the several profiles. C130798 and D210798 are profiles from terrace II and A270698 is from a river cutbank. Isotopic highs represent enrichment of heavy isotopes in surface and near-surface soils. $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values reported vs. PDB.

West et al., 1988; Buchardt and Fritz, 1989; Turi, 1989; Talbot, 1990). These values correspond to expected freshwater and marine carbonate values (Ehleringer and Rundel, 1989). Isotopic signatures of eolian material (mean $\delta^{13}\text{C} = 2.87\text{\textperthousand}$, $\delta^{18}\text{O} = -2.74\text{\textperthousand}$) found within archaeological structures vary from soil carbonate (mean $\delta^{13}\text{C} = -6.17\text{\textperthousand}$, $\delta^{18}\text{O} = -4.67\text{\textperthousand}$), and fresh (mean $\delta^{13}\text{C} = -8.90$, $\delta^{18}\text{O} = -5.65$) and marine (mean $\delta^{13}\text{C} = 1.42\text{\textperthousand}$, $\delta^{18}\text{O} = -2.11\text{\textperthousand}$) limestone parent material signatures (Table 5).

5.0 Discussion

Several factors may be responsible for the shift in $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ isotope values to more positive values from older to younger terraces. The following section will discuss a variety of factors including: soil and rainfall chemistry, groundwater, evaporation, transpiration, leaching, temperature, microbial activity, parent material, composition of carbon dioxide, and diagenetic effects, that influence the $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ value in a semi-arid to arid environment.

5.1 Soil Water/Rainfall Chemistry

Soil carbonate $\delta^{18}\text{O}$ values are primarily determined by soil water (Cerling, 1984; Amundson et al. 1989). Soil water influences the $\delta^{18}\text{O}_{\text{PC}}$ value throughout the entire soil profile. In the absence of groundwater, such as the Eastern Korinthia where the soils are well drained and the groundwater is deep, the $\delta^{18}\text{O}_{\text{PC}}$ is determined by precipitation and evaporation (Amundson et al., 1989). Therefore, change in rainfall chemistry or source of precipitation can influence the isotope

chemistry of pedogenic carbonate (Deutz et al., 2001). Precipitation in central Greece originates from two sources: northwest Europe and northeast Europe with -6‰ $\delta^{18}\text{O}_{\text{RW}}$ and -8‰ $\delta^{18}\text{O}_{\text{RW}}$ respectively (Griffiths et al., 2002). Precipitation in the Korinthia likely is similar to values recorded at the Hellinikon Airport in coastal Athens of -5.7 $\delta^{18}\text{O}_{\text{RW}}$ (rainwater) (ISOHIS, 2003), indicating a northwest European source. Precipitation that enters soil in undisturbed semi-arid and arid regions with little vegetation is primarily lost through evaporation and transpiration, and secondly through leaching (see below) (Amundson, 1989). In semi-arid and arid environments, the $\delta^{18}\text{O}$ of soil water ($\delta^{18}\text{O}_{\text{sw}}$) is typically enriched in heavy isotopes compared to precipitation as a result of evaporation which preferentially removes lighter isotopes from soil water (Allison and Hughes, 1983). Soil-water chemistry plays a significant role in the trend from light to heavy $\delta^{18}\text{O}_{\text{PC}}$ values observed from Terrace VI to Terrace I (Fig. 6). Soil water likely became increasingly enriched in heavy isotopes as a result of increased temperatures and evaporation thus resulting in a positive shift in $\delta^{18}\text{O}_{\text{PC}}$ values from terrace VI to terrace I. Changes in soil and rain water chemistry are directly linked to temperature and will be discussed in greater detail below (Schlesinger, 1989).

5.2 Groundwater

Oxygen isotopic ratio of groundwater influences $\delta^{18}\text{O}_{\text{PC}}$, so long as groundwater is near the surface and interacts with meteoric waters (Amundson, 1989). The effects of groundwater on the terrace sequence $\delta^{18}\text{O}_{\text{PC}}$ values are negligible because of well-drained soils and deep groundwater. The effects of

groundwater at the Loutro Elenis profile are also minimal due to well-drained soils and deep groundwater. Spring activity along the Korinth fault is not present at or near the stratigraphic level of the Loutro Elenis sampling site, and veining, vugs, mineralization, shears, or strong crystallinity of carbonate phases relating to fault-circulating groundwater are not observed.

5.3 Evaporation

Evaporation studies indicate how the drying of an unsaturated soil influences the isotopic composition of soil water (Barnes and Allison 1983, 1984). Two model soil zones are considered in the effect of evaporation on O isotopes: 1) an upper dry zone (or surface soils) dominated by vapor transport that overlies 2) an unsaturated zone dominated by liquid transport (Barnes and Allison, 1983, 1984). Fractionation of the oxygen isotopes occurs due to kinetic enrichment of the heavy isotopes as water vapor moves from the zone dominated by liquid transport to the zone of vapor transport (Barnes and Allison, 1983; Barnes and Allison, 1984; Amundson, 1989). Enrichment of the heavy isotopes near the surface is seen in Figures 4 and 8. Surface horizons are greatly influenced by evaporation (Allison and Hughes, 1983; Barnes and Allison, 1983; Barnes and Allison, 1984; Amundson, 1989). The influence of evaporation decreases down profile. Moving down profile, $\delta^{18}\text{O}_{\text{PC}}$ values become lighter because the effect of evaporation decreases with depth (Allison and Hughes, 1983; Barnes and Allison, 1983; Barnes and Allison, 1984; Dever et al., 1987; Amundson, 1989). This type of scenario is observed in the Loutro Elenis profile, and profiles C130798, D210798 and

A270698 (Figs. 4, 8). The $\delta^{18}\text{O}_{\text{PC}}$ trends in the Loutro Elenis profile are similar to those seen in previous studies and are likely related to evaporation effects near the soil surface (Allison and Hughes, 1983; Barnes and Allison, 1983, 1984; Dever et al., 1987; Amundson, 1989; Pendall and Amundson, 1996). It is likely that the cyclic $\delta^{13}\text{C}_{\text{PC}}$ trend observed in the Loutro Elenis profile and other profiles shown in Figures 4 and 8 is related to evaporation effects (Allison and Hughes, 1983; Barnes and Allison, 1983; Barnes and Allison, 1984; Amundson, 1989).

5.4 Transpiration

Transpiration is the process by which soil water is transported from the soil via plants to the atmosphere. In most cases, water movement from the soil to the roots is nonfractionating, but in water-stressed conditions, fractionation does occur (Allison and Hughes, 1983). Transpiration influences surface horizons as well as subsurface horizons depending on root depth. During soil drying, roots may shrink thus leaving a space between the root in soil (Amundson, 1989). Vapor in the zone between the root and soil, produced by evaporation of soil water, is enriched in heavy isotopes. As a result of fractionation, the area surrounding the root becomes isotopically enriched with the heavier isotope (Allison and Hughes, 1983; Amundson, 1989). It is unlikely that transpiration plays a significant role in the $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ stratigraphy in the Eastern Korinthia based on varying depths of enrichment of heavy isotopes (Figs. 4, 8). If transpiration was the main factor in determining $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values, root depth in the region would control the

depth of isotopic enrichment (Amundson, 1989). However, the depth of enrichment ranges from <20 cm to >50 cm (in non-buried soils).

5.5 Leaching

Leaching is largely considered to be a nonfractionating process for oxygen isotopes (Amundson, 1989). Fractionation can occur when soil water reacts with soil minerals; however these reactions are very slow and minimal fractionation takes place (Amundson, 1989). Leaching plays a negligible role in determining $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values in the Eastern Korinthia. Excess water evaporates quickly in semiarid environments and is not susceptible to leaching. Agricultural and irrigated soils are more susceptible to leaching due to increased vegetation cover and greater soil water content (Amundson, 1989). However, leaching still plays a minimum role in agricultural and irrigated lands in the Eastern Korinthia because the soils have historically not been irrigated, are well drained and water does not stay in the soil profile for extended periods of time. Leaching effects are not observed in the data. If leaching was the main factor in determining the isotope stratigraphy, there would be a positive shift in stable isotope values with depth due to increasing fractionation of soil water with depth (Amundson, 1989).

5.6 Temperature

Soil temperature influences the $\delta^{18}\text{O}$ of rainwater and fractionation of ^{18}O of soil carbonate during precipitation (Schlesinger, 1989). The fractionation factor between water and carbonate is inversely proportional to temperature (Friedman and O'Neil, 1977). The effect temperature has on fractionation during carbonate

formation is small (-0.25‰/°C) compared with its effect on the $\delta^{18}\text{O}$ signature of rainfall (0.85‰/°C) (Schlesinger, 1989). Small changes in $\delta^{18}\text{O}_{\text{PC}}$ values require large soil temperature changes (Friedman & O'Neil, 1977; Schlesinger, 1989). For example, in order to alter the $\delta^{18}\text{O}_{\text{PC}}$ value by 1‰, the soil temperature must change by 4°C. On the other hand, temperature is more influential on $\delta^{18}\text{O}_{\text{RW}}$. For example, a 1.17°C increase would alter the $\delta^{18}\text{O}_{\text{RW}}$ by +1‰ (Friedman and O'Neil, 1977; Schlesinger, 1989). Therefore, temperature plays a minimal role in the fractionation of carbonate, but does play a significant role in the $\delta^{18}\text{O}_{\text{RW}}$ which directly influences the $\delta^{18}\text{O}_{\text{PC}}$ signature (Cerling, 1984; Schlesinger, 1989).

Soil temperature varies little below 30 cm in the Korinthia (Noller, unpublished data) and fractionation of carbonate precipitation from soil solution could not be responsible for a 1.7‰ $\delta^{18}\text{O}_{\text{PC}}$ range such as observed in profile D210798. It is more reasonable that the shift to heavier $\delta^{18}\text{O}_{\text{PC}}$ values reflects the effect temperature has on rain water and a gradual trend toward a warmer mean annual temperature (Schlesinger, 1989). The isotope stratigraphy from the oldest terrace to the youngest terrace shows at most a +2.75‰ shift in $\delta^{18}\text{O}_{\text{PC}}$ values. If temperature is the sole factor in determining $\delta^{18}\text{O}_{\text{PC}}$, the shift would represent a 3.25°C increase in mean annual temperature in the Eastern Korinthia since the formation of the oldest terrace.

5.7 Microbial Activity

It is expected that microorganisms influence isotopic signatures of carbonate in terrestrial environments, but the degree of that fractionation is

unknown. Microbial activity enriches soil water with heavy isotopes, thus resulting in elevated $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values (Sumner, 2001). Elevated $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values would occur in areas of high microbial activity throughout the soil profile (Sumner, 2001). If the $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values were determined solely by microorganisms, the trend observed from the oldest terrace to youngest terrace would reflect a significant increase in microbial activity (Sumner, 2001). Also, if the pedogenic carbonate is microbially fixed and is an extension of the organism, one would expect to see a trend towards less enriched values in younger terraces (Sumner, 2001). It is unknown if microbes are responsible for a +2.75‰ shift in $\delta^{18}\text{O}_{\text{PC}}$ and a +6.83‰ shift in $\delta^{13}\text{C}_{\text{PC}}$ values because of current uncertainty in the degree of fractionation between microbes and carbonate in a terrestrial environment. Changes in $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values, either a product of fixation or enrichment of soil water with heavy isotopes, is indicative of microbial response to long-term climate change. Microbial activity cannot be ruled out as a possible factor in changes in the isotope stratigraphy observed in the Eastern Korinthia.

5.8 Parent Material

Carbonate parent material can influence the stable isotope signatures of pedogenic carbonate throughout the soil profile (Salamons and Mook, 1976; Rabenhorst et al., 1984). Carbon and oxygen derived from lithogenic carbonate can precipitate as soil carbonate if calcium ions are available (Rabenhorst et al., 1984). In the Korinthia, isotope chemistry would reflect marine geochemistry from the bedrock limestone and lithogenic carbonate in the various marine terraces. If

carbonate parent materials significantly contribute greatly to the composition of pedogenic carbonate, the isotope signatures of the Loutro Elenis profile, as well as, C130798, D210798, and A270698, would remain uniform with depth reflecting only parent material chemistry. These patterns are not observed by this study. Seawater chemistry and marine plants determine the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of marine carbonate parent material (Ehlnerger and Rundel, 1989). If parent material composition was the main factor in determining the pedogenic carbonate values in the Eastern Korinthia, the overall trend to heavier $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values from the terrace VI to I would represent a gradual change in seawater chemistry and proportion of marine plants from the time of initial uplift to ~ 70.2 ka. This scenario is unreasonable because it cannot account for the cyclic trends observed in the Loutro Elenis profile and profiles C130798, D210798, and A270698.

The contribution of eolian material to soil could also influence the isotope stratigraphy observed in the Eastern Korinthia (Mizota et al., 1988; Nihlen and Lund, 1995). The cyclic pattern observed in the Loutro Elenis profile and profiles C130798, D210798, and A270698 could be attributed to seasonal deposition and incorporation of eolian material on or into the soil surface. However, this scenario is unlikely, because eolian material is incorporated throughout the soil profile and would therefore influence the $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values at all depths (Mizota et al., 1988). The increasingly positive trend of $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ from terrace VI to I could be related to changing eolian source materials. This scenario is also unreasonable because eolian source materials have been derived consistently from

the Sahara desert (Mizota et al., 1988; Nihlen and Lund, 1995).

5.9 Composition of Carbon Dioxide

The stable isotope composition of soil CO₂ is determined by vegetation, diffusional processes and atmospheric mixing, and is the greatest influence on $\delta^{13}\text{C}_{\text{PC}}$ values (Amundson, 1989; Cerling et al., 1991; Cerling and Quade, 1993; Nordt et al., 1996). The composition of atmospheric ¹³C ranges from -6‰ (pre-industrial conditions) to -8‰ (modern conditions). Atmospheric CO₂ is enriched in heavy isotopes compared to soil respired CO₂ (-27.7‰) (Cerling et al., 1991; Mermut et al., 1999). Soil near the atmosphere/soil interface is influenced by diffusional mixing of atmospheric CO₂, or atmospheric invasion, and soil respired CO₂ (Mermut et al., 1999). Diffusional mixing will shift the $\delta^{13}\text{C}_{\text{PC}}$ signature of soil CO₂ to that of the atmosphere (Mermut et al., 1999).

The $\delta^{13}\text{C}_{\text{PC}}$ records changes in the composition of carbon dioxide, either due to changes in the proportion of C₃ and C₄ plants, or as a result of atmospheric mixing near the soil surface (Amundson, 1989; Nordt et al., 1996). An increase in C₃ produces relatively light $\delta^{13}\text{C}_{\text{PC}}$ values while an increase in C₄ plants produces relatively heavy $\delta^{13}\text{C}_{\text{PC}}$ values (Nordt et al., 1996). There is no evidence to indicate that the population of C₄ vegetation has increased in the Mediterranean or the Korinthia based on present day vegetation. Thus vegetation change is not likely a major factor in accounting for $\delta^{13}\text{C}_{\text{PC}}$ in soils of this study (Cerling, 1984; Griffiths et al., 2002). Enrichment of heavy $\delta^{13}\text{C}_{\text{PC}}$ values observed near the soil surface in the Loutro Elenis and C130798, D210798, and A270698 profiles can be attributed

to increasing atmospheric invasion which directly influences the soil CO₂ composition (Amundson, 1989).

5.10 Diagenetic Effects

Diagenetic effects (dissolution, reprecipitation) of soil carbonate in surface horizons and upper sub-surface horizons may influence isotopic signatures (Salomons and Mook, 1976; Cerling, 1984; Dever et al., 1987). Soil carbonate is most susceptible to dissolution and precipitation in A and B horizons due to change in P(CO₂) and water loss due to evaporation and transpiration (Salomons and Mook, 1976; Cerling, 1984; Dever et al., 1987). It is unlikely that diagenetic effects influenced deep subsurface soils in this study due to the well-drained sites and deep groundwater. Samples from the Loutro Elenis profile with δ¹⁸O_{PC} values ranging from -4.18‰ to -4.21‰ and δ¹³C values from -4.40‰ to -2.48‰ (samples similar to values from Terrace I) (Fig. 6, Table 3) were collected within one meter of the surface and these samples likely represent reprecipitated CaCO₃ due to acidic conditions in the upper soil horizons produced by the regrowth of pine trees along the forested Oneion range (Cerling, 1984; Dever et al., 1987). Coniferous trees create acidic soil conditions which could dissolve soil carbonate, which could then reprecipitate lower in the profile under present climatic conditions (Dever et al., 1987). Other paleosols in the Loutro Elenis profile could have been susceptible to dissolution when they were closer to the surface and these soils could reflect small amounts of reprecipitation by applying methods developed by Salomons and Mook (1976) using known values of oxygen isotope fractionation between CaCO₃ and

water, and known values of carbon isotope fractionation between bicarbonate and CaCO_3 . Large amounts of reprecipitation are more difficult to measure due to the soil water chemistry changing over the course of time (Salomons and Mook, 1976). Small amounts of reprecipitation in horizons near the present day soil surface could be used to identify climatic changes during the Holocene (Dever et al., 1987).

6.0 Conclusions

Atmospheric invasion, evaporation and temperature are major contributors to PIC formation and stable isotope trends in the Eastern Korinthia. Atmospheric CO_2 invasion accounts for the cyclic $\delta^{13}\text{C}_{\text{PC}}$ trend observed in the Loutro Elenis profile, as well as, heavy $\delta^{13}\text{C}_{\text{PC}}$ trends toward surface soils in profiles C130798, D210798 and A270698. Increased atmospheric CO_2 invasion accounts for the overall trend in $\delta^{13}\text{C}_{\text{PC}}$ values from Terrace VI to I. Evaporation and increased temperatures are most likely the main contributors to pedogenic carbonate formation and stable isotope trends in the Eastern Korinthia. The cyclic $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ values in the Loutro Elenis profile and profiles C130798, D210798 and A270698, present strong evidence for enrichment of heavy isotopes in soil water near the soil surface related to evaporation effects (Allison and Hughes, 1983; Barnes and Allison, 1983; Barnes and Allison, 1984; Amundson, 1989; Pendall and Amundson, 1996). As evaporation effects decrease from the soil surface - down profile, enrichment of heavy isotopes lessens (Allison and Hughes, 1983; Barnes and Allison, 1983; Barnes and Allison, 1984; Amundson, 1989). The cyclic pattern repeats itself several times, indicating that each paleosol was influenced by

atmospheric CO₂ invasion and evaporation effects (Allison and Hughes, 1983; Barnes and Allison, 1983; Barnes and Allison, 1984; Amundson, 1989).

The overall positive shift in $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values in the Loutro Elenis profile and the terrace sequence are related (Fig. 9). The Loutro Elenis profile shows a positive shift from the oldest to the youngest horizon and the terrace sequence shows also shows a similar shift from the oldest to youngest terrace (Fig. 9). Figure 9 shows the linear regression of the Loutro Elenis profile and samples collected on the terraces. The linear regression of Terraces A includes all data points, while Terraces B includes all but two points (Fig. 9). Point (a) was removed from the linear regression of Terraces B because it is a surface soil and it likely was altered by diagenetic effects. The point (b) has an atypical $\delta^{18}\text{O}_{\text{PC}}$ vs $\delta^{13}\text{C}_{\text{PC}}$ relationship compared to the majority of other PIC values documented and may represent a contaminated sample. It is most reasonable that the positive shifts in $\delta^{18}\text{O}_{\text{PC}}$ are associated with a gradual increase in temperature (Amundson, 1989). Increased temperatures enrich rainwater with heavy isotopes and, in turn, are reflected in the isotope chemistry of pedogenic carbonate (Amundson, 1989). An increasingly arid environment can also explain the positive shift in $\delta^{13}\text{C}_{\text{PC}}$ as a result of enrichment of heavy isotopes in soil CO₂ due to atmospheric invasion.

It is likely that PIC accumulation in the Eastern Korinthia takes place during interglacial periods, in accordance with Reheis (1987). Therefore the $\delta^{13}\text{C}_{\text{PC}}$ and $\delta^{18}\text{O}_{\text{PC}}$ signatures from Terrace VI to I do not represent a continuous time line, instead the signatures represent discrete interglacial periods and how climate has

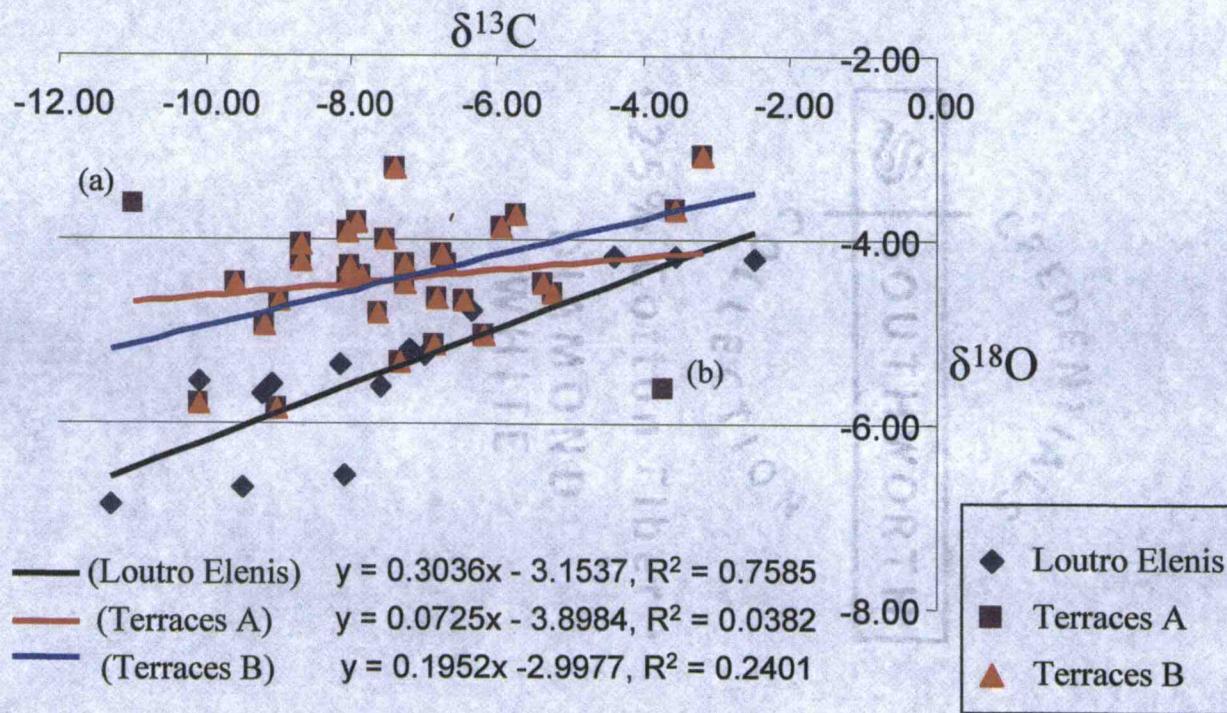


Figure 9: Linear regressions of the Loutro Elenis profile and terraces of $\delta^{13}\text{C}_{\text{PC}}$ vs. $\delta^{18}\text{O}_{\text{PC}}$. Terraces A includes all data points from terraces, while Terraces B includes all but two points. The points removed include a surface soil (a) likely influenced by diagenetic effects and a sample (b) with an atypical $\delta^{13}\text{C}_{\text{PC}}$ vs. $\delta^{18}\text{O}_{\text{PC}}$ relationship. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values vs. PDB.

changed from one interglacial to the next. After peak interglacials, temperatures decreased and precipitation increase in northwestern Greece, thus creating the specific conditions described by Reheis (1987) for carbonate precipitation and clay accumulation.

The findings in this study are partially supported by Griffiths et al. (2002). The Griffiths et al. (2002) study documents a continuous paleoclimatic record from the last interglacial to the Early Holocene using stable isotopes of calcareous sediments and present day aquatic chemistry to establish hydrological changes over the past 126 ka in the Kopais basin of central Greece. Pollen data in the Kopais basin indicates several climatic oscillations, but with an overall long-term downward trend in moisture availability commencing ~126 ka (Griffiths et al., 2002).

7.0 Summary

Stable carbon and oxygen isotope chemistry in the Eastern Korinthia reveal an increasingly arid environment due to increased mean annual temperature and evaporation effects over the past ~600 ka. The terraced Korinthian landscape provides an excellent means to study the carbon and isotope stratigraphy of pedogenic carbonate and shows a positive shift in both $\delta^{18}\text{O}_{\text{PC}}$ and $\delta^{13}\text{C}_{\text{PC}}$ values.

Stable oxygen isotope PIC values in the Eastern Korinthia indicate evaporation and increased temperatures. The cyclic $\delta^{18}\text{O}_{\text{PC}}$ pattern in the Loutro Elenis profile and profiles C130798, D210798 and A270698 show enrichment of heavy isotopes in surface and near-surface soils and provide strong evidence for the

evaporation effect. The positive shift in $\delta^{18}\text{O}_{\text{PC}}$ values with in the Loutro Elenis profile mimic the overall trend in soils formed on the marine terraces and indicates an increase in mean annual temperature and increased evaporation effect.

Stable carbon isotope PIC values indicate diffusional mixing of atmospheric CO₂ and soil respired CO₂ in near surface and surface soils (Mermut et al., 1999). Diffusional mixing will shift the $\delta^{13}\text{C}_{\text{PC}}$ signature of soil respired CO₂ to that of the atmosphere and directly influences the geochemistry of PIC (Mermut et al., 1999). The shift in $\delta^{13}\text{C}_{\text{PC}}$ values from Terrace IV to I indicates increasing atmospheric CO₂ component. Slight isotopic variability of soils on marine terraces VI to IV indicates natural spatial variability and cannot be attributed solely to climatic oscillations.

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