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An Investigation of the Pedogenesis of

Soils Developed in Quaternary Alluvial Deposits

of Eastern Crete

A Dissertation Presented for the

Doctor of Philosophy Degree

The University of Tennessee, Knoxville

Michael Edward Timpson

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DEDICATION

This dissertation is dedicated to my parents, Thomas E. and P. Diane Timpson, who inspired in me a desire to always attempt my best, and never seemed to tire of my incessantly asking: "Why ?".

It is also dedicated to those few teachers and professors, who throughout my academic career, saw something in me which I perhaps did not, and encouraged me to continue pursuing the quest for answers.

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ABSTRACT

A pedologic investigation of an area of highly calcareous Late Quaternary alluvial sediments in northeastern Crete, Greece was undertaken to study the nature and distribution of the soils formed in these deposits and to evaluate the pedogenic processes responsible for their development. The specific objectives of this research were; (i) to describe and classify the soils, (ii) examine the nature and distribution of various forms of iron, manganese and silicon in these soils in order to better understand the weathering processes which had occurred, (iii) characterize the mineralogical properties of the soils and sediments to elucidate the processes responsible for the mineral assemblages identified and (iv) to develop a model of soil and landscape genesis for these alluvial soils.

All four soils exhibited red-colored, clay-rich surface horizons. Calcic horizons had developed in all soils which resulted in paling of subsoil colors. Two pedons were classified as sandy-skeletal, carbonatic, thermic Calcixerollic Xerochrepts and two were sandy-skeletal, carbonatic, thermic Fluventic Xerochrepts. The major pedogenic processes identified were rubification, accumulation of clay and trace elements, notably Ti, and calcic horizon development. Morphological characteristics of the calcic horizons varied from Stage I to III. These features suggested an age of latest Pleistocene to early Holocene for these soils.

Iron, Mn and Si contents were highest in surface horizons, decreasing with depth. Silicate- and dithionite-Fe as a fraction of total-Fe also suggested a maximum upper age limit of Late Pleistocene to early Holocene. Active iron ratios were low (0.05 to 0.15) which suggested rapid conversion of amorphous iron compounds to crystalline phases. Goethite was the dominant secondary iron phase. Manganese in these soils existed primarily as secondary oxides and organically-bound species. Hydroxylamine-HCl extracted an average of 58.8 % of the total Mn, while removing only 0.05 to 4 % of the total iron. This suggested that even in these highly calcareous soils hydroxylamine is still specific for Mn-compounds. Primary silicates were the major source of Si in these soils; however, dithionite,

oxalate and hydroxylamine all extracted varying proportions of Si. These fractions were probably associated with the secondary Fe- and Mn- compounds.

Dolomite, calcite, quartz, illite, chlorite, kaolinite, feldspars (K-spar and plagioclase) and goethite were identified in these soils. Coarse and fine silt fractions were dominated by dolomite, calcite, and quartz. Clay fractions contained chlorite and illite, with minor amounts of kaolinite, quartz, dolomite, calcite and goethite. The extent of clay mineral inheritance, limited expansion of the chlorite and the lack of a chlorite or mica weathering product (vermiculite), as well as the presence of carbonates in the clay fractions all suggested that these soils were relatively young.

The following sequence of events was proposed for development of the sediments and soils of these alluvial deposits. A period of valley-filling followed by stabilization and stream incision, possibly in the Middle Pleistocene, led to the development of marine and fluvial terraces which now exist as conglomeratic inliers surrounded by younger sediments. Continued valley filling and landscape adjustment probably occurred throughout the Late Pleistocene, but the extent of this activity is unknown. One last period of alluviation probably occurred near the transition between the Pleistocene and Holocene, in response to climatic change. This event could have taken place between 8,300 and 9,000 BP based on evidence from southern Crete (Bottema, 1980). Weathering and soil development was probably rapid up to about 7,500 BP, when a shift toward a drier climate would have changed the rate of weathering. Calcic horizon development was probably initiated by about 8,000 BP in response to the shift toward drier conditions. Another period of increased weathering and clay accumulation likely took place between 7,500 and 7,300 BP, as pollen data for this period implied a re-expansion of forests in Crete (Bottema, 1980). Modern soil forming conditions have probably been controlling soil genesis in the area since 4,500 to 4,000 BP. Periods of extreme climate, combined with human population pressure, have likely resulted in brief episodes of landscape instability over the last 4000 to 5000 years.

TABLE OF CONTENTS

INTRODUCTION 1

PART 1. SELECTED LITERATURE REVIEW 3

DEFINITION AND CONCEPTS OF SOIL GENESIS 4

SOILS AS A TOOL IN QUATERNARY STUDIES 5

PEDOGENESIS IN MEDITERRANEAN CLIMATES 6

PEDOGENESIS OF GREEK SOILS 12

CHARACTERISTICS OF THE STUDY AREA 15

Location 15

Climate 15

Geology 18

Soils 23

REFERENCES 25

PART 2. SOIL AND LANDSCAPE GENESIS IN CALCAREOUS HOLOCENE ALLUVIAL SEDIMENTS IN EASTERN CRETE 32

INTRODUCTION 33

LOCATION 34

CLIMATE 34

MATERIALS AND METHODS 37

Field Methods 37

Laboratory Methods 37

RESULTS AND DISCUSSION 39

Soil-Landscape Relationships 39

Soil Morphology and Classification 42
Parent Material Uniformity 45
Physical and Chemical Characteristics 54
Active Pedogenic Processes 68
Late Quaternary Landscape and Soil Development 71
CONCLUSIONS 78
REFERENCES 81

PART 3. CONTENT AND DISTRIBUTION OF IRON, MANGANESE AND SILICON OXIDES IN SOME CALCAREOUS ALLUVIAL SOILS OF EASTERN CRETE 87
INTRODUCTION 88
MATERIALS AND METHODS 89
Field Methods 89
Laboratory Methods 92
RESULTS AND DISCUSSION 93
Iron 93
Manganese 105
Silica 115
CONCLUSIONS 123
REFERENCES 126

PART 4. A MINERALOGICAL INVESTIGATION OF SOME SOILS FORMED IN CALCAREOUS GRAVELLY ALLUVIUM, EASTERN CRETE, GREECE 132
INTRODUCTION 133
MATERIALS AND METHODS 134
RESULTS AND DISCUSSION 137

Soils 137

Silt Mineralogy 140

Clay Mineralogy 142

Iron Oxides 150

Mineral Occurrence and Weathering 150

CONCLUSIONS 152

REFERENCES 154

APPENDICES 158

APPENDIX A. SOIL DESCRIPTIONS FOR THE SOILS INVESTIGATED. 159

APPENDIX B. PARTICLE-SIZE DATA FOR PROFILES 1 THROUGH 4. 168

APPENDIX C. PHYSICAL AND CHEMICAL DATA FOR PROFILE PACHEIA AMMOS 3. 173

APPENDIX D. MAP UNIT DESCRIPTIONS FOR THE SOIL MAP OF THE STUDY AREA. 176

APPENDIX E. GEOLOGY AND LANDFORM RELATIONSHIPS OF THE STUDY AREA. 179

VITA 186

LIST OF FIGURES

PART 1.

Figure 1. Location of the Island of Crete in relation to the Greek mainland and general location of the study area. 16

Figure 2. Generalized geologic section: Neogene and post-Neogene sediments of the Ierapetra region. 21

PART 2.

Figure 1. Location of the study area. 35

Figure 2. Soil map of the study area. 40

Figure 3. Particle-size distributions for the four soils studied. 55

Figure 4. Fine clay: coarse clay ratios from the four soils studied 57

Figure 5. Distribution of soil carbon fractions in the four soils studied. 60

PART 3.

Figure 1. Study site and sampled profiles (indicated by soild triangles). 90

Figure 2. Silicate iron contents (Fe_t - Fe_d) as a percentage of total iron plotted with depth for the four soils studied. 97

Figure 3. The relationship between the crystalline secondary iron oxides and clay content with depth in the four soils studied. 101

Figure 4. Active iron ratios (Fe_o/Fe_d) plotted with depth for all four soils. 104

Figure 5. Silicate manganese (Mn_t - Mn_d) as a percentage of total manganese, plotted with depth for Profiles 1 through 4. 109

Figure 6. Depth distribution of dithionite extractable manganese as a fraction of total manganese for all four profiles. 110

Figure 7. Depth distribution of oxalate manganese as a fraction of total manganese in profiles 1 through 4. 112

Figure 8. Distribution with depth of the ratio of oxalate to dithionite extractable manganese in the four soils investigated. 113

Figure 9. Hydroxylamine extractable manganese as a fraction of total manganese in Profiles 1 through 4 plotted with depth. 114

Figure 10. Relationship between dithionite extractable silica and crystalline iron oxide compounds (Fe_d - Fe_o) in all four soils. 120

Figure 11. Dithionite extractable silica as a fraction of dithionite extractable manganese in the four soils studied. 121

Figure 12. Ratio of oxalate extractable silica to oxalate extractable iron as a function of depth in Profiles 1 through 4. 122

Figure 13. The relationship between hydroxylamine extractable silica and hydroxylamine extractable manganese in Profiles 1 through 4 plotted with depth. 124

PART 4.

Figure 1. Map showing the location of the study area. 135

Figure 2. X-ray diffractograms of the fine silt (2-20 μm) fractions from all four Profiles. 141

Figure 3. X-ray diffractograms of the total clay (<2 μm) fractions from Profile 1 (A) and Profile 4 (B). 143

Figure 4. X-ray diffractograms of the total clay ($<$ 2 μm) from the unweathered phyllite residuum. 145

Figure 5. X-ray diffractogram of HCl-treated clay fraction ($<2\mu$m) from the phyllite. 146

LIST OF TABLES

PART 1.

Table 1. Rainfall, temperature and elevation data for selected locations near the study site. 18

Table 2. Geologic timescale for the upper Phanerozoic eon. 20

PART 2.

Table 1. Profile descriptions for the four soils studied. 43

Table 2. Clay-free particle-size ratios from Profiles 1 through 4. 47

Table 3. Selected total elemental analysis for Profiles 1 through 4. 51

Table 4. Clay accumulation indices for Profiles 1 through 4. 58

Table 5. Content and estimated composition of inorganic carbon fractions in the four soils studied. 61

Table 6. Soil pH and cation exchange characteristics of the four profiles studied. 64

Table 7. Soluble ion compositions from 1:1 water extracts of the four profiles studied. 66

PART 3.

Table 1. Total and extractable iron fractions from Profiles 1 through 4. 94

Table 2. Redness ratings and estimated hematite contents for the four soils studied. 99

Table 3. Total and extractable manganese fractions from Profiles 1 through 4. 106

Table 4. Total and extractable silica fractions from Profiles 1 through 4. 116

PART 4.

Table 1. Selected physical and chemical properties of the four soils studied. 138

INTRODUCTION

In the last twenty to twenty-five years, the investigation of soils has become an important tool in studies of the Quaternary (Pawluk, 1969; Yaalon, 1971; Mahaney, 1978; Pope and van Andel, 1984; Boardman, 1985). Data collected during the study of soil genesis can provide important information with regard to paleoclimates, past weathering environments and processes, and Quaternary landscape evolution. Relatively little information has been reported regarding the Quaternary deposits of northeastern Crete. Dermitzakis (1973) investigated the occurrence of Pleistocene deposits in the southeast Sitea district of eastern Crete. He also discussed neotectonic activity and the existence of old strandlines throughout Crete (Dermitzakis, 1974).

The nature and properties of soils developed from late Quaternary deposits could hold important information with respect to Quaternary paleoclimates and their resulting pedogenic environments. A detailed soil-geomorphic investigation of a group of late-Quaternary-aged fluvial sediments was undertaken to study the nature and distribution of the soils formed in these deposits and to evaluate the possible paleoenvironment(s) and modes of genesis responsible for their development. This information will be useful for environmental interpretations which can be utilized by scientists from allied fields of study (e.g., archaeology, geomorphology).

The objectives of this investigation were (i) to describe and classify the soils developed on a group of late Quaternary-aged sediments on the north coast of the Isthmus of Ierapetra, (ii) to examine the nature and distribution of iron, manganese and silicon oxides in these soils in order to better understand the genesis of these features, (iii) to characterize the mineralogical properties of the soils in an effort to understand and elucidate the processes responsible for the mineral assemblages identified and (iv) to develop a model of soil genesis for the alluvial soils of the region.

The results of this dissertation are presented in four parts. Part 1 reviews some of the scientific literature pertinent to the genesis of soils of the Mediterranean region in general, and Greece in particular. Parts 2, 3, and 4 have been prepared as manuscripts submitted to appropriate scientific journals. Part 2 discusses the genesis of the soils and landforms investigated. Part 3 examines the

nature and distribution of iron, manganese, and silicon oxides in these soils. Part 4 describes the mineralogical characteristics of the soils and sediments and discusses the processes involved in their genesis.

DEFINITION AND CONCEPTS OF SOIL GENESIS

The definition of soil may vary with the viewpoint of the person providing the definition. To an agronomist, soil is often considered a growth medium for higher plants, specifically agricultural crops. To a civil engineer, soil may represent a wide range of materials, from clay minerals to boulders the size of small trucks. To a pedologist, soils are generally considered to be naturally occurring, anisotropic bodies, composed of horizons lying parallel to the earth's surface, which result from climate, organisms and time acting on parent rock and influenced by geomorphic position (Buol et al., 1973, Simonson, 1968, Soil Survey Staff, 1975).

The concept of soil has been thoroughly reviewed by Simonson (1968). Cline (1961) discussed some of the changes in the evolution of the working model of soil. The concept of soils as naturally occurring entities resulting from the interaction of various environmental factors has led to the development of some generalized models to explain their nature and properties.

Probably the best known of these models is the factorial approach first proposed by Dokuchaev and formalized by Jenny (1941). Jenny defined soil as being a function of at least five extrinsic factors plus some undefined number of intrinsic properties. For fifty years Jenny's model has served as the guiding paradigm in soil genesis research (e.g. Yaalon, 1975; Bockheim, 1980; Richardson and Edmonds, 1987).

Simonson (1959) outlined a generalized theory of soil genesis. He proposed that soil genesis could be considered as two overlapping processes; these were the accumulation of parent material and the differentiation of horizons. Horizon differentiation was ascribed to additions, removals, transformations and translocations.

One outgrowth of Jenny's approach has been the study of soil development wherein one factor is observed while the other four major factors are held as constant as possible (e.g. lithosequences, toposequences, biosequences). Another example of this type of study is the chronosequence (Stevens and Walker, 1970), wherein time is the dominant soil forming factor. Yaalon (1975) reviewed the major types of "factorial approach" studies and posed the question: "Can soil-forming functions be

solved ?" Bockheim (1980) presented data for thirty-two chronosequences covering a wide area of the world. He showed that a number of soil properties can be demonstrated to vary quantitatively with time. Johnson et al. (1990) proposed a revised model of soil genesis which emphasized the integrated effects of what they termed "dynamic and passive pedogenic vectors" and the influence of these factors in directing and controlling soil development through time.

SOILS AS A TOOL IN QUATERNARY STUDIES

Over the last twenty-five years, the investigation of soils has become an important and accepted tool in integrated, multi-disciplinary studies of the Quaternary (Pawluk, 1969; Yaalon, 1971; Mahaney, 1978; Shroba and Birkeland, 1983; Boardman, 1985). When studying Quaternary sequences that are not datable using absolute chronometric techniques (e.g. ^{14}C dating) soils can often provide relative age information (Alexander, 1974; Arduino et al., 1984, 1986; Birkeland, 1978). Morrison (1978) discussed the rationale, methodology, and problems associated with the use of soils in Quaternary stratigraphic studies. Rutter et al. (1978) utilized pedological and geomorphological data to estimate climatic trends for a portion of the Quaternary in the central Yukon, Canada. Birkeland (1985) described the use of soils data for dating Quaternary deposits throughout the western United States. He presented examples of soil development and pedogenic processes from various chronosequences and provided examples of the application of these in Quaternary studies. Holocene soil-geomorphological relationships across the southern High Plains of Texas were described by Holliday (1985). The use of soil properties in conjunction with a relatively complete radiocarbon chronology enabled Holliday to discriminate the major intervals of landscape stability in this region throughout the Holocene. Recent studies of various archaeological sites in North America have utilized soils data for reconstruction of Holocene landscape evolution (Foss et al., 1985; Foss, 1991; Timpson et al., 1987a,b).

PEDOGENESIS IN MEDITERRANEAN CLIMATES

Of the five major soil-forming factors, three tend to dominate the soils of Mediterranean regions; climate, parent material and topography (Anastassiades, 1949; Mohr et al., 1972; Nakos, 1979; Papadakis, 1985). The Mediterranean-type climate occurs in a number of areas around the world, although it is best known from the region for which it is named. It is characterized by cool, moist winters and dry, hot summers. Winter precipitation, falling when evapotranspiration is at a minimum, can be quite efficient in promoting leaching and translocation of some materials within soils. Soil Taxonomy (Soil Survey Staff, 1975) defines the Xeric moisture regime, which characterizes "Mediterranean" soils as follows:

> "The soil moisture control section is dry in all parts for 45 or more consecutive days within the 4 months that follow the summer solstice in 6 or more years out of 10. It is moist in all parts for 45 or more consecutive days within the 4 months that follow the winter solstice in 6 or more years out of 10. The moisture control section is moist in some part more than half the time, cummulative, that the soil temperature at a depth of 50 cm is higher than 5° C, or in 6 or more years out of 10 it is moist in some part for at least 90 consecutive days when the soil temperature at a depth of 50 cm is continuously higher than 8° C. In addition, the mean annual soil temperature is lower than 22° C, and mean summer and mean winter soil temperatures differ by 5° C or more at a depth of 50 cm, or at a lithic or paralithic contact, whichever is shallower."

The soil temperature regime is often thermic (Mean Annual Soil Temperature [MAST] = 15-22° C), but it may also be mesic (MAST = 8-15° C).

Mohr et al. (1972) suggested that the severe dessication, caused by the summer moisture deficit common to Mediterranean climates, was the most important factor in the formation of soils in Mediterrranean regions. Nakos (1984) listed the following general characteristics for the Mediterranean bio-climatic zone of Greece: mean annual temperature = 17.3° C; mean annual precipitation = 673 mm; seven months of each year had less than 60 mm of rainfall. This zone commonly extended from sea level to approximately 500 m elevation. Because of the degree of variation in the definition of the

"Mediterranean" climate, Mancini (1966) suggested abandoning the term for describing these soils. In spite of this, soils formed or forming under climatic conditions characterized by cool, moist winters and hot, dry summers are still refered to as "Mediterranean."

There is some disagreement about whether soils in Mediterranean areas (particularly Terra Rossae) are the result of the interaction of modern climate and other soil-forming factors, or relicts of some former set of climatic conditions (Mohr et al., 1972). Because of this, a brief overview of the paleoclimatic data available for the eastern Mediterranean region warrants discussion.

Mariolopoulos (1961) stated that the climate of Greece had not changed appreciably in the past 3500-4000 years, based on comparisons of modern climatic records and climatic descriptions from ancient sources. Wright (1968) on the basis of pollen studies by Beug and some of his own unpublished (at that time) data suggested that little climatic change had taken place in the southern Pelopennese for approximately the last 4000 years.

Farrand (1971) summarized data from a number of studies of the Mediterranean maritime littoral east of about 21° East longitude. From his summary, the climate of the eastern Mediterranean during the last continental glaciation was cooler and more humid than it is now. The mean temperature decrease was 5-7°C, with a definite increase in effective precipitation. Thiede (1978) reported a sea surface temperature map for 18,000 years ago (kya) based on oxygen isotope ratios of foraminifera. A comparison of his 18 kya August (summer) water temperatures with modern water temperatures shows a decrease of approximately 2°C around Crete. Winter water temperatures 18 kya were placed at 17-19°C, but no modern winter temperature data were provided for comparison. Thiede's data also illustrate a large influx of cool, fresh water through the Aegean basin. Vergnaud-Grazzini and Herman-Rosenburg (1969) also noted this influx; they suggested a 1 to 5 per mil decrease in sea water salinity as a result.

A reconstruction of the eastern Mediterranean sea for 18,000 before present (BP) by Thunell (1979) yielded conclusions similar to Thiede's. Thunell's reconstruction was an improvement over Thiede's in that the data set upon which it was based was chosen to more carefully represent conditions

in the Mediterranean. The largest change between 18 kya and present sea surface conditions occurred in the Aegean and immediately south of Crete. The winter temperature anomaly within the Aegean was about 6°C cooler than present. The maximum summer temperature anomaly existed south of Crete and amounted to 4°C cooler than present. Thunell's study also detected the decrease in salinity brought about by the influx of cooler, fresh water due to glacial meltwaters from northeast of the Aegean.

Buckley et al. (1982) noted variations in planktonic foraminifera in sediment cores from the eastern Mediterranean surrounding Cyprus (32°- 35°E long. and 34° - 36°N lat.) which suggested a slow warming from about 24 kya to approximately 4700 BP, near the Holocene climatic optimum. Oxygen isotope composition of the forams changed rapidly between 13 kya and 10 kya. A decrease in ^{18}O during this time period suggests ice melt and increased temperatures accompanying the end of glacial conditions.

Gat and Margaritz (1980) discussed a number of studies that suggested a period of high humidity sometime between 6 and 4 000 B.P. These authors place the transition to modern, arid conditions at about 3000 B.P..

The studies reviewed document the following conditions for the eastern Mediterranean from approximately 20,000 BP to the present: (i) lower temperatures (by 5-7°C) and increased effective precipitation for the last glacial maximum; (ii) wider seasonality of temperatures during the last glacial; (iii) a gradual warming from the end of the last glacial to approximately 4700 BP, culminating in a climatic optimum; (iv) a slight cooling from the climatic optimum, resulting in conditions similar to those of the modern eastern Mediterranean since approximately 4000 BP.

Based on the paleoclimatic data, the soils of the eastern Mediterranean region have formed as a result of varying climatic conditions. Cooler temperatures and increased effective precipitation during the late glacial and early Holocene may have allowed weathering to occur at faster rates than it does now. The onset of "modern" climatic conditions, obtained since 4000 BP, may have had little influence in altering the degree of weathering and soil development that could have occurred in the previous 16 000 years; thus some of the soils in the region could be relict.

The parent materials from which "Mediterranean" soils form vary widely. They range from basalts to granites, hard and soft limestones, rocks exhibiting various grades of metamorphism and alluvial sediments derived from any and all combinations of the sources listed above (Mohr et al., 1972).

In addition to the rock types listed above, another source of parent material that is important for soil development in areas surrounding the Mediterranean basin is eolian sediments (Chester et al., 1977; Yaalon and Ganor, 1973, 1979; Goudie, 1978; Morales, 1979; Prodi and Fea, 1979; Rapp, 1984; Rapp and Nihlen, 1986; Nihlen and Solyom, 1986; Pye 1987; Yaalon, 1987).

A number of authors have reported on the influence of eolian sediments on pedogenesis throughout the Quaternary (Syers et al., 1969; Jackson et al., 1973; Yaalon and Ganor, 1973; Goudie, 1978). Syers et al. (1969) listed the following characteristics for aerosolic dusts and loessial sediments. Aerosolic dusts range in particle diameter from 1-10 μm, they have a transport range of 10^4 - 10^6 km, and are commonly transported in the middle and upper troposphere. Loess, on the other hand, is generally between 10 and 70 μm in diameter, is transported between 10^{-1} - 10^2 km and is generally carried in the lower troposphere. Yaalon and Ganor (1973) suggested that eolian modification of limestone derived soils in many regions should be suspected and investigated. Dust samples collected in Israel indicated that montmorillonite was the dominant clay mineral. Small quantities of kaolinite were also identified. Quartz and carbonates dominated the silt fractions. Chester et al. (1977) reported the average clay mineral composition of the dusts they collected over the eastern Mediterranean to be 50% kaolinite, 40% illite, $<8\%$ chlorite and $<5\%$ montmorillonite.

Although less frequent than easterly or westerly transport, movement of Saharan dust to Europe by cyclonic winds happens occasionally and can contribute significantly to many of the shallow limestone and basalt derived soils in Greece, Italy and Spain (Yaalon and Ganor, 1973; Rapp, 1984; Yaalon, 1987). Dust transported by this mechanism is generally between 1-20 μm in diameter. Residence-time for such material is often several days. "Washout" by rainfall is the primary mode of deposition for these sediments; however, dry deposition can also take place (Yaalon and Ganor, 1973).

Prodi and Fea (1979) reported on an occurrence of Saharan dust transport and deposition over Italy in May of 1979. The size distribution of rainfall residue exhibited two modes, with diameters of 0.2 and 1 μm. X-ray diffraction analyses demonstrated the two modes varied in mineralogical composition. The smaller particles were primarily clays (dominantly kaolinite); whereas, the larger dust consisted of quartz. Deposition from this storm amounted to 833 mg m^{-2}. These authors also noted that similar dust storms were reported in Yugoslavia, Albania and Greece on the same two days. Rapp (1984) posed the question: "Are Terra Rossa soils in Europe eolian deposits from Africa?" He examined sediment from karst pockets in hard limestone from Spain. Particle-size analysis of material from 1-2 m depth showed that 90% consisted of silt plus clay and 10% was fine sand. X-ray analyses indicated that quartz was the dominant mineral phase, followed by chlorite and other clay minerals. The composition of the material he examined was similar to eolian dust from Africa analyzed by others. Haeberli (1977), in a brief review of Saharan dust deposition over the Alps, cited Glawion (1939) who reported the chemical composition of dust from this region to consist of up to 75% SiO_2, 25% Fe_2O_3, 15% Al_2O_3, 5% CaO, and 3% MgO. Only maximum percentages were reported, thus the total adds to greater than 100 percent.

Soils in which slow accretion of dusts ($< 10\mu m\ yr^{-1}$) has not significantly altered the soil forming process, may still contain up to fifty percent (by volume) dust (Yaalon and Ganor, 1973; Yaalon, 1987). Macleod (1980) examined the red soils and limestone bedrock in the Epirus region of NW Greece. The insoluble residue from the limestone amounted to only 0.15% (w/w). He calculated that dissolution of 130 m of limestone would be required to produce the average 40 cm depth of soil overlying the bedrock in this area. The clay mineral composition of the limestone residues was dominated by illite and quartz, whereas the overlying soils contained a predominance of kaolinite (60-90%) with lesser amounts of mica, vermiculite and quartz (approximately 10% each).The occurrence of chert fragments in the coarse sand fraction of these soils suggested some contribution from weathering of the limestone. Macleod advised that in areas affected by Sirocco-type winds, the possibility of dust accretion should be investigated. Jackson et al. (1982) demonstrated through the use of oxygen isotopes

of quartz, that aerosolic-sized quartz (1-10 μm) in some soils derived from limestones in Italy was the result of eolian processes, suggesting these soils were dominantly eolian in nature. Rapp and Nihlén (1986) identified Saharan dust deposition in the central and eastern portions of Crete and on Mt. Taigetos in the southern Peleponnese of Greece. They cited information from the meteorologist at the airport at Iraklion, Crete, that dust laden storms from the south, with wind velocities of 20-30 m s^{-1} (45-67 mph), occur 5-10 times per year. The storms generally occur in the spring and usually last one to two days. Mineralogical analysis of material collected by Rapp and Nihlén indicated that chlorite, illite, kaolinite and quartz dominated the clay-sized fraction; whereas quartz (75%), calcite and feldspars were identified in the silt-sized components.

Danin et al. (1983) provided additional support for the large contribution of eolian sediments in the formation of Terra Rossa soils in some regions of Israel. They regarded the occurrence of weathering patterns formed by endolithic lichens and cyanobacteria on dolomite surfaces covered by as much as 65 cm of soil as evidence of substantial eolian accumulation. Based on dust deposition rates reported by others, Danin et al. suggested that the Terra Rossa soils they investigated could have formed in about 10^4 years.

Topography also influences the development of soils in many areas exhibiting Mediterranean climates. This is particularly true of Greece. Its geologic setting, in an area of active tectonism, results in intermittent episodes of landform upheaval which greatly influence the course of soil and landscape genesis. Much of Greece lies above 200 m elevation. Physiographically, 72% of the country is within 41 km of the sea; thus, stream valleys are relatively short, with steep gradients (Anastassiades, 1949). As a result of the geomorphic setting, approximately 2/3 of the soils of Greece are sloping, shallow and gravelly. In sloping areas soil erosion tends to keep pace with soil development; thus, the soils in these areas remain pedogenically young (Papadakis, 1985). The interaction of the topographic relationships just described and the Mediterranean climatic conditions outlined earlier results in wide variations in landscape stability, leading to intermittent reinitiation of pedogenic activity.

PEDOGENESIS OF GREEK SOILS

The total land area of Greece is 131,990 km^2. Approximately 30% of this is utilized for agriculture. The remainder is classified as forest land which is covered in part by productive forests of fir (*Abies cephalonia*), pines (*Pinus nigra, P. halapensis,* and *P. brutia*), beech (*Fagus silvatica*) and oak (*Quercus spp.*). The largest portion of the so-called forest land is covered by shrubby vegetation which is not utilized for wood production, but grazed extensively by sheep and goats (Nakos, 1979).

Intensive studies of the soils of Greece have been ongoing for approximately fifty years (Papadakis, 1985). Generalized reviews of Greek soils have been given by Anastassiades (1949), Nakos (1977, 1979, 1984), and Papadakis (1985).

Anastassiades (1949) divided the soils of Greece into two main groups, those formed on limestones and those formed on other rocks. The soils derived from calcareous rocks form two groups that are assumed to be closely tied to the parent material; Terra Rossa, and Rendzina. These would include Rhodoxeralfs, Rendolls and Xerochrepts in the current U.S. soil taxonomy. These two broad soil groups are widespread within Greece. He further stated that a division of the limestones into hard (crystalline) and soft rock types is important. The Terra Rossa form more often on the crystalline limestones, whereas the softer sediments give rise to Rendzina.

According to Nakos (1977) the soils of Greece can be divided into 7 main groups, also based on parent material, which comprise varying proportions of the total land-area of the country. These include; soils developed from hard limestone (32%), soils derived from metamorphic rock, mica schist and gneiss (16%), soils developed from Tertiary deposits of calcareous or siliceous nature (21%), soils derived from flysch deposits (9%), those derived from basic igneous rocks (3%) and alluvial soils, which comprise 17% of the total land-area. The island of Crete is dominated by four of these seven groups; hard limestone, metamorphic rocks, Tertiary deposits and flysch sediments. Given the scale of the map produced by Nakos (1: 500 000) only two regions of Crete (the Messara and the region south and west of Chania) were dominated by alluvial soils.

In describing the forest soils of mainland Greece, Nakos (1979) considered parent material to be the dominant factor of soil formation. He further described the interrelationship of lithology and bio-climatic zones among the forest soils of the Greek mainland (Nakos, 1984); four bioclimatic zones (Mediterranean, sub-Mediterranean, Mountainous and Pseudoalpine) were detailed. These zones varied with elevation and natural vegetation. The climate of the Mediterranean zone was characterized by long, hot, dry summers and mild, cool, wet winters. The pseudoalpine climate consisted of cold, wet winters and cool summers. The sub-Mediterranean and Mountainous zones had climates intermediate to the two extremes. The vegetation types and altitudinal zonation of vegetation on mainland Greece do not appear to occur on Crete (G. Nakos, Pers. Commun., 1991).

Soils formed in the Mediterranean climatic zone on hard limestone and calcareous Tertiary deposits consisted of Chromic Luvisols, Calcic Luvisols, Haplic Phaeozems and Rendzina. Under the sub-Mediterranean zone, the same two parent materials resulted in Chromic Luvisols, Luvic Phaeozems, Chromic Cambisols and Rendzina (Nakos, 1984). Approximate equivalents for these soils in the U. S. soil taxonomy would include: Haploxeralfs and Rhodoxeralfs (Chromic and Calcic Luvisols), Hapludolls (Haplic Phaeozems), Rendolls (Rendzina), Argiudolls (Luvic Phaeozems) and Xerochrepts (Chromic Cambisols).

Greek soils in general accumulate little soil organic matter as a result of the climate. The climate is also responsible for the fact that physical weathering processes predominate over chemical weathering in "modern" Greek soils. Sediments weather to sand- and silt-sized components much faster than to clay sized material. This is especially true of the soils of Crete (Anastassiades, 1949). Leaching is limited in many areas of Greece (Anastassiades, 1949; Papadakis, 1985); at Athens, rainfall available for leaching is approximately 86 mm, at Larissa 106 mm and at Thessaloniki it averages about 81 mm. In some regions, notably northwestern Greece, leaching fractions increase (e.g. 898 mm at Corfu). Most leaching takes place in the winter months when temperatures are low, therefore silica removal is low. The limited leaching also results in little removal of carbonates from Greek soils; thus, calcic horizons are quite common and often begin at the soil surface. In many places evapotranspiration

results in net upward movement of solutes. Due to the generally low content of organic matter and clay, the cation exchange capacity (CEC) of many Greek soils is low (Anastassiades, 1949).

Nevros and Zvorykin (1936 and 1937) reported on some soils of Attica. In their 1936 paper they pointed out the effects of sheet and gulley erosion on soil formation and landscape stability. As a result of the action of erosion they divided the "red soils" of Attica into two groups: those that developed "*in situ*" on stable topography and those that formed in transported parent materials (presumably alluvium and colluvium). The 1937 paper described the genesis of a solonetzic soil in the vicinity of the village of Marcopoulo. This soil occupied a stable landscape position and was free of carbonates to a depth of 70 cm, indicating a past environment of greater precipitation.

A small number of soil and landscape studies connected with Greek archaeological sites have been reported (Wagstaff, 1972; Yassoglou and Nobeli, 1972; Yassoglou and Haidouti, 1978; Haidouti and Yassoglou, 1982; Pope and van Andel, 1984; and van Andel et al., 1986). Yassoglou and Nobeli (1972) reported on the soils of the Bronze-aged sites in the Messenia region of the Southern Pelopennese. The soils of the archaeological site at Nichoria were investigated by Yassoglou and Haidouti (1978). Haidouti and Yassoglou (1982) reported further on the soils of Nichoria. The parent materials at the site consisted of unconsolidated Holocene and Pliocene deposits. The authors noted the development of cambic and argillic horizons in these soils. The cambic B-horizons formed in approximately 900 years; whereas, the development of argillic horizons required 2-3000 years. Preferential illuviation of smectitic clays was deemed responsible for the argillic horizon development. Changes in the ratio of oxalate to dithionite extractable iron were found to be indicative of relative soil age.

Wagstaff (1972) investigated the soils associated with the Bronze-age site at Myrtos. The site lies along the south coast of Crete, west of the city of Ierapetra. The soils were for the most part thin (Entisols and Inceptisols) and related to the parent materials from which they formed. More developed soils (probably Inceptisols) were noted under stands of pine near the site.

Investigations of Cretan soils began as early as 1903 (Chalikiopoulos, 1903 in Bintliff, 1977). Chalikiopoulos noted the intensity of the erosive episodes that are initiated by the Mediterranean rainfall pattern. Nevros and Zvorykin (1939) reported on the soil geography of Crete. These authors presented a general soil map for the island. The soils reflected the nature of the parent material from which they formed. The majority of the soils of Crete are calcareous; this is indicative of the carbonate rocks that compose the core of the parent material of the island. It also reflects the limited degree of leaching experienced by these soils.

CHARACTERISTICS OF THE STUDY AREA

Location

The island of Crete lies between 23° 30' and 26° 20' East longitude and 34° 54' 40'' and 35° 41' 34'' North latitude. It is approximately 258 km long and varies between 11 and 56 km in width. The total land area amounts to approximately 8287 km^2 (Allbaugh, 1953); thus, Crete comprises approximately 6.3 percent of the total area of Greece. The study area was located on the northern end of the isthmus of Ierapetra (Figure 1) and covers an area of approximately 4.4 km^2 extending from Pacheia Ammos south to Vasiliki, east toward Monastiraki, north to the Kavousi road and west to Pacheia Ammos again. The soils have developed on fluvial deposits presumed to be late Pleistocene to Holocene in age (Papastamatioy et al., 1959). The sediments have been reworked by stream waters from the Cha River as well as some smaller tributary streams.

Climate

The climate of Crete is very similar to that of southern Turkey, Cyprus and Israel (Zohary and Orshan, 1965). Precipitation falls primarily from September to May; December and January have the highest rainfall. From May to August rainfall is quite rare. Annual precipitation along the north coast



Figure 1. Location of the Island of Crete in relation to the Greek mainland and general location of the study area. Scale approximate.

decreases from west to east, due to orographic effects, from about 600 mm to around 350 mm. Along the south coast the decrease is from 450 mm to approximately 400 mm (west to east) (Allbaugh, 1953; Zohary and Orshan, 1965). The increase in precipitation with increasing elevation also varies from west to east. In the west, the rate is 100 mm/100 m elevation; whereas, in the east the rate decreases to 50-60 mm/100 m elevation. Rosenan (1965, as cited by Zohary and Orshan, 1965) compared weather data from Crete (up to 900 m elevation) with those from Cyprus. He assumed that the rate of increase in precipitation with increasing elevation (up to 1700 m) was of the same magnitude in both locations. These assumptions allowed him to derive the following equations, taken from Zohary and Orshan (1965):

West Crete: $P = 550 - 1.1h$

West Central Crete: $P = 600 - 0.55h$

Messara Plain and East Crete: $P = 400 - 0.6h$

where P = precipitation (mm).

h = elevation above sea level (m).

The inverse relationship between elevation and rainfall implied by the equations as given in Zohary and Orshan (1965) appears at odds with standard interpretations of rainfall and elevation; thus, they appear to be typographical errors.

Table 1 gives selected rainfall and temperature data for some recording stations near the study area. The adiabatic lapse varies between 0.6 and 0.8 °C/100m elevation, depending upon the source of the information.

The prevailing winds are from the north across the Aegean Sea. They blow strongly enough at times to reduce vegetative growth on exposed areas of the north coast. The north winds are steadiest and provide power for irrigation in some parts of the island. In the spring, the prevailing winds often shift to the south bringing the hot, dry, dust-laden Sirocco from Saharan Africa (Allbaugh, 1953). This variable influx of Saharan dust may be a significant factor in the development of some Cretan soils (Chester et al., 1977; Rapp, 1984; Rapp and Nihlén, 1984; Nihlén and Solyom, 1986).

Geology

Crete represents the exposed southern portion of the Hellenides. It consists of an orogenic overthrust belt constructed primarily during the Late Paleogene to Early Miocene (Fortuin, 1977). The overthrust belt consists of a group of six major thrust slices which represent sediments from three or four paleogeographic provinces. The highest thrust sheet is composed of obducted oceanic crust and/or the derivatives of this material (metamorphosed crust). The estimated thickness of this "pile" is

Table 1. Rainfall, temperature and elevation data for selected locations near the study site. (Sources: Allbaugh, L. G. 1953. Crete, a case study of an under developed area. Princeton Univ. Press. Princeton, NJ. and Zohary, M. and G. Orshan. 1965. An outline of the geobotany of Crete. Israel J. Bot. 14:1-49. Suppl.

Location	Elevation	Rainfall	Mean Temperature (°C)	
	- M asl -	- mm -	Jan.	Aug.
Agios Nicolaos	0	356@		
Sitia	0	356@		
		456.2*		
Ierapetra	0	380@	13.2	27.2
Ierapetra	0	206.8*		
Dry Season		23.4*		
Wet Season		138.4*		
Neapolis	400	720@		

@ data from Zohary and Orshan (1965), 1951-1960.
* data are from Allbaugh (1953), 1894-1929.

approximately 6.5 km, representing an unknown palinspastic width (Kopp, 1978). The nappe pile was constructed by north to south thrusts driven by a progressively expanding diapiric mantle uplift, spreading outward from the Aegean Sea (Baumann et al., 1978).

At present, the island forms the upper plate of a subduction zone undergoing extensional faulting with predominantly vertical movements (Kopp, 1978). The folded rocks are separated from the younger Neogene deposits by an angular unconformity.

During the Early Miocene, Crete and the Cretan Sea were part of an exposed mainland and underwent erosive cycles (Buttner and Kowalczyk, 1978). In Middle Miocene time, a general subsidence led to Crete's incorporation into a basin, resulting in the deposition of predominantly fluvio-lacustrine sequences. Tectonism in Late Serravallian to Early Tortonian times (Table 2) resulted in the general configuration of the island today (Meulenkamp, 1985). Early Miocene sediments are largely marine in origin (Buttner and Kowalczyk, 1978). Transitions between marine and continental facies occurred throughout the Neogene in Crete (Buttner and Kowlaczk, 1978). Pliocene tectonic events resulted in an overall regression and the emergence of nearly the entire island. These movements were defined by north-south and east-west trending faults which largely define the modern contours of Crete (Meulenkamp, 1985).

The Neogene (Miocene and Pliocene) sediments of the Ierapetra region have been studied in detail by Fortuin (1977, 1978). The discussion here of these sediments is derived from these two sources.

The Neogene deposits of the Ierapetra region cover approximately 500 km^2, primarily between the Lasithi Mountains in the west and the Sitia Mountains in the east. The late Cenozoic sediments in this area are more than 1 km in thickness. The rock units represent 8 successive depositional episodes and include 9 formations. The formations from oldest to youngest include: the Mithi Formation (Frm); the Males Frm; Prina Complex; Fothia Frm; Kalamavka Frm; Makrilia Frm; Ammoudhares Frm; Mirtos Frm; and the Pakiamos Frm (Figure 2).

Deposition of the oldest sediments began in Middle Miocene times. The Mithi Frm doesn't occur east of the Ierapetra fault and is presumed to represent the oldest Neogene continental facies on Crete. The Males Frm was in place by the close of the Middle Miocene (12 - 12.5 mya). These sediments are terrigenous clastics deposited in fluvatile to lacustrine environments grading to brackish-shallow marine

Table 2. Geologic timescale for the upper Phanerozoic eon. (Source: Faure, G. 1986. Principles of isotope geology. 2nd Edition. J. Wiley, New York, NY.)

Era	Period	Epoch	Age	Age of Boundary (Ma)
Cenozoic	Quaternary	Holocene		
		Pleistocene	Calabrian	0.01
	Neogene (Tertiary)	Pliocene	Piacenzian	1.6
			Zanclean	3.4
		Miocene	Messinian	5.3
			Tortonian	6.5
			Serravallian	11.2
			Langhian	15.1
			Burdigalian	16.6
			Aquitanian	21.8
	Paleogene (Tertiary)	Oligocene	Chattian	23.7
			Rupelian	30.0
		Eocene	Priabonian	36.6
			Bartonian	40.0

conditions by the close of this depositional episode. The Males Frm represents the oldest Neogene marine strata on Crete.

Deposition of the Fothia and Kalamavka formations, the Prina Complex and a portion of the Makrillia Formation occurred between approximately 12.5 and 10 mya (Middle to Late Miocene). The Prina Complex consists of stratified breccias, breccio-conglomerates and conglomerates of continental origin. The largest part of this formation originated from the pre-Neogene Tripolitza limestones. The Fothia Frm consists of poorly rounded polymict conglomerates with sandy and marly intercalations. The formation occurs only east of Ierapetra. The Kalamavka Frm contains alternating marls and regularly stratified calcareous marine sandstones. At various levels conglomeratic channel-fills, pebbly mudstones and large olistoliths occur. The Kalamavka Frm, in contrast to the earlier rock units, consists primarily of fine-grained clastic marine sediments containing alternating bluish gray marls and dark gray calcareous sandstones. A section of this formation outcrops near the town of Vasiliki, within the study area (Figure 1). The Makrillia Frm consists of approximately 450 m of fossiliferous, bluish-gray marls and graded, laminated sands (interpreted as turbidites). Deposition of the Makrillia Frm spanned two sedimentary episodes. Early deposition occurred early in Late Miocene time, whereas later deposition continued into the middle Late Miocene (approximately 10.5 to 9.5 mya). Deposition of the Ammoudhares Frm followed the close of the Makrillia Frm (approximately 9.5 mya). The Ammoudhares Frm is composed of bioclastic calcarenites and marls. The formation typically consists of alternating beds of marl and bioclastic limestones. This formation also outcrops near the village of Vasiliki. The Mirtos formation consists of heterogeneous sediments composed of gypsum, white and greyish marls, marl breccias and sands. The formation occurs in a narrow band along the south coast.

Deposition of the Pakhiamos Frm along the north coast began near the Mio-Pliocene boundary (approximately 6.8 mya). The formation consists of non-fossiliferous, terrigenous-clastic deposits near its base. Following this it becomes primarily whitish algal limestone and whitish marl breccia. The formation occurs only in scattered outcrops along the north coast, where it unconformably overlies pre-

Neogene rocks or conglomerates of the Prina Complex. It was named for the village of Pacheia Ammos, the type section being only 1 km NW of the village. Deposition of this formation occurred in a quiet open marine environment and continued from the beginning of the Pliocene up to approximately the beginning of Late Pliocene times (approx. 4.25 mya).

Near the beginning of the Late Pliocene, active tectonism resulted in uplift of the Ierapetra region. The interior portions of the area probably emerged first. This resulted in distinctly different depositional environments for the north and south coasts with calcareous deposits found in the north and beach deposits and nearshore sands and marls being deposited in the south.

Quaternary-aged sediments in the region include bioclastic limestones, terrigenous clastics, and rockfalls and debris slides. The bioclastic limestones occur throughout portions of the Ierapetra region, including prominent outcrops near Episkopi and Vasiliki. These sediments consist of 2 to 10 m of whitish, grain-packstones of biogenic origin which overlie pre-Neogene or Neogene rocks in an angular unconformity. Near the village of Pirgos along the north coast, west of Pacheia Ammos, the Quaternary limestones are largely composed of marine algal remains. These sediments range in elevation from 160 to 240 m with a gentle northward dip.

Conglomeratic terraces composed of terrigenous clastic sediments are found primarily along the south coast and inland along the isthmus, north of Ierapetra. These terraces are absent along the north coast. The terraces are considered younger than the limestones based on observations east of Ierapetra (Fortuin, 1978). The most outstanding Holocene sediments are represented by the large debris fans associated with the Ierapetra fault scarp.

Soils

The soil survey of the European communities (Commission of the European Communities, 1985), published at a scale of 1:1 000 000, classifies the soils of the study area as Eutric Lithosols (map unit # 47). This map unit consists of 50 % Eutric Lithosols and rock outcrop; 20 % Eutric Cambisols; 20 % Chromic Luvisols and includes other Lithosols, Chromic Cambisols and/or thin

Luvisols. The map utilizes the FAO soil classification system. Equivalent soil groups in the U.S. taxonomic system would include: Lithic subgroups for a variety of great soil groups, most likely those of the Inceptisol and Alfisol orders, (Eutric Lithosols); Eutrochepts without free carbonates in the cambic horizon, (Eutric Cambisols); and Haploxeralfs and Rhodoxeralfs, (Chromic Luvisols).

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PART 2. SOIL AND LANDSCAPE GENESIS IN CALCAREOUS HOLOCENE ALLUVIAL SEDIMENTS IN EASTERN CRETE

LOCATION

The island of Crete lies between 23° 30' and 26° 20' East longitude and 34° 54' 40'' and 35° 41' 34'' North latitude. It is approximately 258 km long and varies between 11 and 56 km in width. The total land area amounts to approximately 8287 km^2 (Allbaugh, 1953); thus, Crete comprises approximately 6.3 percent of the total area of Greece. The study area was located on the northern end of the isthmus of Ierapetra (Figure 1) and covers an area of approximately 4.4 km^2 extending from Pacheia Ammos south to Vasiliki, east toward Monastiraki, north to the Kavousi road and west to Pacheia Ammos again. The soils have developed on fluvial deposits presumed to be late Pleistocene to Holocene in age (Papastamatioy et al., 1959). The sediments have been reworked by stream waters from the Cha river as well as some smaller tributary streams. The area is characterized by level to gently undulating topography; however, slopes become steeper along the sides of the local drainages.

CLIMATE

The climate is Mediterranean, with cool moist winters and hot dry summers. The rainy season extends from October through March. Approximately seven eighths of the yearly precipitation falls during this period. Average precipitation at Sitea (east of the study area) for the period 1894 to 1929 was 457 mm (Allbaugh, 1953). Zohary and Orshan (1965) gave rainfall at Sitea for the period 1951-1960 as 356 mm. At Ierapetra (11 km south of the study area) Allbaugh (1953) listed average rainfall as 206 mm. Wernstedt (1972) listed precipitation at Ierapetra, for an unspecified 35 year period, as 207 mm. At Aghios Nicolaos (approximately 15 km NW of the study area) mean annual rainfall between 1951 and 1960 was 356 mm (Zohary and Orshan, 1965). The prevailing winds are from the north across the Aegean Sea. They blow strongly enough at times to reduce vegetative growth on exposed areas of the north coast. In the spring, the prevailing winds often shift to the south bringing the hot, dry, dust-laden Sirocco from Saharan Africa (Allbaugh, 1953; Mariolopoulos, 1961). This variable influx of Saharan dust may be a significant factor in the development of some Cretan soils (Rapp,

1984; Rapp and Nihlén, 1986; Nihlén and Solyom, 1986). Soil temperature data were only available for Athens and Thessaloniki. At depths less than 25 cm, maximum soil temperatures occurred in July; the minimum occurred in January. Below 25 cm, maxima and minima were delayed by one month. Below 1 meter depth there was no diurnal variation; only an annual variation (Mariolopoulos, 1961).

Evaporation measurements from Athens indicated that average annual evaporation amounted to 1616 mm. Maximum evaporation occurred in July; whereas, the minimum occurred in December (Mariolopoulos, 1961). A comparison of average annual precipitation and evaporation at Athens yielded a moisture deficit of 1207 mm. Papadakis (1985), however, stated that the leaching fraction for Athens is 86 mm. This discrepancy is likely related to the seasonality of rainfall. Because the maximum rainfall occurs during October to March or April, when temperatures and evaporation are low, sufficient soil moisture must accumulate to result in some leaching.

From a review of the data regarding the paleoclimate for the region surrounding Crete (Buckley et al., 1982; Farrand, 1971; Gat and Margaritz, 1980; Mariolopoulos, 1961; Thiede, 1978; Thunnel, 1979; and Wright, 1968) the following conditions may be infered for the eastern Mediterranean from approximately 20,000 years before present (BP) to modern times: (i) lower temperatures (by 5-7°C) and increased effective precipitation for the last glacial maximum; (ii) wider seasonality of temperatures during the last glacial; (iii) a gradual warming from the end of the latest Pleistocene to approximately 4700 BP, culminating in a climatic optimum; (iv) a slight cooling from the climatic optimum, resulting in conditions similar to those of the modern eastern Mediterranean since approximately 4000 BP.

Based on the paleoclimatic data, the soils of the eastern Mediterranean region have formed under the influence of varying climatic conditions. Cooler temperatures and increased effective precipitation during the late glacial and early Holocene probably allowed weathering to occur at faster rates than it may now. The onset of "modern" climatic conditions, obtained since 4000 BP, may have had little influence in altering the degree of weathering and soil development that could have occurred in the previous 16,000 years; thus some soils of the region are probably relict.

MATERIALS AND METHODS

Field Methods

The soils were sampled from preexisting exposures. Efforts were made to minimize the influence of contaminants by choosing recent exposures and removing the weathering faces by excavation. The soils were described using methods outlined in the Soil Survey Manual (Soil Survey Staff, 1981). Bulk samples of each horizon were collected from four pedons representing three landscape positions; an upland shoulder (Profile 1), a lower backslope (Profile 2), and two profiles located in stable uplands (Profiles 3 and 4) (Figure 1). A soil map of the study area was prepared using 1:15,000 scale aerial photographs. Map units were delineated at the Subgroup level of Soil Taxonomy in an effort to differentiate landforms and parent materials and to illustrate the interrelationships between these factors.

Laboratory Methods

Soils were air dried and crushed with a wooden rolling pin to pass a 2 mm sieve. Coarse fragments were separated into fractions > 4.75 mm and 2 to 4.75 mm. These were weighed and volume percent calculations were performed using standard USDA-SCS methods. The fine-earth fraction was subsampled and a portion was ground to pass an 80 mesh sieve. This material was utilized for some of the chemical analyses.

The mineralogical composition of the parent material components was determined using x-ray diffraction and microscopic techniques. Samples of the dolostone gravels from horizons in all four soils were randomly chosen by hand, composited for each soil, finely ground after removal of secondary carbonate accumulations and scanned as random powder mounts using a Scintag XDS-2000 diffractometer and Cu $K\alpha_1$ radiation. Samples of the phyllite material were collected in the upland source-area east of the study sites. Following gentle crushing in a steel mortar, the phyllite material was dispersed using a combination of Na-hexametaphosphate and Na-carbonate. Clay-sized materials

collected following centrifugation (Jackson, 1969) were oriented using a filter-membrane peel technique (Drever, 1973) and scanned using a Phillips model 2500 diffractometer equipped with a graphite crystal monochromator and Cu Kα radiation. Silt and sand-sized components from the phyllite were scanned as random powder mounts, and examined microscopically (Part 3, this dissertation).

Particle-size analyses were performed using the pipette method (Kilmer and Alexander, 1949). One group of samples was treated with 1 M Na-acetate buffered at pH 4.5 to remove the carbonates. Analyses of this material were not representative of the soils as sampled in the field. Because the sediments and soils consisted primarily of dolostone and limestone gravels (20 to 80%), it was decided to determine the particle-size distributions on samples from which the carbonates were not removed (Shields and Meyer, 1964). Pretreatments on these samples consisted only of hydrogen peroxide oxidation of organic carbon from surface samples. No flocculation was observed in any of the sedimentation cylinders; thus, the presence of the carbonates did not appear to affect the results. The sand fraction was dry-sieved into very coarse, coarse, medium, fine and very fine components. The silts were split into fine (2-20 μm) and coarse (20-50 μm) fractions. The fine-clay fraction (< 0.2 μm) was pipetted following centrifugation (Jackson, 1969; Soil Survey Staff, 1984).

Total carbon was determined on $<$ 80 mesh samples using a Leco CR-12 dry combustion furnace. Calcium carbonate equivalent was determined using $<$ 80 mesh samples and the method of Williams (1949). Calcite and dolomite contents were estimated based on the carbonate equivalent and the results of total analyses from each horizon and the dolostone parent materials. Organic carbon was calculated as the difference between total and inorganic carbon.

Dolostone coarse-fragments, saved after sample preparation, were collected as outlined earlier, cleaned to remove secondary carbonate accumulations, ground to pass a 100 mesh sieve and subjected to total analysis using a combination of aqua regia-hydrofluoric acid-boric acid (Nadkarni, 1984). Portions of the phyllite material and soil samples from each horizon were subjected to the same dissolution procedure. A National Bureau of Standards (NBS) dolomite (SRM-88) and two clay mineral standards from the Clay Minerals Society collection (KGa-1, well crystallized and Syn-1, synthetic

Mica-Montmorillonite) were included in the total analysis scheme. This was done to assess the composition of the dolostone relative to a known standard and to provide a check on the recovery of silica from the phyllite and soils. The elemental composition of these materials was determined using inductively coupled plasma (ICP) spectroscopy.

Soil pH was measured in a 1:1 mixture with deionized water and in 2:1 (solution to soil) $CaCl_2$ suspensions. Cation exchange capacities were measured using a modification of the method of Bower et al. (1952). Index ion saturation and replacement were accomplished using a mechanical vacuum extractor (Holmgren et al., 1977). Sodium in the NH_4OAc extracts was determined by atomic emission spectrometry. Extractable bases were determined using 0.25 M $BaCl_2$-TEA (triethanolamine) buffered at pH 8.1 (Mehlich, 1953). This procedure was also modified for use with the vacuum extractor. Calcium and Mg, were determined using atomic absorption spectrophotometry. Na and K in the extracts were determined using atomic emission spectroscopy. To correct the extractable bases, portions of the < 2 mm soils were extracted with deionized water. The water extracts were prepared using a 1:1 mixture of soil and distilled-deionized water (Hogg and Henry, 1984). The samples were mixed thoroughly and allowed to equilibrate for 24 hours. The mixture was gravity filtered through Whatman Number 2 paper and stored for analysis. Electrical conductivity was measured using a conductivity bridge equipped with a dip cell. Solution pH was measured using a Ross combination electrode. The chemical composition of the water extracts was determined using ICP-spectroscopy and ion chromatography. Bicarbonate and carbonate concentrations in the extracts were calculated based on solution pH and atmospheric P_{CO2} using a Personal Computer-based geochemical equilibrium program.

RESULTS AND DISCUSSION

Soil-Landscape Relationships

The study area was dissected by two major drainages, the Cha River, which cuts across the middle of the area, and an unnamed stream which was located along the western margin (Figure 2).

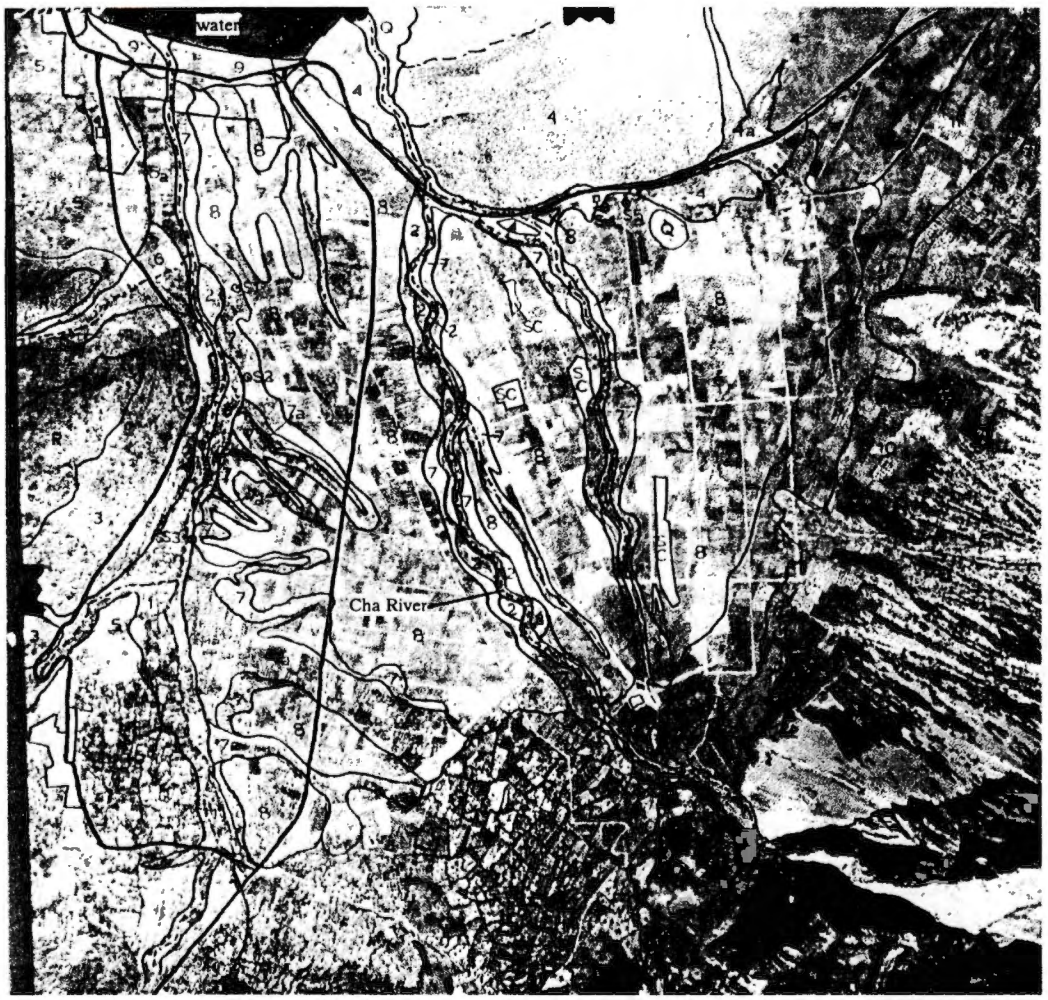


Figure 2. Soil map of the study area. Map Unit designations are given in Appedix D. Soil profiles sampled in the study are located at points S-1 through S-5 on the map. North is to the top of the page.

Two minor drains in the eastern portion of the area appear to have been abandoned as a result of stream piracy by the current Cha River channel. The eastern-most of the two minor drains headed at the base of the scree deposits associated with the Ierapetra Fault. Currently, this drainage probably carries flow in the springtime, and then only in very moist years, because the channel was poorly developed and overgrown with vegetation. The stream terraces along the Cha River and the western drainage (Figure 2, Map Unit 2) were probably formed in response to changes in the baselevel of both streams. The possible timing for these is discussed later.

Major soil taxa identified consisted primarily of Calcixerollic and Fluventic Xerochrepts (Map Units 7 and 8). These taxa were located in stable upland positions and on sloping landscapes. Those soils located in shoulder and backslope positions exhibited varying degrees of erosion and deposition. Due to the alluvial nature of the parent materials, irregular distributions of organic carbon were common in many of these soils. The degree to which calcic horizon development had proceded tended to be the determining factor in placing a soil in a taxonomic unit; thus, the distribution of the fluventic or calcixerollic subgroups was not easily predicted by landscape position.

Headward erosion and landscape dissection were greatest on the western margin of the study area. The western edge represented the furthest extent of alluvial deposition; thus, the sediments were probably thinnest there. The high slopes above, and to the west of this area were relatively parallel. Rainfall on these steep, uniform slopes would likely yield a large amount of runoff which would have added to the volume and intensity of streamflow in the drainage at their base. This added flow would have increased erosion along the base of the alluvial sediments promoting the development of headward erosion. Localized alluvial deposits in the base of these headwardly eroding drains (Figure 2, Map Unit 7a) were intensively cultivated. Erosion from the side-slopes along the drains, and from the drains themselves, was being controlled by agricultural terracing. Where these terraces were well maintained, modern erosion was minimal. In places where the terraces had fallen into disuse however, soil erosion had breached the terrace walls and created small, very local alluvial/colluvial fans. This observation is in-line with similar observations made by van Andel et al. (1986) in the southern Argolid.

Soil Morphology and Classification

The soils were developed in alluvial sediments derived from a combination of Triassic dolostones, Permian-Carboniferous phyllites, and dolostone and limestone breccias and conglomerates of the Prina Complex (Papastamatioy et al., 1959; Fortuin, 1977, 1978). The Prina Complex conglomerates and breccias were formed primarily from materials derived from Pre-Neogene, Tripolitza limestones (Fortuin, 1977, 1978). Abbreviated morphological descriptions for all four soils are given in Table 1. All of the soils exhibited red-colored, clay-enriched surface horizons, indicative of the greater degree of weathering which has occurred in these layers. The lighter hues and higher color values expressed in the lower horizons of Profile 1 were the result of translocation of carbonates causing color paling similar to that noted by Harden and Taylor (1983). This soil contained the most highly developed calcic horizon. Red colors extended to greater depth in Profile 2 as a result of deposition of "pre-weathered" materials from upslope. The gradual increase in color value from 5 in the surface to 7 in the deeper horizons was also indicative of the translocation of carbonates in this soil. Profiles 3 and 4, located in the more stable upland positions, exhibited redder hues over greater depths than did Profiles 1 and 2. The lack of sufficient fine material in the lower portions of Profiles 3 and 4 precluded the determination of color in these horizons. Colors which were observable were the result of iron and carbonate stains and accumulations on gravels and larger sand grains.

Soil structure in the surface horizons was best expressed in the two soils occupying the stable landscape positions. Well expressed structure was also noted in Profile 2, probably as a result of deposition of relatively clay-rich sediments from upslope. Coarse fragment contents were lower in surface horizons than in subjacent layers. Physical and chemical weathering processes have removed or reduced the size of these particles, which were composed primarily of dolostone fragments.

Profiles 2 and 3 were classified as sandy-skeletal, carbonatic, thermic Calcixerollic Xerochrepts. The irregular distribution of organic carbon in Profiles 1 and 4 resulted in these soils being classified as sandy-skeletal, carbonatic, thermic Fluventic Xerochrepts (Soil Survey Staff, 1990).

Table 1. Profile descriptions for the four soils studied. Abbreviations are as given in the Soil Survey Manual (Soil Survey Staff, 1981) except as noted.

Horizon	Depth	Color+		Texture	Structure	Boundary	Consist.	
	- cm -	- moist -	- dry -				- moist -	- dry -
Profile 1								
Ap	0-16	7.5YR 4/4	7.5YR 6/4	gSL	1msbk	CW	fr	h
A/Bk	16-28	(A) 7.5YR 4/4	7.5YR 6/4	gvSL	1m & fsbk	CW	fr	h
		(Bk) 7.5YR 5/4	10YR 6/3					
Bk1	28-46	7.5YR 7/4	7.5YR 7/3	gvSL	0 m	CW	fi	vh
Bk2	46-61	10YR 7/3	10YR 7/3 & 8/2	gSL	0 m	CW	fi	h
Bk3	61-74	10YR 7/3	10YR 7/3 & 8/2	gxSL	0 m	AW	fi	l
Bk4m	74-96	10YR 7/3	10YR 7/3 & 8/2	gxSL	0 m	AW	efi	l
Bk5	96-114	10YR 7/3	10YR 8/2 & 7/3	gvSL	0 m	CW	efi	l
Bk6m	114-132	10YR 7/3	10YR 8/2	gvSL	0 m	AW	efi	l
Bk7m	132+	10YR 7/3	10YR 8/2	ND	0 m	_	efi	eh
Profile 2								
A	0-16	7.5YR 3/4	7.5YR 5/4	gL	2fsbk	CW	fr	h
Bw	16-31	5YR 3/4	7.5YR 5/4	gL	1&2 fsbk	AW	fr	h
Bk1	31-50	7.5YR 5/4 & 5/6	7.5YR 6/4	gxSL	0 m	CW	l	h
Bk2	50-68	7.5YR 6/6	7.5YR 7/4	gvSL	0 sg	CW	l	h
Bk3	68-78	7.5YR 6/4	7.5YR 7/4	gvSL	0 sg	CW	l	h
Bk4	78-108	7.5YR 6/4	7.5YR 7/4	gvSL	0 sg	CW	l	h
Bk5	108+	7.5YR 6/4	7.5YR 7/4	gvSL	0 sg	-	l	h

Table 1 (continued)

Horizon	Depth	Color+		Texture	Structure	Boundary	Consist.	
	- cm -	- moist -	- dry -				- moist -	- dry -
Profile 3								
Ap	0-14	5YR 3/4	5YR 5/4	gCL	2msbk	CS	fr	sh
Bw	14-27	2.5YR 3/4	5YR 5/4	gCL	2msbk	CW	fr	sh
Bk1	27-35	5YR 5/6	5YR 6/6	gvLS	0 sg	CS	fr	h
Bk2	35-44	5YR 5/6 & 4/6	7.5YR 6/4	gvLS	0 m	CS	sh	vh
BCk1	44-54	10YR 6/4 & 4/6	10YR 6/4	gvLS	0 sg	CW	fr	l
BCk2	54-72	ND	ND	gxLS	0 sg	AW	l	l
C	72-83	ND	ND	gvS/SL	0 sg	-	l	l
Profile 4								
Ap	0-10	5YR 4/4 & 3/4	5YR 5/4	gCL	1 & 2 fsbk	CS	fr	sh
Bw	10-34	5YR 3/4	5YR 4/4	gCL	2 f & msbk	CS	fr	h
Bk1	34-48	5YR 4/6	5YR 4/6 &5/6	gvSL	0 sg	AS	fi	l
Bk2	48-59	ND	ND	gvSL	0 m	AS	fi	l
Bk3	59-74	ND	ND	gvSL	0 sg	AS	fi	l
Bk4	74-91	ND	ND	gvSL	0 sg	CW	fi	h
Bk5	91-112	ND	ND	gxLS/SL	0 m	CW	fi	h
C	112-130	ND	ND	gvSL	0 sg	-	fi	l

+ For some horizons colors were not determinable because of a lack of sufficient fine material. The only color obtainable was derived from individual mineral grains. ND = not determined.

Parent Material Uniformity

In order to evaluate the development of a soil profile it is necessary to define and evaluate the initial status of the parent material (Barshad, 1964). Because the soils in this study formed from parent materials derived from multiple sources, the degree of uniformity or non-uniformity of this material was determined in order to better assess and compare changes in soil profile development among the four soils.

A variety of techniques have been utilized to assess parent material uniformity. Barshad (1964) listed a number of these which have been widely used. Most of these methods are based on the assumption that particular minerals or groups of minerals are resistant to chemical weathering processes and are therefore stable in pedogenic environments. Commonly utilized minerals occur in the heavy fraction of soil separates (S.G. > 2.96) and include zircon, rutile, ilmenite, tourmaline, magnetite and sphene. Quartz has also been used, although it is not considered a heavy mineral. Quantification of these minerals is generally achieved by direct measurement (grain counts) of various particle-size fractions, or by determination of an element specific to a mineral or group of minerals (e.g. Zr for zircon, or Ti for rutile, anatase and/or ilmenite). Because the heavy minerals have been demonstrated not to be stable under all circumstances (e. g. Khan, 1959), a number of other supporting lines of evidence have been suggested to estimate the degree of uniformity of parent materials.

The ratio of various particle-size fractions, calculated on a clay-free basis, has been used by some researchers as a measure of parent material uniformity (Raad and Protz, 1971; Thompson et al., 1981; Ajmone Marsan et al., 1988). In this study, a combination of visual observation, elemental analysis, x-ray diffraction techniques and particle-size ratios were utilized to assess the uniformity of the parent sediments.

Visual observation of the soils and sediments in the field and during sample preparation suggested that the parent materials were similar in lithology. The dominant lithologic components were dolostone, limestone (calcite inclusions in the dolostone and phyllite) and phyllite. Particle-counts of the > 2 mm fractions indicated that the phyllite composed approximately 1 percent of the parent

sediments. Phyllite fragments were identified in the parent sediments and soils throughout the study area, indicating that the sediments have been transported and mixed by fluvial processes across the entire basin.

X-ray diffraction techniques were utilized to determine the mineralogical composition of the parent materials. The dolostones were composed of dolomite which contained quartz and a trace of feldspar (primarily albite). The phyllite consisted of a trioctahedral, ferrous chlorite, mica and kaolinite, as well as quartz and a small quantity of feldspars (Part 3, this dissertation). Separation of the magnetic fraction indicated that only a trace of magnetite was present in both rock types.

Calcium oxide contents of the dolostones averaged 30.79 percent and magnesium oxide averaged 22.27 percent. Analysis of the standard dolomite material yielded 30.49 percent CaO and 22.43 percent MgO. The NBS standard contained 30.49 percent CaO and 21.48 percent MgO (Burgess, 1928). The differences in these oxides between what was analyzed and the published data were 0 and 0.95 percent for CaO and MgO, respectively. Differences between the dolostone and the NBS standard were 0.30 percent and 0.79 percent for CaO and MgO, respectively. These data indicated that the analytical accuracy of this analysis was quite good and that the dolostones were very similar in composition to the standard dolomite.

Various particle-size ratios were calculated to further test the uniformity of the soils and sediments (Table 2). Barshad (1964) suggested that this method was as reliable as many of the other methods and was particularly useful in sedimentary materials. Ratios were calculated based on uncorrected particle-size distributions and also on a clay-free basis. Because of the coarse-textured nature of the sediments there were no differences in the ratios; however, data in Table 2 are based on the clay-free calculations.

The ratio of medium to (very coarse + coarse) sand (Harden, 1982) demonstrated the closest agreement among the four locations investigated (Table 2). This ratio ranged from 0.14 to 0.16, on a whole-soil basis. The standard deviations were within 0.01, and coefficients of variation (CV) were all

Table 2. Clay-free particle-size ratios from Profiles 1 through 4.

Horizon	Ratio			
	MS/(VCOS+COS)[+]	FS/Silt[@]	Silt/Sand	Fine Silt/Total Silt
Profile 1				
Ap	0.20	0.38	0.57	0.48
A/Bk	0.18	0.24	0.65	0.44
Bk1	0.14	0.19	0.63	0.41
Bk2	0.16	0.20	0.70	0.39
Bk3	0.09	0.34	0.28	0.55
Bk4m	0.11	0.34	0.41	0.50
Bk5	0.12	0.40	0.30	0.46
Bk6m	0.12	0.29	0.39	0.32
Bk7m	ND	ND	ND	ND
Mean	0.14	0.30	0.49	0.44
Std. Dev.	0.04	0.08	0.17	0.07
CV	28.6%	26.8%	33.8%	16.2%
Profile 2				
A	0.18	0.29	0.82	0.54
Bw	0.22	0.36	0.73	0.54
Bk1	0.14	0.47	0.35	0.55
Bk2	0.17	0.46	0.41	0.55
Bk3	0.15	0.40	0.42	0.55
Bk4	0.12	0.35	0.44	0.53
Bk5	ND	ND	ND	ND
Mean	0.16	0.39	0.53	0.54
Std. Dev.	0.04	0.07	0.20	0.01
CV	21.9%	17.7%	36.9%	1.5%

Table 2 (continued)

Horizon	Ratio			
	MS/(VCOS+COS)+	FS/Silt@	Silt/Sand	Fine Silt/Total Silt
Profile 3				
Ap	0.16	0.26	0.69	0.59
Bw	0.15	0.31	0.58	0.57
Bk1	0.08	0.61	0.10	0.48
Bk2	0.19	1.36	0.09	0.45
BCk1	0.17	0.84	0.13	0.41
BCk2	0.24	1.18	0.15	0.43
C	0.16	1.84	0.07	0.41
Mean	0.16	0.91	0.26	0.48
Std. Dev.	0.05	0.58	0.26	0.07
CV	29.9%	63.7%	100.1%	15.5%
Profile 4				
Ap	0.17	0.23	0.81	0.56
Bw	0.18	0.29	0.73	0.62
Bk1	0.17	1.23	0.10	0.60
Bk2	0.12	1.09	0.09	0.45
Bk3	0.17	1.79	0.06	0.30
Bk4	0.16	2.14	0.05	0.36
Bk5	0.09	1.17	0.07	0.42
C	0.08	1.35	0.05	0.48
Mean	0.14	1.16	0.25	0.47
Std. Dev.	0.04	0.66	0.33	0.11
CV	28.5%	56.7%	130.1%	24.3%

+ MS/(VCOS + COS) = Medium Sand/ (Very Coarse + Coarse Sand).
@ FS/Silt = Fine Sand/Silt.
ND = not determined.

within 8 percent (absolute) of each other. When taken as an aggregate the mean ratio was 0.15 (n=29) with a CV of 26.6 percent.

The ratio of fine sand to total silt (Ajmone Marsan et al., 1988) varied considerably among the four profiles, but based on the CV values this ratio suggests that there were two populations of sediments. These two modes occur on opposite sides of the study area. Profiles 1 and 2 exhibited an overall mean (n=14) of 0.34 with a CV of 25.5 percent. Profiles 3 and 4 exhibited an overall mean (n=15) of 1.05 with a CV of 58.4 percent. The variation noted here is probably related to the location of the pedons within the study area. Profiles 1 and 2 occurred along the western edge of the study area and are associated with a stream which drains a region of Prina Complex rocks to the west of that area. Profiles 3 and 4 are more closely related to the drainage of the Cha River, which drains an area dominated by the dolostones and phyllites. Differences in the fluvial regimes and parent rocks of these two drainages could explain the bimodal nature exhibited by this ratio.

Total silt to total sand ratios also implied two populations. Profiles 1 and 2 exhibited means within 0.04 percent of each other; with CV's ranging from 33.8 to 36.9 percent. Profiles 3 and 4 had means of 0.26 and 0.25, respectively. The CV's were 100 percent for Profile 3 and 130 percent for Profile 4. The high silt content of the upper two horizons appeared to be responsible for the wide variation of this ratio in both soils. If the two surface horizons were excluded from the calculations, the mean for Profile 3 was reduced to 0.11 with a standard deviation of 0.03 and CV of 29 percent. Exclusion of the two surface horizons in Profile 4 yielded a mean of 0.07, with a standard deviation of 0.02 and CV of 30 percent. These CV values are closer to those of Profiles 1 and 2, although they were still somewhat different.

Fine silt to total silt ratios were similar in all four profiles. The highest values of this ratio generally occurred in the surface horizons of all four soils. Two hypotheses could explain this: (i) the proportion of fine silt in surface horizons is greater due to eolian additions or (ii) physical weathering processes have produced more fine silt particles in surface horizons. The generally close agreement of this ratio in the surface horizons of all four soils suggests that eolian additions are probably the best

explanation. The distribution of this ratio in Profile 2 is rather uniform with depth. This most likely resulted from the landscape position this profile occupied. Deposition of eroded materials in this position should reflect the nature of the eroded sediments. Because silt-sized particles are easily eroded, they should comprise a large proportion of the depositional materials. If fine silt makes up the largest portion of the total silt in surface horizons (as demonstrated earlier) then deposition of such material would result in a relatively constant value of this ratio in depositional positions. The higher values of this ratio in the Bk3 and Bk4m horizons of Profile 1 probably reflect the presence of a buried surface horizon. This seems plausible given the close agreement of the ratio in these two horizons when compared with the modern soil surfaces. Other physical and chemical data supported the presence of this buried surface, and will be discussed later.

With the exception of the medium to (very coarse + coarse) sand ratio, the particle-size ratios demonstrated the variability one would expect in coarse-textured alluvial sediments. Because physical weathering processes dominate these soils (Anastassiades, 1949; Part 3, this dissertation) one would expect wider variation in particle-size ratios calculated for the finer fractions. From these data, the ratio of medium to (very coarse + coarse) sand appeared to be the best physical measure of the uniformity of these sediments.

Selected total elemental compositions of all horizons from each profile and the parent sediments are listed in Table 3. The dolostone materials contained only a trace of titanium and zirconium. The phyllite contained trace amounts of zirconium, but contained an average of 929 mg kg^{-1} Ti (0.16% TiO_2). Both parent materials contained less than 5.0 mg kg^{-1} phosphorous. As a result, the elemental ratios commonly utilized in parent material uniformity analyses could not be calculated. Inspection of the data for the parent materials and soils suggested the use of a number of other such ratios for the purpose of assessing the uniformity of the soils and sediments.

The two ratios chosen for this purpose were those of barium to lead (Ba/Pb) and calcium to strontium (Ca/Sr). Barium and lead were chosen because both elements are heavy metals and should

Table 3. Selected total elemental analysis for Profiles 1 through 4. ND represents analyses not determined.

Horizon	Al_2O_3	Ba	K_2O	Na_2O	Pb	SiO_2	Sr	TiO_2	ZrO_2	Ba/Pb	Ca/Sr
	%	mg kg^{-1}	%	%	mg kg^{-1}	%	mg kg^{-1}	%	%		
Profile 1											
Ap	4.10	83.7	0.61	0.21	21.4	32.67	92.3	0.087	0.001	4.35	4274
A/Bk	2.68	46.7	0.43	0.14	12.3	25.35	73.7	0.037	tr	3.88	7202
Bk1	1.23	19.4	0.18	0.08	19.6	6.93	58.3	tr	tr	1.04	10633
Bk2	1.22	19.6	0.19	0.07	21.8	6.59	51.3	tr	tr	0.90	12364
Bk3	2.27	41.5	0.39	0.13	29.5	26.51	87.9	0.017	tr	0.74	5310
Bk4m	3.14	53.2	0.53	0.15	29.2	29.41	88.9	0.024	tr	2.01	5164
Bk5	1.68	27.8	0.29	0.11	13.3	18.16	81.8	0.005	tr	3.11	6337
Bk6m	1.45	22.8	0.27	0.13	11.1	18.71	69.1	0.005	tr	2.21	8326
Bk7m	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Profile 2											
A	7.75	161.1	1.19	0.38	55.2	37.37	84.0	0.197	0.003	2.92	3160
Bw	8.06	158.1	1.18	0.35	36.5	37.88	79.7	0.171	0.002	4.33	3356
Bk1	3.24	55.7	0.54	0.14	25.7	21.32	96.7	0.042	tr	2.17	5001
Bk2	2.51	39.5	0.43	0.17	25.9	21.62	102.0	0.040	tr	1.53	4851
Bk3	2.39	38.0	0.43	0.13	23.7	19.52	98.5	0.028	tr	1.60	5364
Bk4	2.85	44.9	0.48	0.18	18.3	23.65	93.8	0.036	tr	2.46	5284
Bk5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 3 (continued)

Horizon	Al_2O_3	Ba	K_2O	Na_2O	Pb	SiO_2	Sr	TiO_2	ZrO_2	Ba/Pb	Ca/Sr
	%	mg kg^{-1}	%	%	mg kg^{-1}	%	mg kg^{-1}	%	%		
Profile 3											
Ap	12.29	242.2	1.60	0.42	61.3	37.52	80.0	0.298	0.007	3.95	2014
Bw	11.34	223.4	1.47	0.42	68.4	42.62	82.0	0.264	0.006	3.27	2363
Bk1	2.94	52.6	0.47	0.17	33.3	19.54	99.1	0.036	0.001	1.58	4353
Bk2	2.19	36.7	0.37	0.17	32.2	18.42	99.0	0.020	0.001	1.14	4460
BCk1	2.65	44.4	0.48	0.17	11.2	19.97	95.1	0.022	tr	3.98	4493
BCk2	2.74	43.2	0.45	0.34	11.4	25.58	96.3	0.026	0.002	3.80	4410
C	1.76	29.4	0.32	0.13	19.1	20.67	96.2	0.013	tr	1.54	4589
Profile 4											
Ap	12.61	264.6	1.68	0.53	44.6	35.92	79.3	0.325	0.007	5.93	1639
Bw	12.50	261.0	1.66	0.49	50.4	46.07	85.4	0.322	0.007	5.18	1733
Bk1	3.78	63.7	0.56	0.17	33.3	29.81	102.2	0.064	0.001	1.91	3948
Bk2	2.64	45.4	0.45	0.14	23.1	21.30	104.3	0.032	tr	1.96	4321
Bk3	1.36	23.3	0.25	0.11	4.5	13.38	107.0	0.012	tr	5.15	4330
Bk4	1.48	25.4	0.26	0.11	22.1	14.50	107.7	0.010	tr	1.15	4181
Bk5	1.85	50.1	0.32	0.11	40.5	30.18	107.6	0.010	tr	1.24	4234
C	1.18	20.6	0.21	0.10	39.1	9.69	100.4	0.007	tr	0.53	4656
Dolostone	0.15	3.4	0.02	0.04	25.6	3.09	67.2	tr	tr	0.12	7191
Phyllite	17.68	457.8	3.76	1.12	102.2	47.05	22.2	929.0	tr	4.86	356

not therefore be removed to any large extent by weathering reactions in these highly calcareous soils. Calcium and strontium are both constituents of dolostones. The molar ratio of these two elements in dolostones varies widely depending upon the age of the rock. Mesozoic dolostones generally contain an average of 100 to 200 mg kg^{-1} Sr , and are non-stoichiometric with respect to calcium, having about five mole percent excess Ca (Dr. L. S. Land, Pers. Commun., 1992). Because the dolostones were the dominant rock-type in the parent sediments, the ratio of these two elements in the soils should provide an indication of the influence of the dolostones and the degree of uniformity among the four soils.

The Ba/Pb ratio of the dolostone was 0.12 (Table 3), (n = 6) with a standard deviation of 0.03 and a coefficient of variation (CV) of 21.9 percent. The same ratio in the phyllite material was 4.86. No meaningful standard deviation could be calculated for this ratio because it was based on only two analyses. The means of the Ba/Pb ratio for each soil on a whole-profile basis were 2.28, 2.50, 2.75, and 2.88 for Profiles 1 through 4, respectively. Coefficients of variation for this ratio ranged from 41.5 to 75.1 percent.

The Sr content of the dolostones varied from 62 to 73 mg kg^{-1}. These values are somewhat lower than the average content in Mesozoic dolomites listed earlier. The molar ratio of Ca to Mg in the parent dolomites was 0.99 (standard deviation = 0.006, CV = 0.63 percent); thus, they appear to be very close to stoichiometric dolomites. The molar Ca/Sr ratio in the parent dolostones averaged 7191, with a standard deviation of 429 and CV of 5.96 percent. The Ca/Sr ratio of the phyllite was 356. The Sr content of the soils ranged from 79 to 110 mg kg^{-1}. The increase in Sr content in the soils probably reflected the influence of the phyllite component, which contained an average of 22 mg kg^{-1} Sr. The Ca/Sr ratio in the four soils averaged 7451, 4502, 3812, and 3630 for Profiles 1 through 4, respectively. The CV's ranged from 20 to 36 percent.

There is little agreement in the literature about the magnitude of the difference in any ratio sufficient to constitute a lithologic discontinuity. Chapman and Horn (1968) chose a value of 100% difference in Ti/Zr between any two horizons in a profile. Drees and Wilding (1973) suggested a shift of 60% for the same ratio in Wisconsinan-aged outwash materials. A study by Murad (1978) suggested

(FC/CC) were calculated by subtracting the measured fine clay from the total clay and dividing the fine clay value by this difference. This ratio varied widely in the four soils studied (Figure 4). In Profiles 2 and 4, FC/CC ratios were highest in the surface horizons and generally decreased with depth, suggesting little or no translocation of fine clay. The distribution of this ratio in Profile 3 was lower in the upper horizons and increased to a maximum of 0.55 in the C-horizon. The FC/CC ratios in Profile 1 varied widely with depth. In the upper four horizons the ratio increased from 0.26 to 0.56. It dropped again in the Bk3, to 0.24, and increased to the bottom of the profile. The dual distribution of this ratio in Profile 1 may represent the presence of a buried soil. The total clay content of the Bk3 horizon represented a second maxima within this profile, further suggesting the existence of a paleo-weathering surface. The interpretation of the fine clay coarse clay ratios in these soils is somewhat problematic because the carbonates were not removed prior to particle-size analysis. Clay-sized carbonates were identified in these soils (Part 3, this dissertation) thus, some of the fine clay materials were carbonates; however, x-ray analyses indicated that the greatest portion of the $< 2\ \mu m$ size fraction consisted of phyllosilicates.

To further assess the changes in the clay contents of these soils, the clay accumulation index (CAI) of Levine and Ciolkosz (1983) was computed. This index compares the clay content of a horizon of interest with that of the presumed parent material. The index is calculated by subtracting the clay content of the C-horizon (or lowest BC horizon) from the percentage of clay in the horizon of interest and then multiplying this difference by the thickness of the horizon in question (CAI = [B - C] * T). The values for this index ranged from -21.6 to 631 (Table 4). No values are listed for the lowest horizon in each soil as these were the values used to calculate the index. The CAI values were highest in the surface horizons of all four soils, indicating these were the locations of maximum clay accumulation. The generally lower values for this index in the subsurface horizons suggested that little clay had been translocated from the surfaces of these soils. The distribution of the clay accumulation index in Profile 1 appeared to further substantiate the presence of a buried soil in this profile. When compared with the modern surface, the CAI values of the Bk3 and Bk4m horizons suggested a zone of

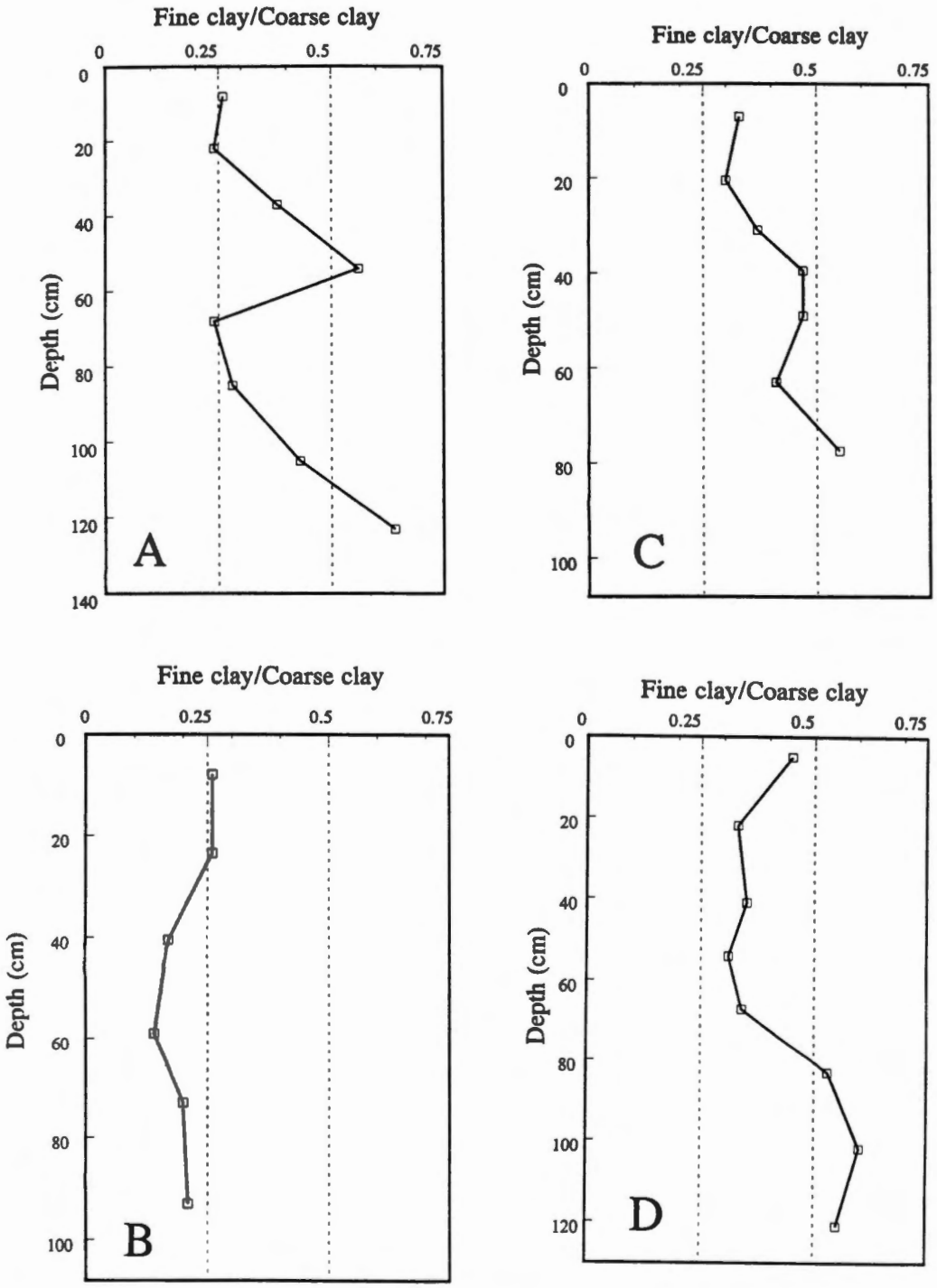


Figure 4. Fine clay: coarse clay ratios from the four soils studied: (A) = P-1; (B) = P-2; (C) = P-3; (D) = P-4.

Table 4. Clay accumulation indices for Profiles 1 through 4.

Horizon	CAI	Horizon	CAI
Profile 1		**Profile 3**	
Ap	128	Ap	372
A/Bk	43.2	Bw	354
Bk1	-21.6	Bk1	36.0
Bk2	-19.5	Bk2	16.2
Bk3	40.3	BCk1	18.0
Bk4m	70.4	BCk2	37.8
Bk5	21.6	C	-
Bk6m	-	**Profile 4**	
Bk7m	ND	Ap	254
Profile 2		Bw	631
A	202	Bk1	125
Bw	218	Bk2	45.1
Bk1	17.1	Bk3	13.6
Bk2	-3.6	Bk4	-3.4
Bk3	14.0	Bk5	2.1
Bk4	-	C	-
Bk5	ND		

ND = not determined.

clay accumulation which could have been related to weathering at a former soil surface. The highly negative values in the Bk1 and Bk2 horizons are due in-part to the presence of the calcic horizon. The influx of translocated carbonates probably served to dilute the clay content in these two horizons, thus, lowering the CAI.

The highly calcareous nature of these soils was reflected in the inorganic carbon distributions (Figure 5). Inorganic carbon contents ranged from 26 to 118 g kg^{-1}. They were lowest in the surfaces and increased with depth, reflecting both the dissolution of carbonates in surface horizons and translocation of carbonates, with subsequent calcic horizon formation. Whereas the parent materials were dominantly dolostone sands and gravels, the bulk of the inorganic carbon was derived from this source. Organic carbon contents (Figure 5) ranged from 0 to 34 g kg^{-1}. Because the organic carbon values represented the difference between the total and inorganic carbon measurements, any error in the previous determinations would be expressed as an error in the estimate of organic carbon. The zero values determined for some horizons may have represented underestimations of the actual organic carbon contents. The organic carbon content in Profile 1 exhibited two maxima, one at the surface and the other coinciding with the Bk3 horizon. The deep accumulation of organic carbon in Profile 2 provided further evidence of the depositional nature of this soil.

Limited spectrochemical data, collected from secondary carbonate accumulations using energy dispersive x-ray analysis, indicated that these materials were comprised almost exclusively of calcite, with little or no magnesium substitution. Based on these data plus the measured carbonate equivalents and the results of total chemical analyses, the proportions of dolomite and calcite were estimated. As expected, dolomite comprised the largest portion of the inorganic carbon. The distribution of calcite (Table 5) illustrates the zones of secondary carbonate accumulation, indicating the presence of calcic horizons in all four soils. The most highly developed of these horizons was in Profile 1. The calcite content in this soil increased from 0 to 312 g kg^{-1} in the Bk2 horizon. The distribution of calcite with depth in Profile 1 further substantiated the presence of a buried soil, as did the distribution of organic

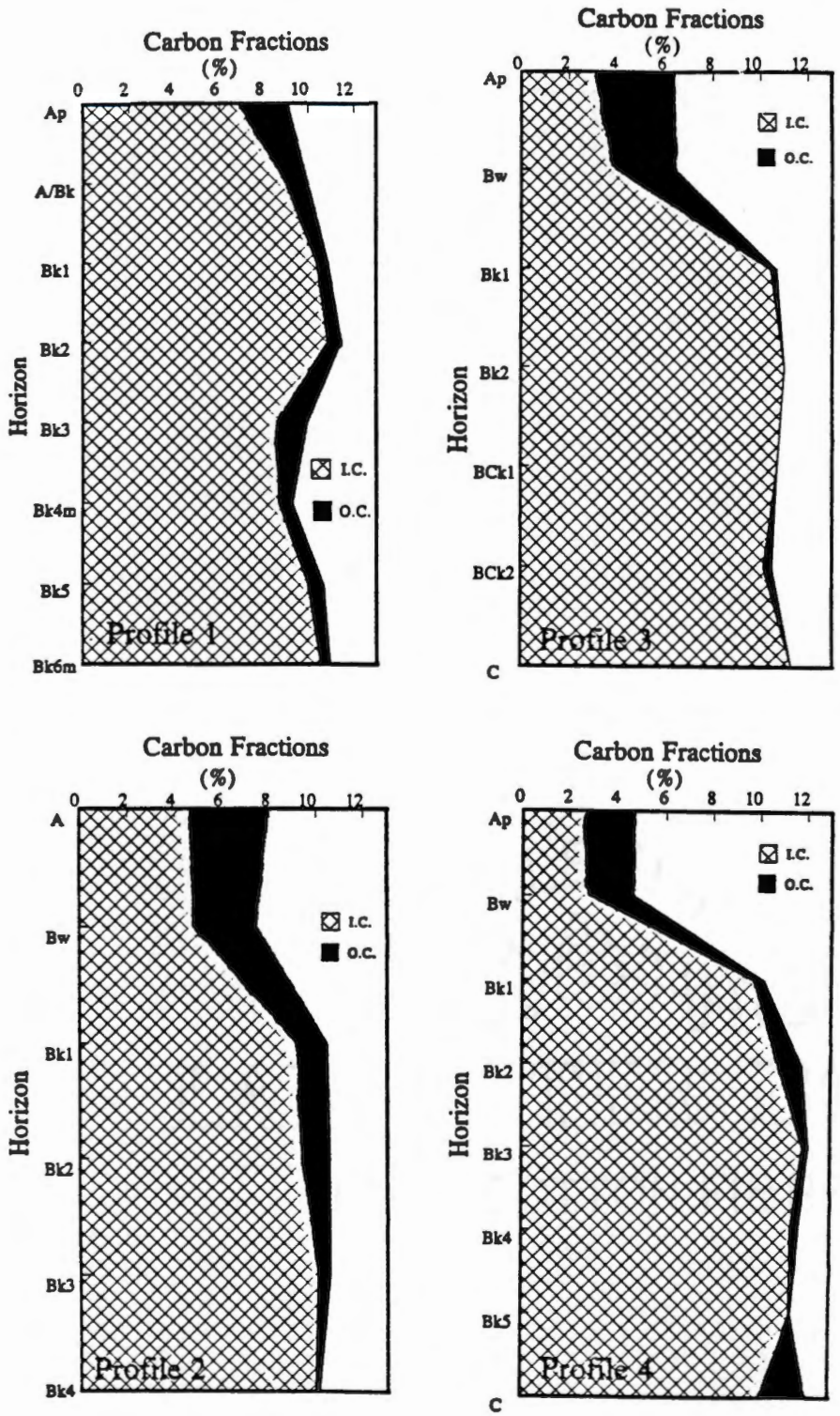


Figure 5. Distribution of soil carbon fractions in the four soils studied.

Table 5. Content and estimated composition of inorganic carbon fractions in the four soils studied.

Horizon	Lower Depth	Calcium Carbonate Equivalent	Estimated Calcite	Estimated Dolomite
	-- cm --	g kg^{-1}		
Profile 1				
Ap	16	570	0	570
A/Bk	28	745	123	622
Bk1	46	855	188	667
Bk2	61	901	312	589
Bk3	74	710	2	708
Bk4m	96	716	12	703
Bk5	114	826	4	822
Bk6m	132	871	98	773
Bk7m	132+	ND	ND	ND
Profile 2				
A	16	385	3	382
Bw	31	395	1	394
Bk1	50	756	6	751
Bk2	68	775	1	774
Bk3	78	835	10	825
Bk4	108	827	18	809
Bk5	108+	ND	ND	ND
Profile 3				
Ap	14	255	11	244
Bw	27	326	6	320
Bk1	35	867	21	846
Bk2	44	918	10	908
BCk1	54	894	11	883
BCk2	72	839	13	826
C	83+	940	11	930

Table 5 (continued)

Horizon	Lower Depth	Calcium Carbonate Equivalent	----- Estimated ----- Calcite	Dolomite
	-- cm --	---------- g kg^{-1} ----------		
Profile 4				
Ap	10	214	2	212
Bw	34	221	3	219
Bk1	48	806	38	768
Bk2	59	888	75	813
Bk3	74	979	48	931
Bk4	91	945	41	904
Bk5	112	945	64	882
C	130+	832	0	832

ND = Not Determined.

carbon in this profile (Figure 5). The generally low calcite contents with depth in Profile 2 probably resulted from additions of materials with low inorganic carbon contents. Additions of materials from upslope which had been largely leached of their original carbonate, resulted in dilution of the carbonates already present in this soil profile.

Soil pH ranged from 7.9 to 9.0 in H_2O and 7.5 to 8.3 in $CaCl_2$ suspensions (Table 6). The alkaline reaction in these soils reflected their calcareous nature, and probably influenced the weathering reactions in these soils. In another study (Part 3, this dissertation) limited weathering of the clay minerals in these soils was in-part related to these high pH values. Cation exchange capacity (CEC) varied from 2.1 to about 24 cmol (Na^+) kg^{-1} (Table 6). The CEC was highest in the surfaces, reflecting the higher clay and organic carbon content of these horizons, and decreased greatly with depth. Extractable Mg^{2+}, Na^+, and K^+ contents were generally low throughout all four soils (< 1 cmol(+) kg^{-1}). As would be expected, extractable Ca^{2+} dominated the exchange complex. All four soils had base saturations above 100 percent, indicating the presence of free calcium carbonate. Exchangeable sodium percentages were low in all soils, but tended to be highest in the surfaces; reflecting the addition of airborne salts (Yaalon, 1964) or perhaps evaporation.

The concentration of soluble salts in these soils, as indicated by electrical conductivity (EC) measurements of dilute 1:1 soil extracts, was quite low (Table 7). The EC ranged from 0.13 to 0.67 dS m^{-1}, indicating that none of these soils was saline (U. S. Salinity Laboratory Staff, 1954). The dominant anion in these soils was chloride. It varied in concentration from 5.9 to 9.6 mmol(-)L^{-1}, and was highest in surface horizons. The small range in Cl concentration with depth was probably due to a combination of low annual precipitation and the presence of the calcic horizons. Plugging of the available pore space by carbonates would result in decreased hydraulic conductivity. This combined with the low precipitation could have been responsible for the distribution pattern of Cl with depth in these soils. The dominant cations in the dilute extracts were Ca^{2+} and Na^+. The concentration of both ions was highest in the surfaces and decreased with depth. The distribution patterns of Na^+ and Cl^- both

Table 6. Soil pH and cation exchange characteristics of the four profiles studied.

	------ pH ------		---------- Extractable Cations ---------						
Horizon	1:1 H_2O	2:1 $CaCl_2$	Ca	Mg	Na	K	CEC	ESP	SAR
			---------- cmol (+) kg^{-1} ----------				cmol (Na^+) kg^{-1}	--- % ---	
Profile 1									
Ap	8.1	7.7	11.7	1.4	0.53	0.20	8.7	6.1	1.24
A/Bk	8.5	7.9	7.7	0.6	0.31	0.13	5.0	6.2	1.56
Bk1	8.8	8.1	7.9	0.3	0.02	0.03	2.1	0.8	0.85
Bk2	8.9	8.1	6.9	0.3	0.06	0.03	2.5	2.3	0.93
Bk3	8.5	8.0	7.7	0.4	0.05	0.06	4.7	1.1	0.69
Bk4m	8.7	8.0	12.7	0.6	0.02	0.09	4.6	0.3	0.71
Bk5	8.6	8.0	11.4	0.5	0.02	0.06	3.9	0.6	0.48
Bk6m	8.8	8.1	9.6	0.5	0.04	0.03	2.5	1.6	0.75
Bk7m	ND	ND	ND	ND	ND	ND	ND	ND	ND
Profile 2									
A	8.0	7.8	17.5	2.4	0.66	0.68	13.2	5.1	2.7
Bw	8.1	7.8	15.9	1.8	0.61	0.53	11.3	5.5	1.9
Bk1	8.5	7.9	11.8	1.1	0.12	0.14	4.5	2.7	0.83
Bk2	8.6	8.0	11.7	0.9	0.10	0.08	3.8	2.6	0.98
Bk3	8.6	8.0	18.5	1.1	0.12	0.08	3.4	3.7	0.80
Bk4	8.6	8.0	17.4	1.3	0.17	0.09	3.5	4.8	1.3
Bk5	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 6 (continued)

Horizon	------ pH ------		---------- Extractable Cations ---------						
	1:1 H_2O	2:1 $CaCl_2$	Ca	Mg	Na	K	CEC	ESP	SAR
			---------- cmol (+) kg^{-1} ----------				cmol (Na^+) kg^{-1}	--- % ---	
Profile 3									
Ap	8.0	7.7	23.7	4.0	0.35	0.46	23.9	1.5	1.1
Bw	8.2	7.8	22.6	4.3	0.32	0.22	23.5	1.4	1.2
Bk1	8.4	7.9	4.4	0.7	0.04	0.09	6.4	0.6	0.92
Bk2	8.7	8.0	3.6	0.7	0.02	0.07	2.7	0.7	0.97
BCk1	8.7	8.0	3.4	0.6	0.00	0.08	2.2	0.2	0.99
BCk2	8.6	8.0	5.1	0.7	0.01	0.08	3.1	0.5	0.79
C	8.8	8.1	3.1	0.5	0.02	0.05	1.8	1.2	0.89
Profile 4									
Ap	7.9	7.5	19.2	3.7	0.23	0.77	16.3	1.4	0.99
Bw	8.1	7.7	18.7	4.0	0.26	0.34	15.3	1.7	1.0
Bk1	8.4	8.0	6.4	1.5	0.10	0.14	5.0	2.0	0.79
Bk2	8.7	8.1	4.5	0.7	0.06	0.10	3.1	2.1	0.82
Bk3	8.9	8.2	3.0	0.5	0.00	0.04	1.5	0.2	0.82
Bk4	8.9	8.2	4.5	0.6	0.00	0.03	1.3	0	0.74
Bk5	8.9	8.2	5.8	0.7	0.00	0.04	2.3	0	0.73
C	9.0	8.3	5.4	0.7	0.04	0.03	1.3	3.0	1.0

ND = not determined.

Table 7. Soluble ion compositions from 1:1 water extracts of the four profiles studied.

			Water Extractable Ions									
Horizon	pH	EC	CO_3	HCO_3	Cl	NO_3	SO_4	Ca	Mg	Na	K	SAR
		dS m^{-1}	mmol (+/-) L^{-1}									
Profile 1												
Ap	7.1	0.39	0.0	0.07	7.01	0.48	0.40	3.04	0.70	1.70	0.13	1.24
A/Bk	7.3	0.33	0.0	0.10	6.57	0.49	0.42	1.94	0.42	1.69	0.14	1.56
Bk1	7.1	0.18	0.0	0.06	6.01	0.50	0.23	1.21	0.25	0.72	0.08	0.85
Bk2	7.0	0.16	0.0	0.05	5.98	0.50	0.24	1.06	0.22	0.74	0.07	0.93
Bk3	7.4	0.26	0.0	0.12	6.19	0.47	0.22	1.98	0.48	0.76	0.13	0.69
Bk4m	7.5	0.22	0.0	0.15	6.07	0.61	0.19	1.59	0.48	0.73	0.14	0.71
Bk5	7.5	0.19	0.0	0.16	6.12	0.79	0.18	1.46	0.44	0.47	0.07	0.48
Bk6m	7.5	0.22	0.0	0.16	6.24	0.84	0.22	1.36	0.47	0.72	0.08	0.75
Bk7m	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Profile 2												
A	7.3	0.67	0.0	0.10	9.60	0.51	0.96	3.07	0.96	3.77	0.35	2.7
Bw	7.6	0.54	0.0	0.02	8.87	0.55	0.76	2.84	0.87	2.62	0.20	1.9
Bk1	7.7	0.24	0.0	0.03	6.21	0.52	0.27	1.72	0.51	0.88	0.08	0.83
Bk2	7.7	0.23	0.0	0.02	6.41	0.54	0.26	1.49	0.45	0.96	0.06	0.98
Bk3	7.7	0.19	0.0	0.02	6.06	0.54	0.19	1.31	0.43	0.75	0.05	0.80
Bk4	7.7	0.27	0.0	0.24	6.76	0.71	0.25	1.40	0.55	1.26	0.05	1.3
Bk5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 7 (continued)

Horizon	pH	EC	Water Extractable Ions									
			CO_3	HCO_3	Cl	NO_3	SO_4	Ca	Mg	Na	K	SAR
		dS m^{-1}	mmol (+/-) L^{-1}									
Profile 3												
Ap	7.8	0.60	0.0	0.34	8.67	0.49	0.65	4.16	1.61	1.89	0.11	1.1
Bw	7.9	0.38	0.0	0.43	7.09	0.49	0.58	2.39	0.93	1.55	0.05	1.2
Bk1	7.9	0.23	0.0	0.40	6.45	0.53	0.35	1.47	0.53	0.92	0.06	0.92
Bk2	6.9	0.17	0.0	0.04	6.08	0.50	0.23	0.99	0.32	0.78	0.05	0.97
BCk1	7.3	0.17	0.0	0.09	6.08	0.52	0.25	0.97	0.30	0.79	0.06	0.99
BCk2	7.6	0.18	0.0	0.20	6.06	0.53	0.24	1.23	0.41	0.71	0.06	0.79
C	7.6	0.15	0.0	0.21	5.99	0.51	0.26	0.84	0.29	0.67	0.07	0.89
Profile 4												
Ap	7.6	0.51	0.0	0.22	7.17	0.51	0.69	3.66	1.61	1.61	0.18	0.99
Bw	7.8	0.36	0.0	0.30	6.69	0.52	0.54	2.44	1.06	1.37	0.05	1.0
Bk1	7.8	0.24	0.0	0.34	6.43	0.50	0.31	1.51	0.64	0.82	0.04	0.79
Bk2	6.9	0.16	0.0	0.04	6.02	0.50	0.21	0.99	0.37	0.67	0.05	0.82
Bk3	7.0	0.14	0.0	0.05	6.03	0.50	0.21	0.79	0.29	0.60	0.04	0.82
Bk4	7.1	0.13	0.0	0.06	5.92	0.49	0.19	0.81	0.32	0.56	0.05	0.74
Bk5	7.2	0.15	0.0	0.08	5.89	0.49	0.19	0.87	0.43	0.59	0.05	0.73
C	7.3	0.14	0.0	0.09	5.90	0.52	0.23	0.67	0.32	0.72	0.04	1.0

ND = not determined.

suggested additions by aerosolic salts. The prevailing northerly winds in the region likely pick up sea-spray from the Aegean, and locally from the Bay of Merabellou, and deposit these salts at the soil surface. All of the soils sampled lay within one kilometer of the coast. Seager (1916) stated that this portion of the Cretan coast "suffers greatly from winter storms which drive salt spray far inland blighting the crops." Yaalon (1964) noted EC values of 225 dS m^{-1} at Ashdod in Israel. This city is located only 100 m from the coast. Yearly deposition of chloride and sodium at Ashdod amounted to 124 and 73 kg ha^{-1}, respectively. Muhs (1982) also noted the occurrence of aerosolic salt additions in a group of Quaternary soils in California.

Despite the addition of soluble Na to these soils, the sodium adsorption ratios (SAR) were all very low (Table 7). The SAR ranged from 0.48 to 2.7, being highest in the surface horizons and generally decreasing with depth. These data imply that sodium probably played little or no part in the genesis of these soils.

Active Pedogenic Processes

The pedogenic processes active in the soils of the Cha River region included rubification, dissolution and translocation of carbonates, color paling, eolian additions of both solid and dissolved materials, and physical and chemical weathering processes leading to the accumulation of clay in the surface of these soils.

Rubification, as defined by Kubiena (1970), involves the crystallization of amorphous iron compounds into goethite and hematite which are freely suspended in the groundmass of the soil matrix. These compounds result in the development of red soil colors. The 7.5YR and 5YR color hues present in the surface layers of these soils indicated that rubification has been and still is an active process in their development. Rubification has been identified as a significant process in Quaternary soils by other investigators (Harden, 1982; McFadden and Hendricks, 1985).

The development of calcic horizons in these soils was one of their significant features. Gile et al. (1966) developed a morphologic sequence of calcic horizon development for desert soils of the southwestern U.S. This scale has been utilized by some authors to infer climate change and to estimate the age of Quaternary deposits exhibiting calcic horizons (e.g. McFadden, 1982; Taylor and Shroba, 1986). The development of calcic horizons in gravelly soils has been shown to require less time than it does in non-gravelly soils (Gile et al., 1966; Flach et al., 1969). The calcic horizons developed in the Cha River soils exhibited Stage I, II and III development as defined by Gile et al. (1966).

Stage I development in gravelly soils was identified by Gile et al. (1966) in soils associated with a geomorphic surface which was late to middle Holocene in age. Stage II accumulations were identified in soils associated with a surface which ranged in age from middle Holocene to latest Pleistocene. Stage III accumulations were identified in association with a late Pleistocene surface. These data indicate that the soils of the Cha river area may range in age from late middle Holocene to latest Pleistocene. Similar age estimations were determined based on iron oxide:total iron data (Part 2, this dissertation).

Taylor and Shroba (1986) found that little or no secondary carbonates had accumulated in soils formed in gravelly noncalcareous alluvium in Nevada which were less than 3000 years old. They identified calcic horizons ranging from 20 to 50 cm thick in soils formed in similar alluvium which was between about 3000 and 20,000 years old. They noted that the sequence of accumulation of carbonates and secondary silica in the Nevada soils was somewhat different than that identified by Gile et al. (1966) for the Las Cruces area of New Mexico. Taylor and Shroba suggested that the seasonality of precipitation in the Las Vegas area of Nevada was probably responsible for these differences. The rainfall pattern in the Las Vegas area is similar to that of Crete with regard to timing; i.e. most of the rainfall occurs during the cool winter months when carbonates would be most soluble. The observations of Taylor and Shroba (1986) may also imply an age of perhaps latest Pleistocene to Holocene for some of the Cha River soils.

The thickness of the calcic horizons in the soils of the present study ranged from 33 to 78 cm. Profile 2 contained a calcic horizon which was approximately 77 cm in thickness and exhibited Stage I and II morphology. The calcic horizon in Profile 3 was 45 cm thick and exhibited morphologic characteristics associated with Stage II. Profile 4 contained a calcic horizon which was thicker (78 cm) than the one in Profile 3, even though these two soils occupy similar landscape positions. Morphological characteristics of the calcic horizon in Profile 4 were of Stage II development also. This indicated that in spite of the greater thickness of this horizon in Profile 4 the degree of development was similar. Calcic horizons in Profile 1 were the most variable. The upper calcic horizon sequence exhibited the greatest degree of morphological development (Stage III). The lower sequence of calcic horizons in this profile exhibited Stage I and II development. Despite the younger age of the upper sequence in this profile, it displayed the greatest degree of development, suggesting that some intrinsic property influenced the development of this horizon. The degree of calcic horizon development in the upper portions of this soil could be explained by feed-back processes (Torrent and Nettleton, 1978). The preexistence of a calcic horizon at depth in this profile (Bk3) could have reduced the hydraulic conductivity in the profile sufficiently to speed the development of the overlying calcic horizon (a feed-back process). Further plugging of the pore space by translocated carbonate could have led to a more rapid build-up of calcic materials and reduced the amount of time required to reach Stage III morphology.

In conjunction with the development of calcic horizons, color paling, as noted by Harden and Taylor (1983) was also a significant process in two of the soils examined. Carbonates tend to impart a lighter color to sediments in which they accumulate (Taylor, 1982; Birkeland, 1984 p. 12). The lighter hues and higher color values noted in Profiles 1 and 2 were the result of translocated carbonates in these soils.

The addition of solid and soluble airborne constituents to these soils was suggested by the presence of higher quantities of Na and Cl (Table 7) and the presence of measurable quantities of Zr in the modern surfaces (Table 3). As previously discussed, the addition of airborne salts resulted from

sea-spray carried inland by the prevailing northerly winds. The presence of measurable amounts of Zr in the surfaces of all four soils (Table 3) may have indicated eolian additions of Zr-bearing minerals, because the parent materials contained only trace amounts of Zr. Alternatively, the increase in Zr in the surface horizons could have been the result of weathering. If sufficient weathering had occurred in the surface horizons, Zr in the parent materials could have been concentrated to a degree that would allow its measurement. The later mechanism probably explains the occurrence of Zr in these soils because long-distance eolian transport of Zr-containing minerals is not likely. The high specific gravity of these minerals probably limits their transport over long distances by eolian processes.

Physical and chemical weathering processes have resulted in the development of clay-enriched surface horizons in all four soils. Rostad et al. (1976) noted the importance of dissolution of carbonates and physical disintegration of shale lithorelicts in the formation of argillic horizons in some soils formed from calcareous glacial sediments. In addition to clay enrichment, the release and concentration of Ti also occurred in the Cha River soils (Table 3). Elemental analysis of the phyllite indicated that it contained 0.16 percent TiO_2. Yaalon et al. (1974) stated that losses of Ti in the Mediterranean environments of Israel were small. The distribution of this element should therefore provide an indication of the zones of maximal weathering. The data in Table 3 indicated that the highest concentrations of Ti occurred in the surface horizons of all four soils. The distribution of Ti in Profile 1 provided further evidence of the existence of a buried weathering surface.

Late Quaternary Landscape and Soil Development

The following sequence of events is proposed for the development of the sediments of the Cha River region. Throughout the Pleistocene, alluvial processes led to accumulation of sediments in the Cha River basin. At sometime, possibly the Middle Pleistocene, a period of valley filling probably occurred, followed by a period of landscape stability and stream incision. These events probably led to the formation of the marine and fluvial terraces identified by Papastamatioy et al. (1959) (Appendix E). Middle to late Pleistocene, post-depositional tectonism has uplifted these deposits because the marine

terraces are now as much as 60 m above modern sea level. The remnants of these terraces consisted of breccio-conglomeratic sediments which were almost completely lithified with secondary carbonate cements. Further sequences of valley filling and sediment reworking probably occurred throughout the Late Pleistocene in response to glacial and interglacial cycles. The extent of these processes is unknown at present.

Shackleton et al. (1984) presented paleogeographic maps of the central and western Mediterranean for 18,000 and 9,000 BP. Based on sea level data for the last 125,000 years (i.e. most of the Late Pleistocene), they suggested that the 18,000 BP map was probably a reasonable representation of preceding cold stadials, while the map for 9,000 BP depicted the shorelines during intervening warm periods. The 18,000 and 9,000 BP shorelines, -120 m and -35 m, respectively, were similar to those proposed by van Andel and Shackleton (1982) for Greece and the Aegean. This could suggest that the 125,000 year record given by Shackleton et al. (1984) may serve as a proxy record for Greece and the Aegean for the same time interval. These data could provide an initial framework for the Late Pleistocene alluvial sequences suggested above.

Sea level reconstructions for Greece and the Aegean placed the 18,000 BP shore at -130 m and the 9,000 BP shore -36 m (van Andel and Shackleton, 1982). Due to tectonic instability, no shoreline was proposed for Crete by those authors. They did however indicate the position of the -100 m isobath for Crete. This much of a decrease in sea level surrounding Crete does not seem unreasonable. By 9,000 BP the shoreline around Crete had risen to nearly its modern level. The change in sea level between 18,000 and 9,000 BP provided a shift in baselevel which the streams carrying the late glacial and Holocene sediments of the Cha River area would have responded to. Rising sea level would have led to stream aggradation and channel-filling. Tectonically induced sea level changes since 9,000 BP have been identified in the Pacheia Ammos area and along the north shore of central and eastern Crete (Hood and Leatham, 1959; Boekschoten, 1963; Davaras, 1974; and Dermitzakis, 1974). Hood and Leatham (1959) suggested a rise of about 1 m since Roman times. This was based on observations of submerged fish tanks at Mochlos (ca. 6 km northeast of Pachiea Ammos) and drowned coastal

constructions at Chersonisos (ca. 60 km west of Pachiea Ammos). Submergence of some building walls at Priniatikos Pirgos (ca. 10 km west of Pachiea Ammos) was noted by Hayden et al. (1992).

A sequence of Holocene uplifts was responsible for the terrace deposits noted along both the Cha drainage and the stream which drained the western margin of the study area (Map unit 2, Fig. 2). Observations in the Gourniapotamos and Xeropotamos River basins west of Pachiea Ammos further substantiated this conclusion, as a sequence of late glacial to Holocene terraces with elevations similar to those in the Cha basin were noted in these two drainages. A wave-cut notch approximately 1 m above modern sea level at the beach at Tholos (ca. 4 km northeast of Pachiea Ammos) as well as the sequence of Holocene terraces in the Cha, Gourniapotamos and Xeropotamos drainages suggest that this portion of the north Cretan coast has not undergone the post-Roman submergence noted in other locations. Given the tectonic nature of these sea level adjustments this sort of local variation is not surprising.

Emplacement of the majority of the parent sediments in the Cha basin had probably occurred by 8-9,000 BP and initial soil formation had probably begun somewhat before this. Bottema (1980) noted the deposition of a coarse-textured sediment between 9,000 and 8,300 BP from a core sampled near Aghia Gallini in south central Crete. Deposition of this sediment followed a marine incursion near the mouth of the Platys River. This marine transgression appeared to coincide with van Andel and Shackleton's 9,000 BP shoreline reconstruction. It also implied a period of fairly significant landscape instability which could have resulted in deposition of coarse-textured sediment throughout Crete. This episode may mark the alluviation event which was noted in Profile 1. Late glacial (10 to 12,000 BP) soil development may have been sufficient to create the paleo-weathering surface marked by the Bk3 horizon in Profile 1. Deposition around 9000 BP could have led to reinitiation of soil development which resulted in the buried soil identified in this profile.

Climatic reconstructions for the last 18,000 years, based on various analyses, document the following conditions for the region surrounding Crete: (i) lower temperatures (by 5 to 7° C) and increased effective precipitation (at least through the early Holocene); (ii) wider seasonality of

Ritchie et al. (1985), on the basis of lake sediment and pollen analyses in northwest Sudan, proposed a period of humid conditions for the eastern Sahara during early to middle Holocene times. From 8,500 to 6,100 BP they suggested a period of humid tropical climate with monsoonal precipitation. Reduced rainfall or increasing evaporation, beginning around 6,100 BP, led to drier conditions and a transition to a savannah, scrub-grassland vegetation, which shifted further south by 4,500 BP, when the lake basin dried out entirely. The timing of this drying coincides fairly closely with the climatic optimum identified by Buckley et al. (1982). The moist period between 8,500 and 6,100 BP identified by Ritchie et al. (1985) may be related to the re-expansion of forest in Crete noted by Bottema (1980) between 7,300 and 6,300 BP. Gat and Margaritz (1980) suggested a period of increased humidity for the eastern Mediterranean sometime between 6,000 and 4,000 BP; however, this is not supported by pollen evidence from Crete. Bryson et al. (1974) provided evidence of a period of extreme drought for portions of eastern Greece and Crete sometime around 3,200 BP. They suggested that this may have been the cause of the decline of Mycenaean culture. Watrous (1982) noted a sharp decrease in the population of the Lasithi Basin of eastern Crete at about the same time.

Based on the geologic scenario proposed earlier and the combined climatic analyses, a sequence of major soil forming intervals likely resulted in development of the soils and landforms of the Cha River region. Weathering and soil development, under the influence of warm, moist conditions, had probably begun before the Holocene transition (ca. 10 to 12,000 BP). Initial weathering of these coarse-textured, carbonate-rich sediments under a moist climatic regime would have resulted in relatively rapid translocation of carbonates and enrichment of finer materials in the surface layers. Eolian additions of fine material were also likely, although data regarding late glacial to Holocene dust fluxes in the eastern Mediterranean are lacking. Translocated carbonates would not have accumulated to any great extent during this period because rainfall would likely have been sufficient to leach much of the dissolved carbonate. As the climate became less humid however, accumulation of carbonates, initially as clast coatings, would have increased. Based on Bottema's (1980) data, the increase in carbonate accumulation probably began sometime around 8,000 BP. Calcic horizon development

probably continued up to approximately 7,300 BP when increasing humidity likely initiated a renewed period of parent material dissolution, with concomitant clay accumulation. Clay accumulation and limited accumulation of carbonates probably continued up to about 6,300 BP or slightly later. Throughout the period from 9,000 to 6,300 BP hydrolysis and oxidation of divalent iron from the phyllites, and to a limited extent from the carbonates, would have resulted in an increase of pedogenic iron oxides, leading to rubification of the surficial soil horizons.

The climate for the period between 6,300 and about 5,000 BP is somewhat uncertain, but data from Buckley et al. (1982), Ritchie et al. (1985) and Bottema (1980) imply a period of increasing aridity for the eastern Mediterranean and the eastern Sahara. The preceding studies imply a period of decreased dissolution of carbonates in the soils of the Cha River area. Conversely, carbonate accumulation throughout this period would have increased, in response to the limited leaching regime. Rubification and clay accumulation would also have decreased in response to the same decrease in moisture.

Relatively steady-state conditions, punctuated by limited though perhaps significant periods of increased humidity and drought, have probably persisted since about 4,000 BP. Thus, modern rates of soil formation have likely been controlling the development of the Cha River soils for approximately 4,000 years. One such period of increased aridity has been postulated for approximately 3,200 BP (Bryson et al., 1974). This period of extreme aridity (perhaps as much as 40 percent lower than normal rainfall) would have greatly reduced the rate of soil development. It would also have set the stage for a period of landscape instability when "normal" climatic conditions returned.

Cultural Impacts

Watrous (1982) provided evidence of population expansion in the Lasithi Basin of eastern Crete beginning in Late Neolithic times and extending up through Middle Minoan III (ca. 5,000 to 3,500 BP). Pendlebury (1963) identified Neolithic remains at Vasiliki. Sakellaraki (1975) cited evidence for increasing human occupation in the Cha River area throughout Early Minoan times (5,000 to 4,000

BP). Relatively large settlements existed at Vasiliki, Mochlos and Psyera during this time-span. A sequence of burials at Pacheia Ammos was noted by Seager (1916). The burials were used fairly continuously from Early Minoan III (4,200 BP) up to Late Minoan I (ca. 3,500 BP) (Pendlebury, 1963). Seager (1916) suggested that the village associated with these burials, which were very near the coast, was probably located some distance inland. Based on archaeological survey work in the summer of 1992 (Dr. L. V. Watrous, pers. commun., 1992) the actual location of this settlement was the hilltop directly to the west of the modern harbor at Pacheia Ammos.

Watrous (1982) suggested a continuous occupation of the Lasithi Basin up to the Late Minoan period (ca. 3,500 BP). Pendlebury (1963) provided evidence of continual occupation of the Pacheia Ammos area throughout the same period of time. A sharp decrease in the population of the Lasithi Basin during Late Minoan III (Watrous, 1982) was probably contemporaneous with the period of drought postulated by Bryson et al. (1974). The population of the Cha River area likely responded to the same climatic shift. Much lower population densities were common throughout the Dark Ages (ca. 3,100 to 2,900 BP) in the Cha River area. Settlements at Vronda, Kastro and Vrokastro supported smaller populations during this period. Information regarding post-Iron Age settlement patterns for this region of Crete are somewhat limited. Archaeological survey projects currently underway in the area should provide detailed data regarding settlement patterns and landuse practices which may have influenced regional post-Iron Age soil and landscape development.

Climatically-induced landscape instability, perhaps exacerbated by the impact of increasing human population growth, may have led to landscape readjustment and renewed cycles of pedogenesis in some portions of the drainage basin. Previous investigations have identified recurrent periods of landscape instability in Greece (Pope and van Andel, 1984; van Andel et al., 1986; van Andel et al., 1991). Pope and van Andel (1984) suggested that a stable landscape existed in the Southern Argolid until about 4500 BP, when debris flows and other mass-wasting processes resulted in valley aggradation. These authors felt that this period of instability was initiated by extensive land clearance during the Early Bronze Age. The timing of these events however, also coincides with the climatic

optimum identified by Buckley et al. (1982); thus, the two factors in combination could also have explained these phenomena.

As noted earlier, a long period of population expansion from late Neolithic (ca. 5000 B.P.) to Middle Minoan times (ca. 3500 B.P.) occurred throughout much of eastern Crete. Extensive land clearance associated with this expanding population could have led to a period of human-induced landscape instability. Preliminary results from one of the archaeological survey projects (The Gournia Project, Dr. L. V. Watrous, Director) have identified a settlement located just to the north of Profile 1 (Figure 2). Pottery remains suggested that the site was inhabited from the Early Minoan through the Middle Minoan periods (Drs. L. V. Watrous and D. Haggis, Pers. Commun., 1992). These results suggest that culturally induced soil erosion in the Cha Basin since the Early Bronze Age has probably not been extensive.

CONCLUSIONS

An investigation was undertaken to determine the nature and properties of a sequence of soils developed in an area of late Quaternary alluvial sediments in eastern Crete, Greece. All four soils exhibited red-colored, clay-rich surface horizons which indicated maximum weathering had occurred in these zones. Calcic horizons had developed in all soils resulting in paling of subsoil colors, especially in Profiles 1 and 2. Two of the pedons were classified as sandy-skeletal, carbonatic, thermic Calcixerollic Xerochrepts (Profiles 2 and 3). The remaining soils, Profiles 1 and 4, were classified as sandy-skeletal, carbonatic, thermic Fluventic Xerochrepts due to the irregular distribution of organic carbon in each of these pedons.

Various methods utilized to assess the uniformity of the soil parent materials indicated a reasonable degree of similarity among the sediments and soils studied. The ratio of medium to (very coarse + coarse) sand was the most reliable physical means of determining parent material uniformity. The ratios of barium to lead and calcium to strontium proved most useful as chemical indicators of parent material uniformity.

The clay accumulation index of Levine and Ciolkosz (1983) indicated that maximum clay accumulation had occurred in the surface of all four soils. This was related to dissolution and translocation of carbonates and disaggregation and concentration of phyllite lithorelicts. Translocation of carbonates resulted in the development of calcic horizons in each soil. These horizons exhibited varying degrees of morphological development ranging from Stage I to Stage III (Gile et al., 1966). The addition of solid and soluble constituents by eolian processes was indicated by higher levels of Na and Cl in dilute H_2O extracts. The presence of measurable quantities of Zr in the surface horizons of all four soils may have been related to weathering processes or a result of eolian additions. Release and concentration of Ti from the phyllite provided additional evidence of surficial weathering processes. The relatively high levels of this element in the Bk3 horizon of Profile 1 helped to confirm the existence of a buried weathering surface in this soil.

The morphological development exhibited by the calcic horizons in all four soils suggested a late Pleistocene to early Holocene age for this group of soils. Data from another study (Part 2, this dissertation) suggested a similar age for these soils. The Stage III morphology identified in the upper sequence of calcic horizons in Profile 1 may have formed in the last 3000 to 5000 years under the influence of feed-back processes specific to this soil.

The following sequence of events was proposed for development of the sediments and soils of these alluvial deposits. A period of valley-filling followed by stabilization and stream incision, possibly in the Middle Pleistocene, led to the development of marine and fluvial terraces which now exist as conglomeratic inliers surrounded by younger sediments. Continued valley filling and landscape adjustment probably occurred throughout the Late Pleistocene, but the extent of this activity is unknown. One last period of alluviation probably occurred near the transition between the Pleistocene and Holocene, in response to climatic change. This event could have taken place between 8,300 and 9,000 BP based on evidence from southern Crete (Bottema, 1980). Weathering and soil development was probably rapid up to about 7,500 BP, when a shift toward a drier climate would have changed the rate of weathering. Calcic horizon development probably increased by about 8,000 BP in response to

the shift toward drier conditions. Another period of increased weathering and clay accumulation likely took place between 7,500 and 7,300 BP, as pollen data for this period implied a re-expansion of forests in some portions of Crete (Bottema, 1980). Modern soil forming conditions have probably been controlling soil genesis in the area since 4,500 to 4,000 BP. Periods of extreme climate, combined with human population pressure, have likely resulted in brief episodes of landscape instability over the last 4000 to 5000 years, although archaeological data implied that these episodes were probably not extensive.

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PART 3. CONTENT AND DISTRIBUTION OF IRON, MANGANESE AND SILICON OXIDES IN SOME CALCAREOUS ALLUVIAL SOILS OF EASTERN CRETE

INTRODUCTION

The nature of various metal oxides in soils is relevant to both soil genesis and soil behavior. Iron oxides and oxyhydroxides in soils have been investigated by numerous authors (Blume and Schwertmann, 1969; Alexander, 1974; Torrent et al., 1980; Arduino et al., 1984; McFadden and Hendricks, 1985; Torrent and Cabedo, 1986). Schwertmann (1985) reviewed the effect of pedogenic environments on iron oxides. Schwertmann and Murad (1983) reported on the effect of pH on the transformation of ferrihydrite to goethite and hematite. A number of researchers have related the content of various forms of iron to soil age (Alexander, 1974; Torrent et al., 1980; McFadden and Hendricks, 1985; Aniku and Singer, 1990). Still others have investigated the process of rubification, the relationship between iron content and soil color (Soileau and McCracken, 1967; Hurst, 1977; Bowman, 1982; Schwertmann et al., 1982; Torrent et al., 1983). Loeppert (1988) presented a review of the chemistry of iron in calcareous soil systems.

Manganese oxides in soils have generally been reported as being amorphous. This is due in large measure to their small crystallite size which results in broad, diffuse x-ray diffraction patterns. In addition, the platy crystal habit of many manganese minerals yields characteristic x-ray peaks which overlap with a number of other mineral species commonly associated with them (McKenzie, 1989). Manganese oxides commonly occur as coatings on other soil particles, deposits in fissures and veins and in association with iron and other metal oxides in concretions and segregations.

Despite the problems associated with identification and characterization of Mn-minerals, a number of researchers have reported on their occurrence (Taylor, et al., 1964; Ross et al., 1976; Tokashiki, et al., 1986). Dixon et al. (1990) presented a review of the occurrence, composition and mineralogy of manganese oxides in soils and other sediments. Blume and Schwertmann (1969) evaluated the distribution of iron and manganese in soils in relation to pedogenic processes. Yaalon et al. (1972) investigated the content and distribution of manganese in three soil catenas from the Mediterranean region of Israel. These authors discussed only total Mn. Singer (1977) discussed the distribution of iron, manganese and aluminum in soils developed from basalt and scoria in the

Mediterranean region of the Golan Heights in Israel. McBride (1979) discussed chemisorption and precipitation of divalent manganese at $CaCO_3$ surfaces. Precipitation of $MnCO_3$ was observed to follow saturation of the adsorbing surfaces. The carbonate surfaces served as initial nucleation sites for Mn precipitation.

Silica in soils is most abundant as a major component of silicate minerals. Wilding et al. (1977) reviewed the relationships among quartz and its polymorphs in soils. McKeague and Cline (1963a) discussed the nature and properties of silica in soils. Beckwith and Reeve (1963 and 1964) and McKeague and Cline (1963b, c) investigated the solubility and sorption behavior of silica in soils. Weaver et al. (1968) discussed the association of silica and iron oxides extractable in citrate-bicarbonate-dithionite. A number of other investigators have reported on the relationship between various forms of extractable silica and bonding mechanisms in soils (Harlan et al., 1977; Norton and Franzmeier, 1978; Hallmark and Smeck, 1979; Ajmone Marsan and Torrent, 1989).

With the exception of the investigations by Yaalon et al. (1972) and Torrent and Cabedo (1986) few studies have examined the nature or distribution of iron, manganese or silica in highly calcareous soil systems. The objective of the present study was to investigate the content, nature and distribution of the iron, manganese and silicon oxides occurring in a group of highly calcareous alluvial soils from eastern Crete, Greece in order to better infer the type and direction of the pedogenic processes which led to their development and to provide an estimate of relative soil-age based on the composition of the Fe fractions in these soils.

MATERIALS AND METHODS

Field Methods

The study area was located along the north coast of eastern Crete (Fig. 1). The soils have been described in detail in a previous study (Part 2, this dissertation). The profiles investigated represented three landscape positions; an upland shoulder (Profile 1), a lower backslope (Profile 2), and two

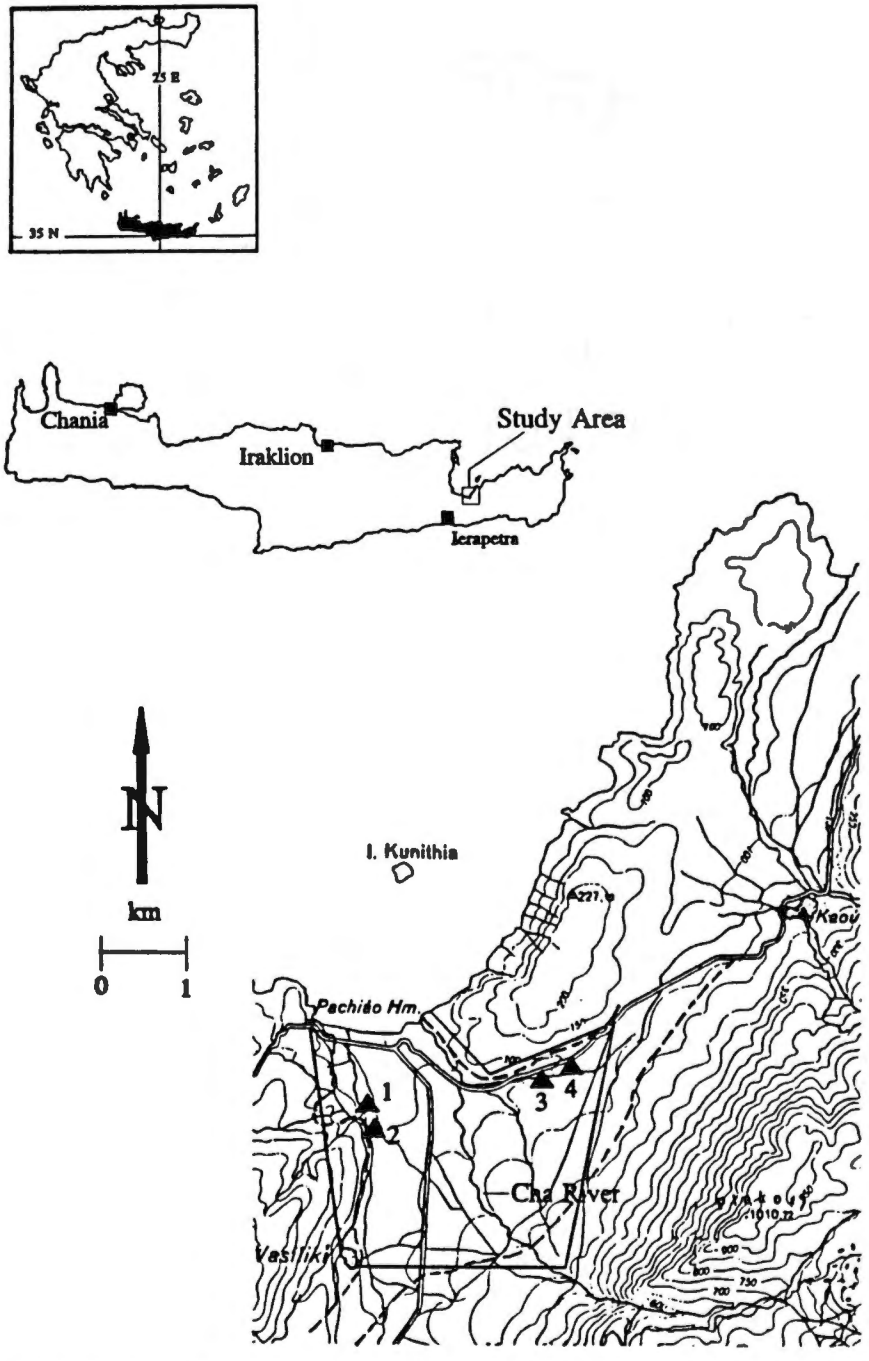


Figure 1. Study site and sampled profiles (indicated by soild triangles). Solid line indicates the boundary of the study area. Dashed line represents the approximate boundary of the Holocene alluvial deposits according to Papastamatioy et al., 1959. Scale is approximate. Elevation is in meters above sea-level.

profiles located in stable uplands (Profiles 3 and 4). The parent material consisted of dolostone alluvium which contained approximately 1 percent phyllite gravels. The phyllite consisted of a trioctahedral, ferrous chlorite, illite, quartz and minor amounts of kaolinite and feldspar (Part 3, this dissertation). Trace amounts of magnetite were also identified in the phyllite, dolostones and soils.

Climate

The climate is Mediterranean, with cool moist winters and hot dry summers. Annual precipitation at two nearby recording sites varied between 356 and 380 mm for the period 1951-1960 (Zohary and Orshan, 1965). Wernstedt (1972) reported annual precipitation at Ierapetra, 11 km south of the study area, to be 207 mm. The prevailing winds are from the north across the Aegean Sea. They blow strongly enough at times to reduce vegetative growth on exposed areas of the north coast. In the spring, the prevailing winds often shift to the south bringing the hot, dry, dust-laden Sirocco from Saharan Africa (Allbaugh, 1953; Mariolopoulos, 1961). This variable influx of Saharan dust may be a significant factor in the development of some Cretan soils (Rapp,1984; Rapp and Nihlén, 1986; Nihlén and Solyom, 1986).

Although the modern climate is typically Mediterranean, with relatively low rainfall, previous climates were probably not. The soils investigated here may have formed in-part in response to a variety of climatic conditions. From a review of the data regarding the paleoclimate for the region surrounding Crete (Buckley et al., 1982; Farrand, 1971; Gat and Margaritz, 1980; Mariolopoulos, 1961; Thiede, 1978; Thunnel, 1979; and Wright, 1968) the following conditions may be infered for the eastern Mediterranean from approximately 20,000 years before present (BP) to modern times: (i) lower temperatures (by 5-7°C) and increased effective precipitation for the last glacial maximum; (ii) wider seasonality of temperatures during the last glacial; (iii) a gradual warming from the end of the latest Pleistocene to approximately 4700 BP, culminating in a climatic optimum; (iv) a slight cooling from the climatic optimum, resulting in conditions similar to those of the modern eastern Mediterranean since approximately 4000 BP.

Laboratory Methods

Samples of soil and parent materials ground to pass an 80 or 100 mesh sieve were extracted using the following methods: total analysis by dissolution in aqua regia - hydrofluoric acid - boric acid (Nadkarni, 1984); sodium citrate-dithionite (Holmgren, 1967); acid ammonium oxalate (Schwertmann, 1964 and McKeague, 1981); and hydroxylamine hydrochloride (Chao, 1972).

Quantities of soil and parent sediments dissolved for total analysis varied between 100 and 300 mg. In the dithionite extracts quantities of soil were adjusted to account for expected iron contents. Soil weights varied from 1.5 to 3 g. Acid oxalate extracts were carried out with a 100:1 solution:soil ratio. Samples were shaken for two hours in the dark, centrifuged, decanted and stored for analysis. The solution to soil ratio used for the hydroxylamine extractions was 50:1. The samples were shaken for 30 min., centrifuged, decanted and stored for analysis.

Iron and manganese in the chemical extracts were determined by atomic absorption spectrophotometry. Total elemental compositions were determined using Inductively Coupled Plasma-spectroscopy. Silica in the chemical extracts was determined using the method of Weaver et al. (1968). Color development was achieved using a modification of the standard procedure (Dr. B. R. James, personal commun., 1992). The modification is outlined below.

Four ml of 0.5 M H_2SO_4 were added to 2 ml of extract in a 20 ml test tube. This solution was mixed on a vortex mixer and allowed to stand for 30 min. Following this 2 ml of tataric acid was added and the mixture was vortexed once more. During the mixing process 0.4 ml of reducing agent were added and the final mixture was vortexed for an additional period of time (generally 30 s). After allowing the color to develop for approximately 30 min., absorbance was measured at 810 nm on an Hitachi Model 100-20 spectrophotmeter. Samples were compared to a standard curve prepared using appropriate standards.

Duplicate samples were extracted using the total, dithionite and hydroxylamine treatments. Samples were extracted in triplicate on the acid oxalate extracts.

RESULTS AND DISCUSSION

Iron

Total analysis of the dolostone and phyllite parent materials indicated that the dolostone contained only 0.17 percent iron as Fe_2O_3; whereas, the phyllite contained 10 percent Fe_2O_3. The total and extractable iron contents of all four soils are given in Table 1. Iron values recovered by all extractions were greatest in the upper 30 cm and decreased with depth.

The content of silicate iron (total minus dithionite) (Blume, 1988) in the four soils examined ranged from 0.34 to 2.95 percent Fe_2O_3 (Table 1). The low iron content of the dolostones should make the assumption that total minus dithionite iron equals silicate iron reasonable. Silicate-Fe levels were highest in the surfaces of most soils, indicating the concentration effect of dissolution and translocation of carbonates. Conversely, lower levels of silicate-Fe in some subsurface horizons (notably the Bk1 and Bk2 of Profile 1) were the result of dilution by the same translocated carbonates. Profile 2, located in the backslope exhibited relatively high silicate-Fe contents throughout the entire profile. This was likely the result of colluvial additions in this landscape position. As a percentage of the total iron, silicate-Fe varied between 51 and 82 percent (Figure 2). Silicate iron:total iron ratios were lowest in surface horizons and increased with depth, indicating that a greater proportion of iron in the surfaces of these soils existed as secondary iron compounds. Redder colors in the surface horizons further substantiated this conclusion.

Arduino et al. (1984) reported silicate iron values that ranged from 50 to 78 percent in soils of upper Pleistocene - Holocene river terraces in northwestern Italy. Silicate iron contents in late middle Pleistocene terrace soils varied from 33 to 62 percent. In a later study, (Arduino et al., 1986) silicate iron contents of soils developed on upper Pleistocene-aged terrace sediments ranged from 51 to 85 percent. These data imply an upper Pleistocene to Holocene age for the Cha River soils investigated here. Comparisons with the Italian data would require that all three groups of soils had undergone similar weathering conditions over the span of time involved. The weatherability of the parent materials in the two areas should also be considered. The carbonates and iron-bearing phyllites of the Cha River

Table 1. Total and extractable iron fractions from Profiles 1 through 4.

Horizon	Total-Fe	Dithionite-Fe	Oxalate-Fe	Hydroxylamine-Fe	Silicate-Fe
	Fe_2O_3 %	mg/kg			Fe_2O_3 %
Profile 1					
Ap	2.33	7860	689	15	1.20
A/Bk	1.56	5029	374	15	0.85
Bk1	0.66	2231	157	20	0.34
Bk2	0.72	2548	208	19	0.35
Bk3	1.61	5028	267	29	0.89
Bk4m	1.64	5295	242	33	0.88
Bk5	0.96	2643	166	24	0.59
Bk6m	0.92	1980	148	24	0.63
Bk7m	ND	ND	ND	ND	ND
Prof. Wt. Mean	1.29	4043	274	ND	0.71
Profile 2					
A	3.85	12005	1312	12	2.14
Bw	3.88	12420	1212	13	2.10
Bk1	1.71	4447	279	6	1.08
Bk2	1.50	3591	187	6	0.98
Bk3	1.35	2320	141	4	1.02
Bk4	1.60	3958	223	24	1.31
Bk5	ND	ND	ND	ND	ND
Prof. Wt. Mean	2.12	5819	468	ND	1.34

Table 1 (continued)

Horizon	Total-Fe	Dithionite-Fe	Oxalate-Fe	Hydroxylamine-Fe	Silicate-Fe
	Fe_2O_3 %	---------- mg/kg ----------			Fe_2O_3 %
Profile 3					
Ap	5.53	18922	2032	16	2.83
Bw	5.13	17402	1738	9.0	2.64
Bk1	1.46	3826	459	53	0.92
Bk2	1.18	2553	329	70	0.82
BCk1	1.33	2949	371	53	0.91
BCk2	1.30	2870	364	46	0.89
C	1.04	1847	290	49	0.78
Prof. Wt. Mean	2.03	5638	652	40	1.22
Profile 4					
Ap	5.76	19924	2004	13	2.91
Bw	5.79	19919	2159	19	2.95
Bk1	2.03	5662	622	46	1.22
Bk2	1.44	3120	380	47	0.99
Bk3	0.86	1774	284	55	0.61
Bk4	0.93	1802	259	70	0.67
Bk5	0.99	2032	248	64	0.70
C	0.85	1400	228	57	0.65
Prof. Wt. Mean	2.35	7046	790	47	1.34

ND = not determined.

sediments may be more easily weathered than the igneous and acid-metamorphic sediments in the Italian studies; thus, the age estimates can only be considered maximum values. The Cha River soils could be Holocene in age.

Dithionite extractable iron in these soils was derived primarily from secondary oxides because the low content of iron in the dolostones would not contribute a significant proportion of iron to the extractable iron fractions. Secondary iron oxides probably resulted from a combination of release of silicate iron from the phyllite component of the parent material, release of iron accompanying weathering of any iron-bearing material added as eolian dusts and eolian additions of pre-existing iron oxides.

The degree of weathering in soils may be assessed by examining the ratio of ditionite-extractable to total iron (Schwertmann, 1985). As a percentage of total iron (Fe_t), dithionite extractable iron (Fe_d) in the Cha River soils ranged from 17 to 49 percent. Data presented by Torrent and Cabedo (1986) for two soils formed from calcarenites in southern Spain produced Fe_d to Fe_t ratios that varied from 27 to 61 percent. The ratio was highest in the surface horizons of their soils and decreased with depth. Using data given in Arduino et al. (1984), calculated Fe_d/Fe_t ratios ranged from 22 to 50 percent in soils developed on some upper Pleistocene to Holocene-aged river terraces in Italy. Soils formed on terraces of late middle Pleistocene age yielded Fe_d/Fe_t ratios which varied between 36 and 63 percent. Ratios from the soils of the present study fall in the range of both age brackets, but are closer to the younger of the two age groups. In another study (Arduino et al., 1986) upper Pleistocene terrace soils yielded Fe_d/Fe_t ratios which ranged from 15 to 51 percent; whereas, soils formed on middle Pleistocene terraces yielded ratios that varied from 33 to 78 percent. Once again, Fe_d/Fe_t ratios from the present study overlap both age ranges, but are closer to the range given for the upper Pleistocene terrace sediments. These comparisons also suggest that the soils of the Cha River area could be upper Pleistocene to Holocene in age, assuming that they formed under climatic conditions similar to those obtained for the same period in Italy.

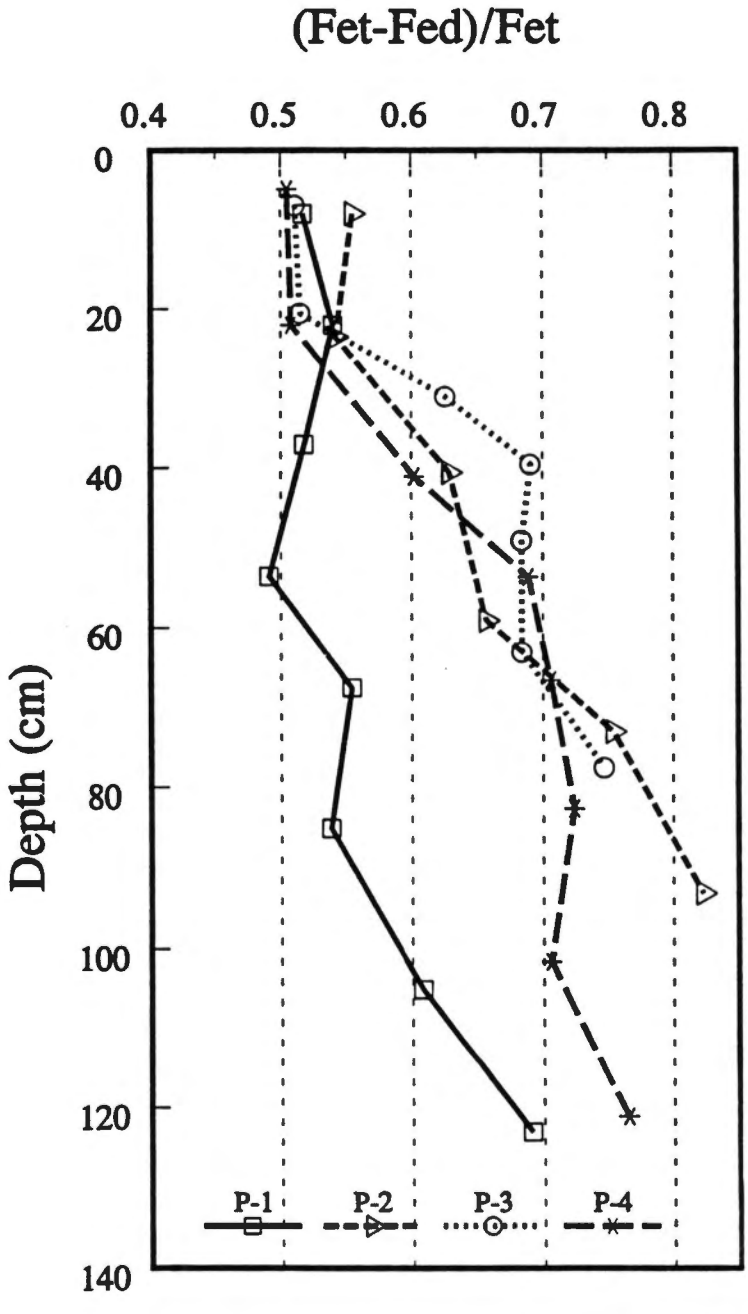


Figure 2. Silicate iron contents (Fe_t - Fe_d) as a percentage of total iron plotted with depth for the four soils studied.

If the upper 30 cm of each profile is examined, the ratio of Fe_d to Fe_t is relatively constant (44.5 to 49.5 percent). This suggests that the surfaces of all four profiles have undergone a similar degree of weathering. The surface of Profile 2, which has received colluvial additions from upslope, represented a combination of *in situ* weathering and additions of "pre-weathered" material.

Differences among profiles, related to landscape position and relative soil age, were assessed by comparing weighted profile iron contents (Oertel, 1961; McFadden and Hendricks, 1985). The approach outlined by McFadden and Hendricks (1985) was not possible because bulk density values were not measured in the extremely coarse-textured soils studied here. The means were calculated according to Oertel (1961); by multiplying the metal content (mg/kg) by horizon thickness, summing over the depth of the soil and dividing the sum by the total depth of each profile. To facilitate inter-pedon comparisons, the weighted profile means were normalized to 1.3 m. Metal contents of the lowest horizon in soils not sampled to 1.3 m were extrapolated to this depth (Harden, 1982; Birkeland, 1984, p.25). The weighted means are listed in Table 1.

The weighted profile Fe_d contents were lowest in the relatively unstable shoulder position. This is likely the result of soil erosion. The low content of Fe_d in the surface horizons of this profile relative to the other soils investigated suggests losses due to erosion. Despite the lower overall Fe_d content of this soil compared with the other three profiles, the proportion of Fe_d relative to total iron is similar to that in the other three soils; indicating that a similar degree of weathering has taken place in this soil. The soil located in the backslope position contained appreciably more Fe_d than did the shoulder position. This could be due to two factors. Deposition of iron bearing, weathered materials from upslope and lateral water movement through this pedon. Additional soil moisture would allow a greater degree of weathering to occur in this profile, liberating more iron. The two profiles from the stable upland positions contained nearly the same amount of Fe_d. The stability of the landscape occupied by these two profiles permitted increased weathering and greater profile development.

Redness ratings calculated using the method of Torrent et al. (1983) closely follow the Fe_d distributions in each profile (Table 2). The ratings listed here were obtained by calculating the values

Table 2. Redness ratings and estimated hematite contents for the four soils studied. Ratings were calculated using the method of Torrent et al. (1983). Rating data represent means of values calculated for moist and dry soils. Hematite contents were estimated using equations given in Torrent et al. (1983), (H-1) and Torrent and Cabedo (1986), (H-2).

Horizon	Rating	Fe_2O_3d	Hematite		Horizon	Rating	Fe_2O_3d	Hematite	
		-- % --	-- % --				-- % --	-- % --	
			H-1	H-2				H-1	H-2
Profile 1					**Profile 3**				
Ap	2.1	1.12	0.85	0.75	Ap	5.3	2.71	2.1	2.1
A/Bk	2.1	0.72	0.85	0.75	Bw	7.0	2.49	2.7	2.9
Bk1	0.7	0.32	0.31	0.15	Bk1	5.5	0.55	2.2	2.2
Bk2	0	0.36	0	0	Bk2	3.8	0.37	1.5	1.5
Bk3	0	0.72	0	0	BCk1	ND	0.42	ND	ND
Bk4m	0	0.76	0	0	BCk2	ND	0.41	ND	ND
Bk5	0	0.38	0	0	C	ND	0.26	ND	ND
Bk6m	0	0.28	0	0					
Bk7m	ND	ND	ND	ND					
Profile 2					**Profile 4**				
A	2.4	1.72	0.96	0.88	Ap	4.5	2.85	1.8	1.8
Bw	4.3	1.78	1.7	1.7	Bw	5.8	2.85	2.3	2.4
Bk1	2.3	0.64	0.92	0.84	Bk1	7.5	0.81	2.9	3.1
Bk2	2.0	0.51	0.81	0.71	Bk2	ND	0.45	ND	ND
Bk3	1.6	0.33	0.65	0.54	Bk3	ND	0.25	ND	ND
Bk4	1.6	0.28	0.65	0.54	Bk4	ND	0.26	ND	ND
Bk5	ND	ND	ND	ND	Bk5	ND	0.29	ND	ND
					C	ND	0.20	ND	ND

ND = not determined.

based on moist and dry field colors which were then averaged for each horizon. Redness ratings for some horizons equaled zero; in other cases, notably in Profiles 3 and 4, ratings were not calculatable because color could not be determined for some horizons. The coarse-textured nature of the subsoils resulted in colors which were due only to individual mineral grains and iron or carbonate stains on larger sand particles.

Hematite contents estimated using the data in Torrent et al. (1983) and the redness ratings calculated for the Cha River soils varied between 0.31 and 2.9 percent (Table 2). Hematite contents calculated from data given in Torrent and Cabedo (1986) for soils derived from calcarenites, were in the same range. The soils investigated here would appear to be reasonable approximations to those examined by Torrent and Cabedo. Despite this, the hematite contents estimated in this way overestimated the Fe_d content in half of the soil horizons investigated.

In an other study (Part 3, this dissertation) x-ray diffraction analyses identified only goethite in these soils. These findings suggest that an independent regression equation is necessary to estimate the hematite content in the soils studied here. It also suggests that hematite, if present in these soils, existed as a very finely divided component which was likely to be x-ray amorphous. Gangas et al. (1973) identified hematite in some Greek soils using Mössbauer spectroscopy. They found that hematite existed as discreet particles of very fine size (1.31 nm). Torrent et al. (1980) suggested that failure to identify hematite in the clay fraction of soils by XRD could be attributed to low contents and/or poor crystallinity. Further studies using differential x-ray diffraction and Mössbauer spectroscopy would be required to positively identify hematite in the soils investigated here.

Figure 3 illustrates the relationship between the crystalline secondary iron oxides and clay contents with depth in these soils. The ratios were calculated by subtracting the oxalate iron values from the dithionite iron values and dividing the resulting iron content (as % of < 2 mm soil) by the clay content. The values ranged from 0.02 to 0.08. Haidouti and Yassoglou (1982) reported similar results for a group of soils near Nichoria in southwestern Greece. The low values of this ratio imply

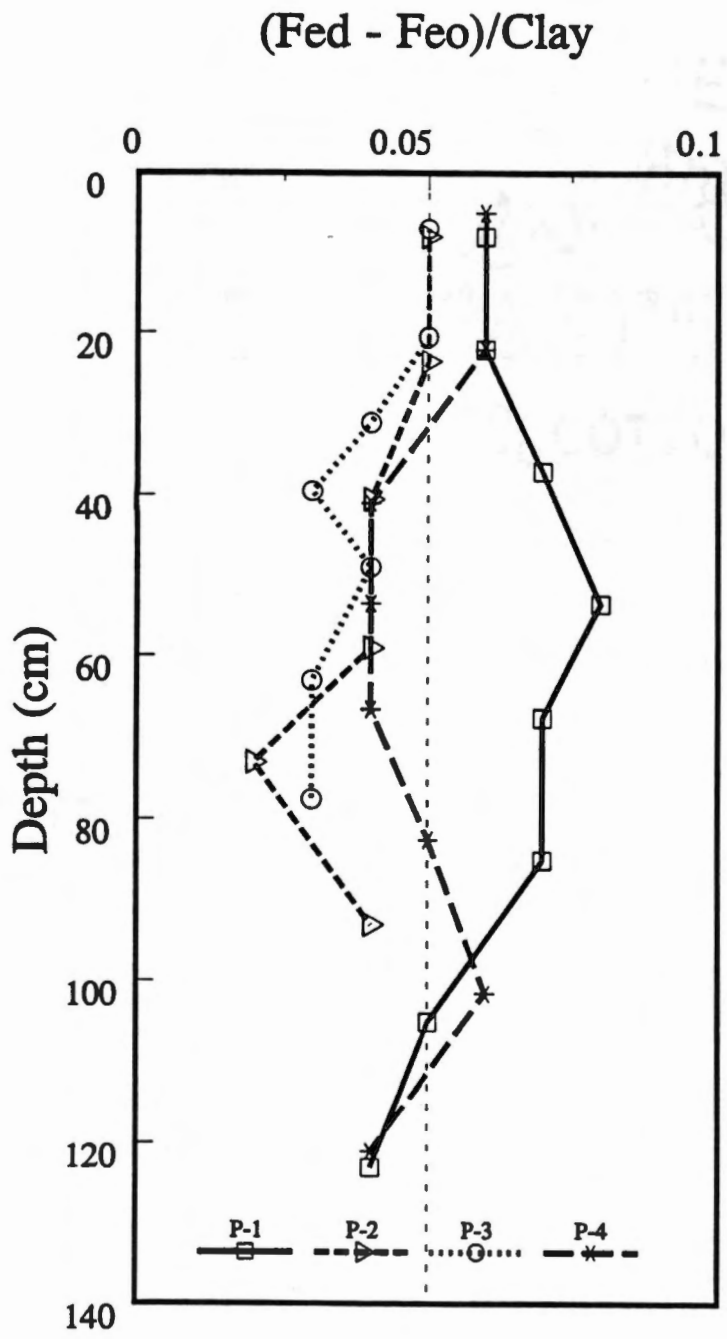


Figure 3. The relationship between the crystalline secondary iron oxides and clay content with depth in the four soils studied.

that little of the crystalline secondary iron oxides in these soils was associated with the clay fraction; therefore, the majority of the secondary iron compounds existed as discrete particles.

The content of oxalate extractable iron in soils has been shown to be affected by soil mineralogy. Schwertmann (1964) suggested that oxalate extracted the amorphous iron fraction. This fraction has been demonstrated to consist primarily of ferrihydrite (Schwertmann and Taylor, 1977). Other investigators have found that the presence of magnetite and/or iron-bearing trioctahedral clay minerals can influence the content of iron extractable in acid oxalate (Baril and Bitton, 1967; Arshad et al., 1972; Pawluck, 1972; Walker, 1983). Baril and Bitton (1967) advised removal of magnetite from soils prior to analysis of free iron oxides if more accurate values of amorphous iron were desired. Walker (1983) suggested that when using Fe_o/Fe_d ratios for relative age dating, the ratio of magnetite-free oxalate to untreated dithionite iron should be utilized. Arshad et al. (1972) advised caution when interpreting the Fe_o content of soils relative to pedogenesis when iron-bearing trioctahedral silicates were present. Pawluck (1972) indicated that NH_4-oxalate extractable iron was probably useful as an indicator of relative quantities of "amorphous" iron oxides, but the use of this extractant was questionable as a measure of absolute amounts of this iron fraction. Both Arshad et al. (1972) and Pawluck (1972) found particle-size to be an important factor in the extractability of Fe_o.

The soils examined in this investigation contained only trace amounts of magnetite; therefore, the contribution of oxalate extractable iron from magnetite is probably negligible. However, mineralogical analysis (Part 3, this dissertation) identified iron-bearing trioctahedral chlorite in these soils. As a result, the Fe_o and "active iron ratio" (Fe_o/Fe_d) data should be interpreted with some caution.

The oxalate extractable iron (Fe_o) contents followed the same pattern as dithionite iron (Table 1), being highest in the surface and decreasing with depth. The higher content of Fe_o in the surface horizons suggested that the greatest degree of weathering occurred in the surface layers of these soils. Weathering of primary minerals (most likely the chlorite present in the clay fraction) released iron which was probably initially converted to ferrihydrite and iron-organic matter complexes. Loeppert

(1988) suggested that a ferrihydrite-like phase probably controlled $Fe_{(aq)}$ concentrations in calcareous, oxidizing environments.

Singer (1977) found Fe_o contents were highest in the argillic horizons of soils formed from basalt and scoria in Israel. He suggested this was the result of translocation of amorphous iron compounds associated with the clay fraction. The data presented in Table 1 and Figure 3, imply that translocation of clay and associated amorphous iron was not a significant process in the soils investigated here. Due to the calcareous nature of these soils, limited translocation of clay would not be unexpected.

Oxalate iron contents as a percentage of total iron varied from 1.3 to 5.3 percent. Percentages were highest in the surface layers and generally decreased with depth. The ratio was similar in the surface layers of all four soils, suggesting a similar degree of weathering for the upper portions of these soils.

Arduino et al. (1986) examined Fe_o to Fe_t ratios from complete profiles of soils formed on upper Pleistocene to middle Pleistocene terrace sequences; thus, the Fe_o to Fe_t ratios from the present study may be comparable with those analyzed by Arduino et al. (1986). Soils from upper Pleistocene terraces exhibited Fe_o/Fe_t ratios that ranged from 7 to 23 percent. Soils developed in middle Pleistocene terrace sediments had Fe_o/Fe_t ratios ranging from 5 to 23 percent. In general, the Italian soils exhibited much higher ratios of oxalate to total iron than did the soils of the Cha River region. These results may be due to the large difference in parent materials between the two locations. Based on the data of this study and those presented by Arduino et al. (1986), it appears that the ratio of oxalate to total iron is not an effective means of separating soils based on their relative age.

The ratio of Fe_o to Fe_d is often used to assess the "active" fraction of soil iron (Blume and Schwertmann, 1969; Birkeland, 1984). The active iron ratio values in general were low, varying from 0.05 to 0.16 (Figure 4). Haidouti and Yassoglou (1982) found similar results (0.03 to 0.17) for a group of soils in southwestern Greece. Torrent et al. (1980) reported that for red soils in Spain, the Fe_o/Fe_d ratio rarely exceeds 0.15 and is generally less than 0.07 irrespective of parent material or environment.

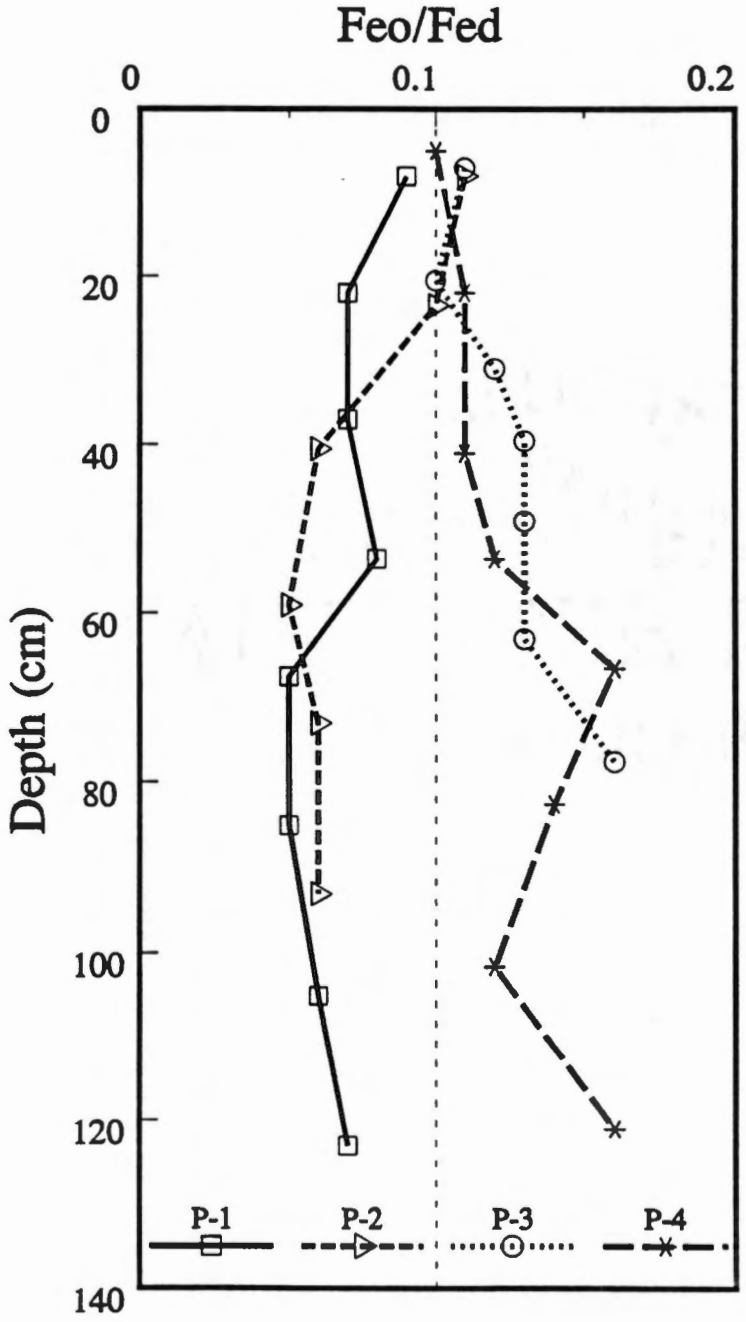


Figure 4. Active iron ratios (Fe_o/Fe_d) plotted with depth for all four soils.

Singer (1977) also reported low values for this ratio (generally < 0.1). The low ratio of Fe_o to Fe_d in the present soils and the general agreement of this value with data published for other Mediterranean soils suggests that little structural iron was removed from the chlorites by this extractant.

The active iron ratios in the least stable landscape positions were highest in the surface horizons and decreased with depth. Conversely, in the two most stable positions the ratio was lowest in the surface and increased with depth. One explanation for these results could be that erosion of material from the shoulder position and subsequent deposition of the partially weathered sediments in the lower backslope position may be maintaining a higher Fe_o level in the least stable positions. Conversely, the greater stability of the two upland positions probably allowed sufficient time for conversion of the amorphous iron components into crystalline phases, thus producing lower Fe_o/Fe_d ratios in the surface horizons of these two soils. The higher ratios with depth in the stable uplands may have been indicative of active weathering.

Manganese

Total analyses of the dolostones and phyllite yielded values of 0.002 percent MnO for the dolostones and 0.22 percent MnO for the phyllite. Total Mn (Mn_t) in the soils ranged from 0.015 to 0.160 percent MnO (Table 3). These values lie on both sides of the world soil-average of 850 mg kg^{-1} (0.110% MnO) (Yaalon et al., 1974). Total Mn was highest in surface horizons and generally decreased with depth. Yaalon et al. (1972) reported total soil Mn contents for two separate catenary sequences formed on dolomite and limestone. Manganese contents from soils of the dolomite catena ranged from 950 to 1950 mg kg^{-1} (0.116 to 0.238% MnO). Soils of the limestone catena averaged 750 to 1800 mg kg^{-1} (0.091 to 0.219% MnO). The data of Yaalon et al. (1972) are generally higher than those listed in Table 3 for the soils of the Cha River region. Because no data were presented for the Mn content of the dolomite or limestone in the Israeli study it is difficult to determine why such large differences existed between their soils and those investigated here. Singh et al. (1988) reported total Mn

Table 3. Total and extractable manganese fractions from Profiles 1 through 4.

Horizon	Total-Mn	Dithionite-Mn	Oxalate-Mn	Hydroxylamine-Mn	Silicate-Mn
	MnO %	mg/kg			
Profile 1					
Ap	0.048	263	220	156	39
A/Bk	0.029	169	148	108	11
Bk1	0.015	74	66	53	19
Bk2	0.015	59	75	56	33
Bk3	0.025	116	103	100	41
Bk4m	0.028	138	143	110	42
Bk5	0.019	111	82	73	12
Bk6m	0.015	72	59	58	24
Bk7m	ND	ND	ND	ND	ND
Prof. Wt. Mean	0.024	124	111	89	ND
Profile 2					
A	0.090	456	531	334	116
Bw	0.088	441	538	338	115
Bk1	0.027	124	117	97	48
Bk2	0.025	102	110	87	57
Bk3	0.019	87	67	57	31
Bk4	0.033	167	146	133	42
Bk5	ND	ND	ND	ND	ND
Prof. Wt. Mean	0.043	213	223	164	ND

Table 3 (continued)

Horizon	Total-Mn	Dithionite-Mn	Oxalate-Mn	Hydroxylamine-Mn	Silicate-Mn
	MnO %	mg/kg			
Profile 3					
Ap	0.141	725	946	506	169
Bw	0.126	651	934	455	149
Bk1	0.027	113	88	106	56
Bk2	0.021	69	59	84	64
BCk1	0.028	97	99	118	79
BCk2	0.023	70	69	85	73
C	0.019	57	48	77	67
Prof. Wt. Mean	0.045	197	354	167	ND
Profile 4					
Ap	0.160	846	1268	589	164
Bw	0.154	813	1169	592	164
Bk1	0.036	184	118	146	44
Bk2	0.027	129	90	97	45
Bk3	0.019	81	43	65	41
Bk4	0.020	82	32	72	42
Bk5	0.021	95	60	81	41
C	0.016	61	25	54	39
Prof. Wt. Mean	0.057	290	356	216	ND

ND = not determined.

contents in surface horizons of some calcareous soils of India which varied from 207 to 409 mg kg^{-1} (0.025 to 0.050% MnO). These values were much lower than those observed in the surfaces of the Cha River soils.

An estimate of the silicate-Mn contents was obtained by subtracting the dithionite-Mn from the total-Mn. As with the Fe, the low content of Mn in the dolostones made this a reasonable assumption. Silicate-Mn contents were highest in surface layers and decreased with depth (Table 3). These distributions resulted from the combined effect of dissolution and translocation of the carbonates from the surface horizons of these soils. The net effect of these two processes was a concentration of the phyllite materials in surface layers. A lower content of silicate-Mn in subsoils was due in-part to dilution effects caused by translocation of carbonates. The source of the silicate-Mn in the phyllite is probably the interlayer hydroxide sheet of the chlorite mineral identified in this rock (Bailey, 1975; Moore and Reynolds, 1989; Weaver and Pollard, 1973). The distribution of silicate-Mn as a percentage of the total-Mn (Figure 5) indicated that the majority of Mn compounds in the surfaces of these soils existed as secondary oxides and organically complexed Mn species.

The dithionite extractable Mn (Mn_d) contents ranged from 57 to 846 mg kg^{-1} and followed the same general trend as total-Mn (Table 3). Singer (1977) reported Mn_d levels close to 1000 mg kg^{-1} in some soils formed from basalt and scoria in Israel. The distribution of this Mn fraction was uniform in the soils examined by Singer. The higher content of manganese in the Israeli soils was due in-part to the parent materials and partly to the climate. Singer reported the rainfall for that portion of Israel was between 600 and 800 mm per year; nearly twice that for the Cha River region.

Profile weighted Mn contents were also utilized to assess differences among the various landscape positions (Table 3). These data were effective in discriminating the least stable and most stable landscape locations, but were not effective in separating Profiles 2 and 3 (the lower backslope and the shallower of the two upland positions). This is most likely related to the effect that long-term deposition of Mn-bearing sediments has had on the whole-soil content of Mn in Profile 2.

As a fraction of the total-Mn, Mn_d ranged from 46 to 94 percent (Figure 6). The relatively

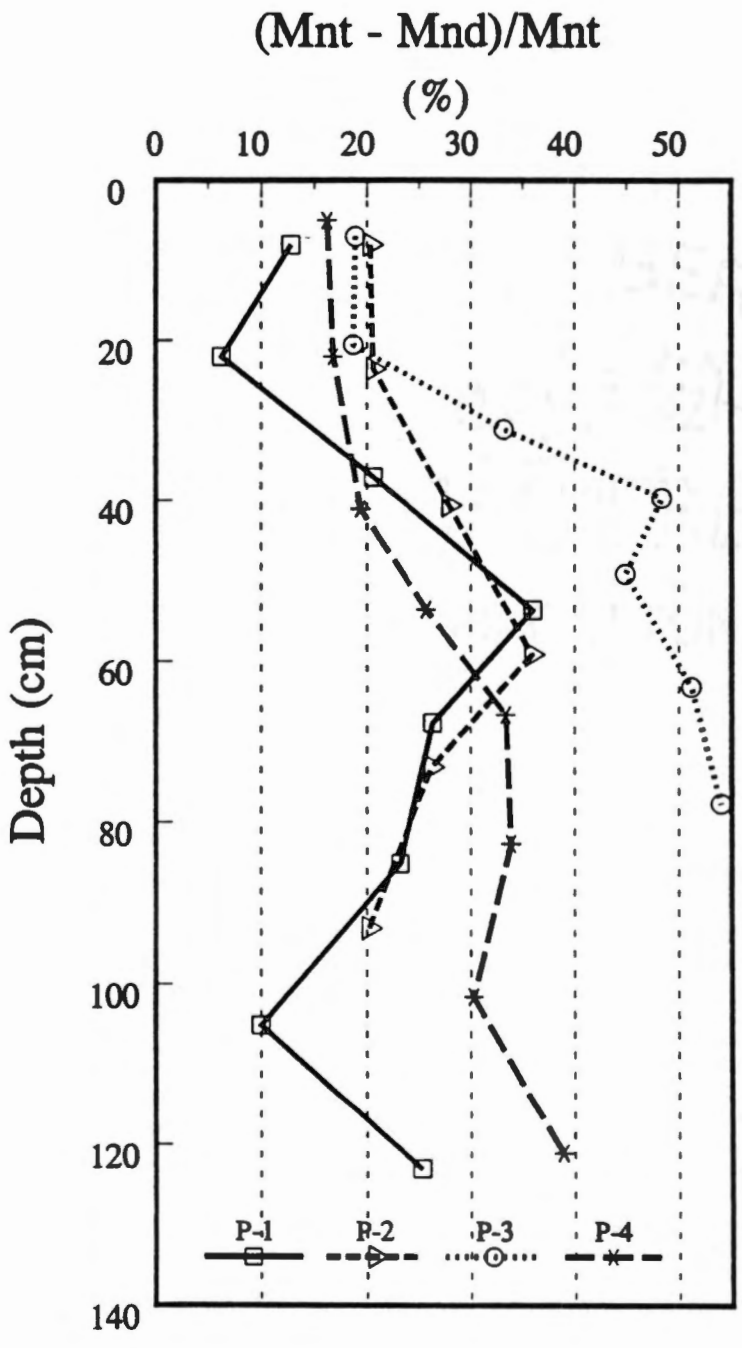


Figure 5. Silicate manganese (Mn_t - Mn_d) as a percentage of total manganese, plotted with depth for Profiles 1 through 4.

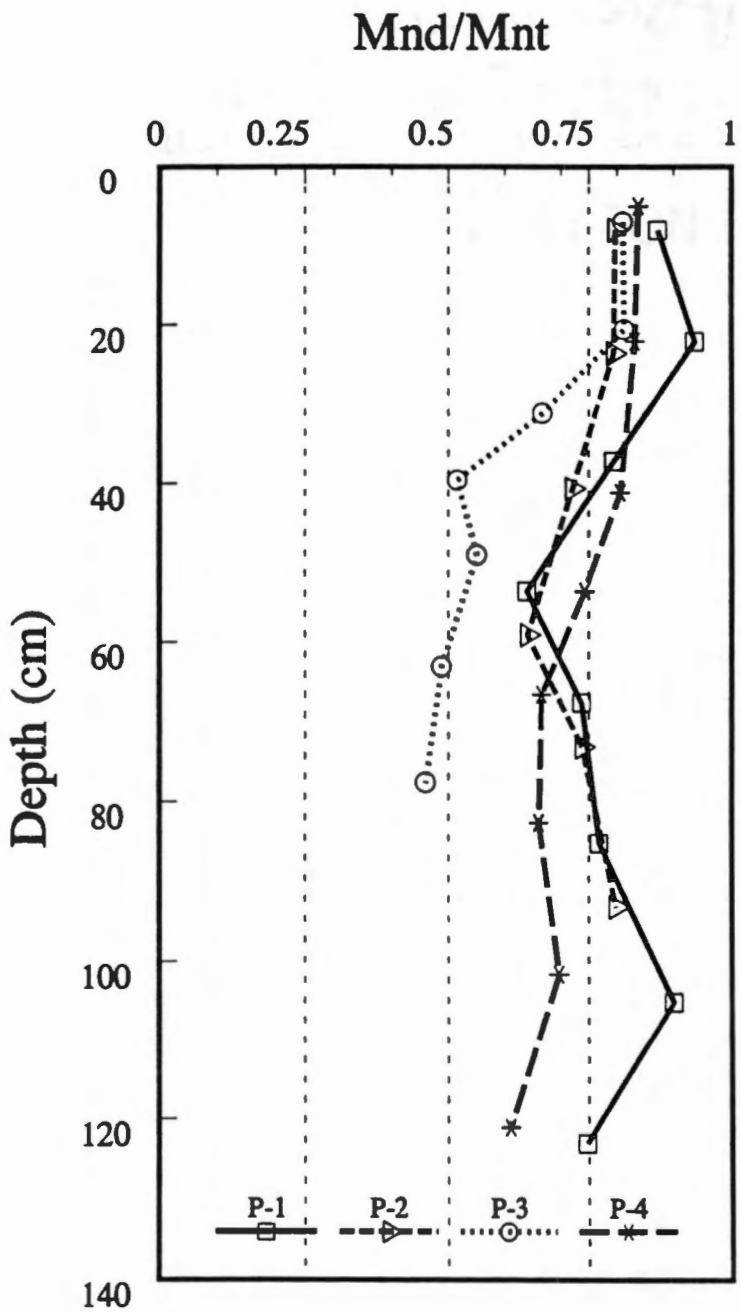


Figure 6. Depth distribution of dithionite extractable manganese as a fraction of total manganese for all four profiles.

high Mn_d contents throughout all four profiles substantiates the earlier finding that most of the Mn in these soils existed as secondary oxide species and organically complexed forms.

The content of oxalate-extractable Mn (Mn_o) in general paralleled that of the total and dithionite extractable forms (Table 3). In non-calcareous soils, Blume and Schwertmann (1969) suggested that NH_4-oxalate extracted approximately the same soil Mn fraction as Na-dithionite. Figure 7 illustrates the distribution with depth of Mn_o as a percentage of total Mn. These percentages varied from 25 to 125; whereas Mn_d as a percentage of total Mn varied only from 46 to 93 percent (Figure 6). The differences in the extractability of Mn by these two solutions may represent random variability, or they may suggest that oxalate is extracting Mn from the chlorite present in these soils. The ratio of Mn_o to Mn_d as a function of depth varied from 0.39 to 1.5 (Figure 8). The range of these data is equivalent to that for Mn_o relative to total Mn. These results indicate that further analysis should be conducted to determine the effectiveness of NH_4-oxalate relative to dithionite in extracting secondary Mn-compounds in highly calcareous soils and/or in soils containing Mn-bearing trioctahedral clays.

Hydroxylamine-HCl - HNO_3 solutions at pH 2 have been demonstrated to extract the secondary Mn-compounds that are not closely associated with the Fe-oxide fraction of soils (Chao, 1972). The hydroxylamine extractable Mn (Mn_h) contents ranged from 54 to 589 mg kg^{-1} (Table 3). As with the other Mn fractions, the Mn_h contents were generally highest in the surface horizons and decreased with depth. The difference between the Mn_d and Mn_h contents indicated that the majority of the Mn compounds in these soils existed as discrete forms not associated with secondary Fe-oxides, or were complexed by organic matter.

When viewed as a percentage of total Mn, Mn_h varied from 49 to 67 percent (Figure 9). Singh et al. (1988) found that on average only 22 percent of the total Mn in a group of calcareous soils in India was extractable in hydroxylamine. The overlap of the data in the four soils examined here (Figure 9) suggested that the same fraction of Mn was being removed from all four soils. Chao (1972) reported an average of 85 percent of the total manganese was extracted by hydroxylamine from the sediments he

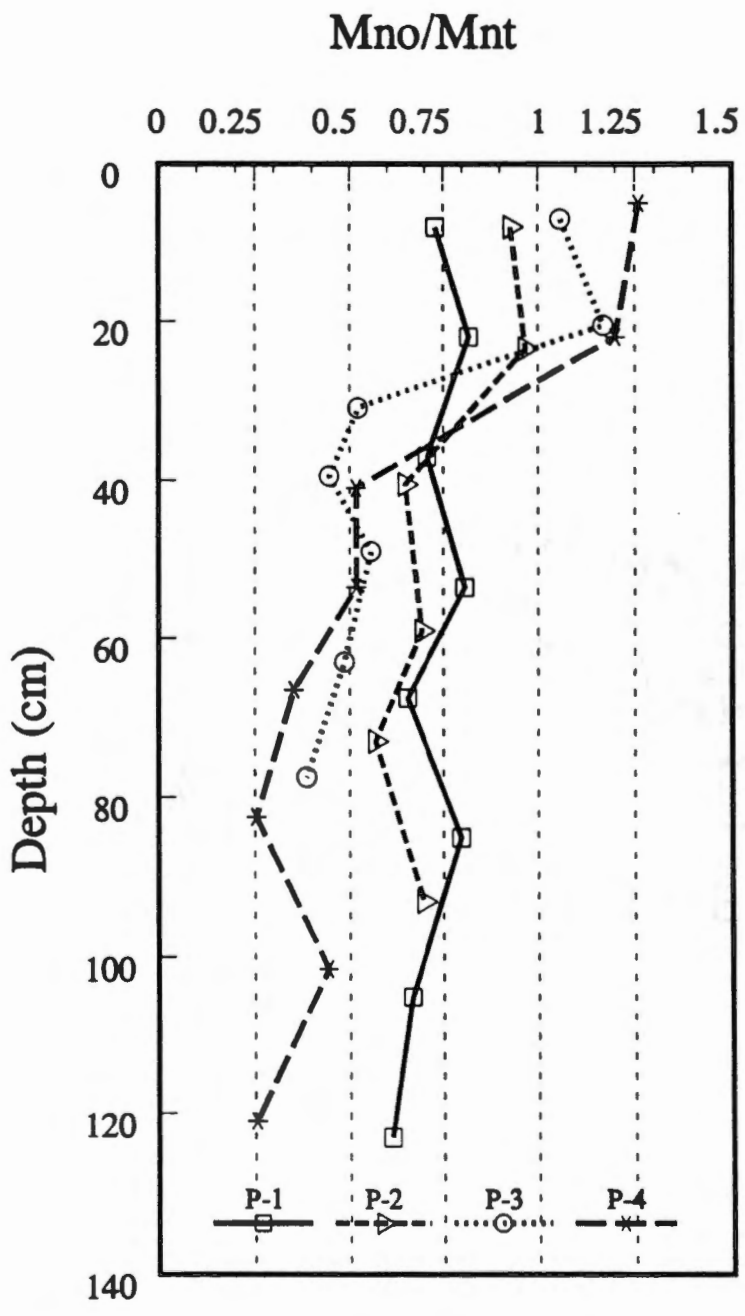


Figure 7. Depth distribution of oxalate manganese as a fraction of total manganese in profiles 1 through 4.

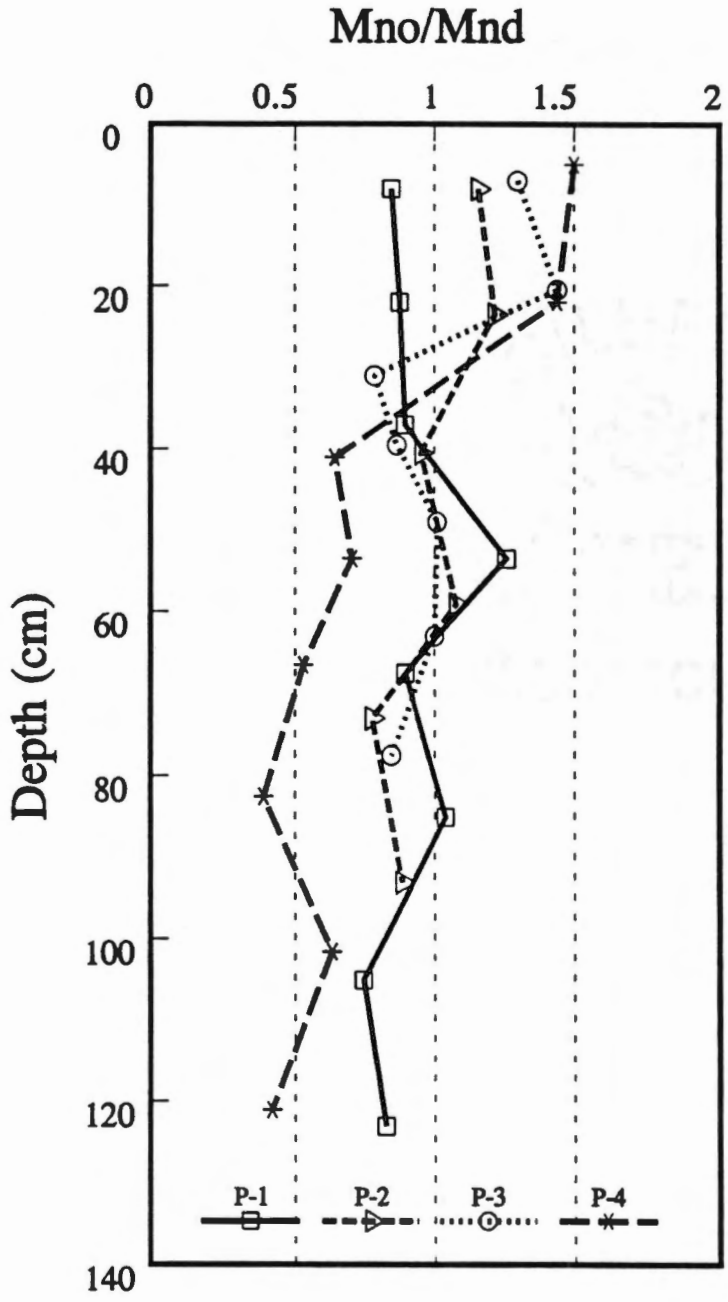


Figure 8. Distribution with depth of the ratio of oxalate to dithionite extractable manganese in the four soils investigated.

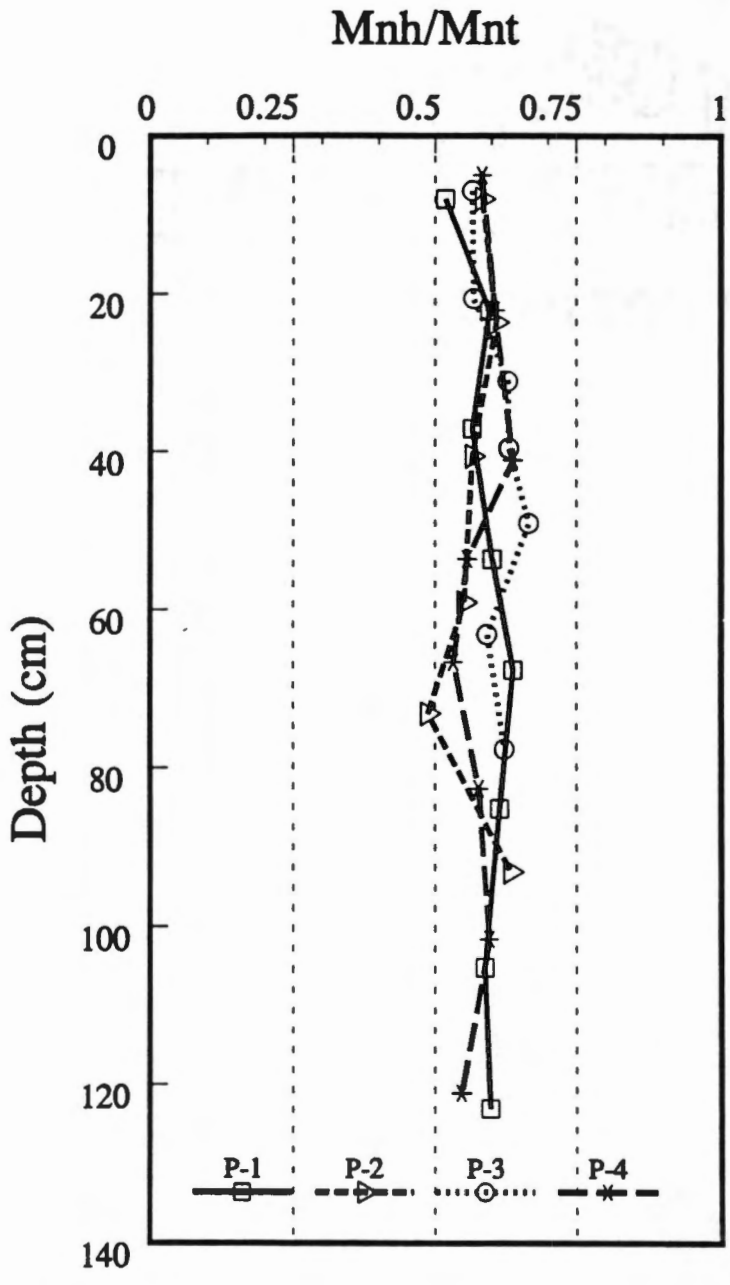


Figure 9. Hydroxylamine extractable manganese as a fraction of total manganese in Profiles 1 through 4 plotted with depth.

examined. The average extractable Mn_h content relative to total Mn in the Cha River soils was 58.8 percent. These data, as well as the low content of iron extractable in hydroxylamine (0.05 to 4.1 percent of total Fe) indicated that the same fraction of Mn is being extracted from these soils as was extracted from the group which Chao used. The content of Mn_h in the present soils may be lower on average because the high carbonate contents neutralized the extracting solution. This probably reduced the effectiveness of the extractant to some degree. Assuming that 85 percent recovery of total Mn is an upper limit, this reduction amounted to about 31 percent. These results suggest however, that even in highly calcareous soils, hydroxylamine-HCl at pH 2 is an effective extractant for estimating the proportion of Mn that is not closely associated with secondary iron compounds.

Silica

Total analysis of the parent materials indicated that the dolostone contained only 3.1 percent SiO_2; whereas the phyllite component contained 47.1 percent SiO_2. Mineralogical analysis of the phyllite showed it was composed of chlorite, mica, quartz, and a small amount of kaolinite and feldspars. Analysis of the insoluble residue of the dolostone showed it was dominantly quartz (Part 3, this dissertation).

Total Si in these soils ranged from 6.5 to 46 percent as SiO_2 (Table 4). Because the quantity of other forms of extractable Si was quite small, total Si was assumed to equal silicate-Si. The distribution of this element paralleled that of both Fe and Mn; being highest in the surfaces, where dissolution and translocation of carbonates have concentrated it, and lower in the subsoils, where the proportion of phyllite materials was lower and translocated carbonates further diluted its content.

Weaver et al. (1968) suggested an association between the Si extractable in citrate-bicarbonate-dithionite (CBD) and the iron and aluminum compounds extracted by the same solution. Gamble and Daniels (1972) argued that silica extracted by CBD was the result of partial dissolution of quartz and kaolinite present in the soils they examined. The solubility of quartz in water can vary from 0 to 14

Table 4. Total and extractable silica fractions from Profiles 1 through 4.

Horizon	Total-Si	Dithionite-Si	Oxalate-Si	Hydroxylamine-Si
	SiO_2 %	---------- mg/kg ----------		
Profile 1				
Ap	32.67	477	457	53
A/Bk	25.33	423	314	37
Bk1	6.93	294	203	26
Bk2	6.59	298	228	25
Bk3	26.51	322	271	38
Bk4m	29.40	441	244	28
Bk5	18.15	344	232	24
Bk6m	18.71	329	218	25
Bk7m	ND	ND	ND	ND
Prof. Wt. Mean	20.52	368	267	31
Profile 2				
A	37.37	931	686	108
Bw	37.88	820	714	117
Bk1	21.32	410	319	41
Bk2	21.62	383	272	31
Bk3	19.52	372	249	31
Bk4	23.64	468	235	37
Bk5	ND	ND	ND	ND
Prof. Wt. Mean	26.04	538	364	54

Table 4 (continued)

Horizon	Total-Si	Dithionite-Si	Oxalate-Si	Hydroxylamine-Si
	SiO_2 %	---------- mg/kg ----------		
Profile 3				
Ap	37.51	1015	922	219
Bw	42.62	998	877	179
Bk1	19.54	256	389	67
Bk2	18.42	128	328	51
BCk1	19.97	227	334	54
BCk2	25.58	91	328	56
C	20.67	289	305	36
Prof. Wt. Mean	25.08	393	441	77
Profile 4				
Ap	35.91	1016	887	209
Bw	46.07	1106	900	216
Bk1	29.80	463	502	92
Bk2	21.30	187	390	59
Bk3	13.40	305	322	43
Bk4	14.50	252	301	41
Bk5	30.17	234	283	39
C	9.69	220	253	34
Prof. Wt. Mean	25.94	484	478	92

ND = not determined.

mg L^{-1} Si (Wilding et al., 1977). The solubility increases however as a result of excessive grinding or shaking the suspension during the extraction process. This increase in solubility has been attributed to a disordered or amorphous layer at the surface of quartz grains (McKeague and Cline, 1963b; Wilding et al., 1977). Removal of this layer using pretreatments of NaOH or HF generally yields soluble quartz values within the range mentioned earlier (Henderson et al., 1970 in Wilding et al., 1977). The CBD-Si values attributed to dissolution of quartz and kaolinite by Gamble and Daniels (1972) may have been derived, in-part, from this disordered layer. Data presented in Wada (1977) indicated that CBD is a rather poor extractant for amorphous silica and/or short-range order aluminosilicates. These studies suggest that CBD extractable Si probably represents that portion of soil Si which is associated with secondary iron, manganese and/or aluminum compounds.

McKeague and Cline (1963c) and Beckwith and Reeve (1963) demonstrated that the adsorption of monosilicic acid by soil sesquioxides was maximal between pH 8 and 10. At these pH levels sesquioxides may act as sinks for soluble silica (Wilding et al.,1977). Whereas the pH of the soils in the present study varied between 7.9 and 9.0, sorption of silica by sesquioxide compounds could represent a source of extractable Si in these soils.

Dithionite extractable Si (Si_d) ranged from 91 to about 1000 mg kg^{-1} (Table 4). It was generally highest in the surface horizons and decreased with depth. Dithionite extractable-Si data for soils of the Mediterranean region are very limited. Weaver et al. (1968) reported a value of 383 mg kg^{-1} for the A-horizon of a soil from northeastern Iraq.

The majority of reports of this silica fraction have come non-calcareous soils from humid temperate regions. Harlan et al. (1977) reported values of 467 to 1402 mg kg^{-1} CBD extractable Si in some loess soils in southwestern Indiana. In a study of loess-derived soils of late Wisconsinan age in the same area of Indiana, Norton and Franzmeier (1978) reported Si_d levels between 0.75 and 4.0% SiO_2. Ajmone Marsan and Torrent (1989) reported dithionite extractable Si values between 170 and 1020 mg kg^{-1} for an Aquic Fragiudalf in northwestern Italy. The Si_d contents of the Cha River soils were within the range of values reported in these previous investigations, suggesting that even in

calcareous soils under Mediterranean climatic conditions, dithionite extracts approximately the same fraction of soil silica.

Profile weighted means (Table 4) discriminated between the most stable and least stable landscape positions, but as with the other elements examined, this value was ineffective at separating Profiles 2 and 3, probably for the same reasons outlined earlier.

The relationship between the Si extractable in dithionite and the crystalline iron compounds in the Cha River soils is illustrated in Figure 10. The ratio of Si_d to (Fe_d - Fe_o) varied widely in these soils but never exceeded 0.2, suggesting that only about 20 percent of the Si_d is associated with these iron compounds. Secondary Mn species may also be acting as sites of Si sorption. A plot of the dithionite extractable Si and Mn is illustrated in Figure 11. These data indicate that Si_d contents were high enough to completely saturate the secondary Mn compounds; thus, Mn species may be only a minor source of sorbed or occluded Si in these soils.

Oxalate extractable Si (Si_o) ranged from 218 to 922 mg kg^{-1} (Table 4). Hallmark and Smeck (1979) reported Si_o levels between 100 and 600 mg kg^{-1} in some fragipan soils of northeastern Ohio. The Si_o values of the present study were comparable to those identified by Hallmark and Smeck. The relationship between Si_o and Fe_o is shown in Figure 12. The ratio of these two fractions varied from about 0.5 to 1.8, suggesting a higher affinity between the amorphous and organic iron species and silica in these soils than was demonstrated for the crystalline iron components. Cornell et al. (1987) suggested that under alkaline conditions, silicate species were adsorbed to ferrihydrite particles, linking them into an immobile network. Alternatively, iron-organic matter complexes could be serving as sites of sorption for the extractable silica in these soils.

Silica sorbed to carbonate surfaces may also explain some of the variation in the extractable Si contents in the present study (Beckwith and Reeve, 1963). Because most of the extractants utilized in this investigation were acidic they would have dissolved some portion of the carbonates present in the sample, thus, releasing silica sorbed to their surfaces. Due to the highly calcareous nature of the soils

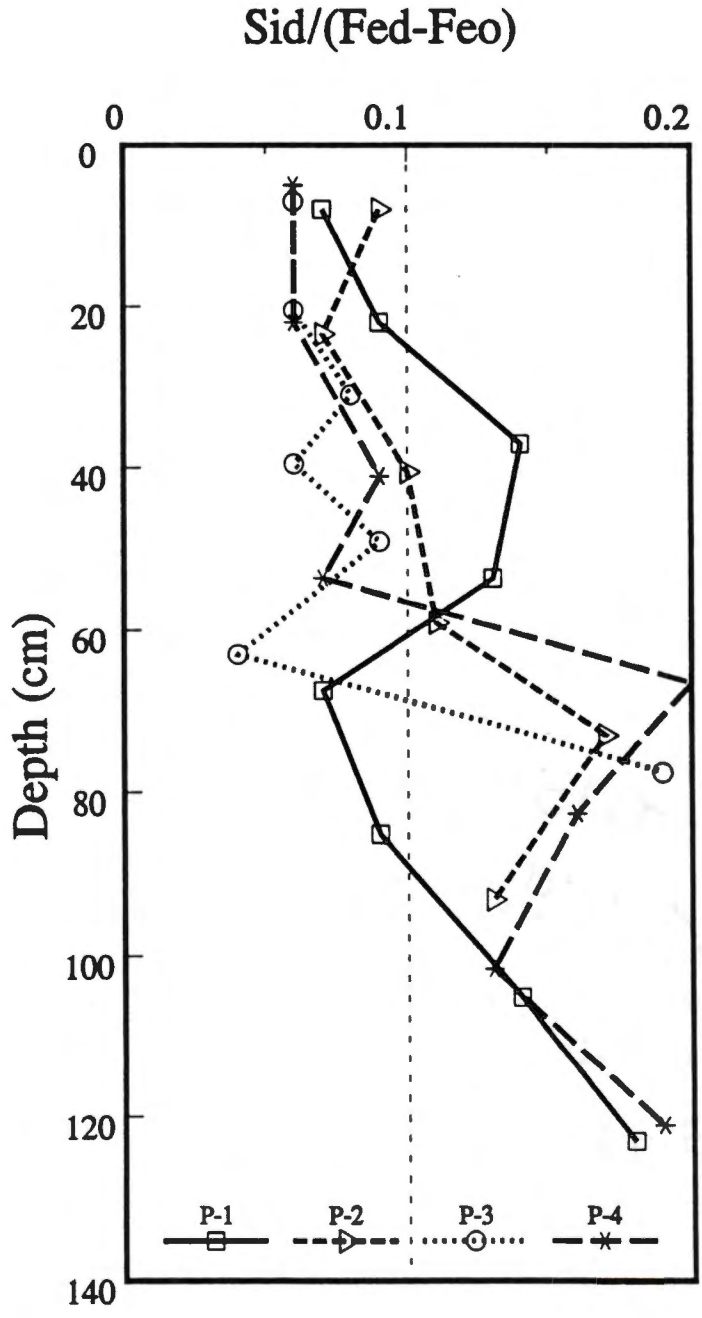


Figure 10. Relationship between dithionite extractable silica and crystalline iron oxide compounds (Fe_d - Fe_o) in all four soils.

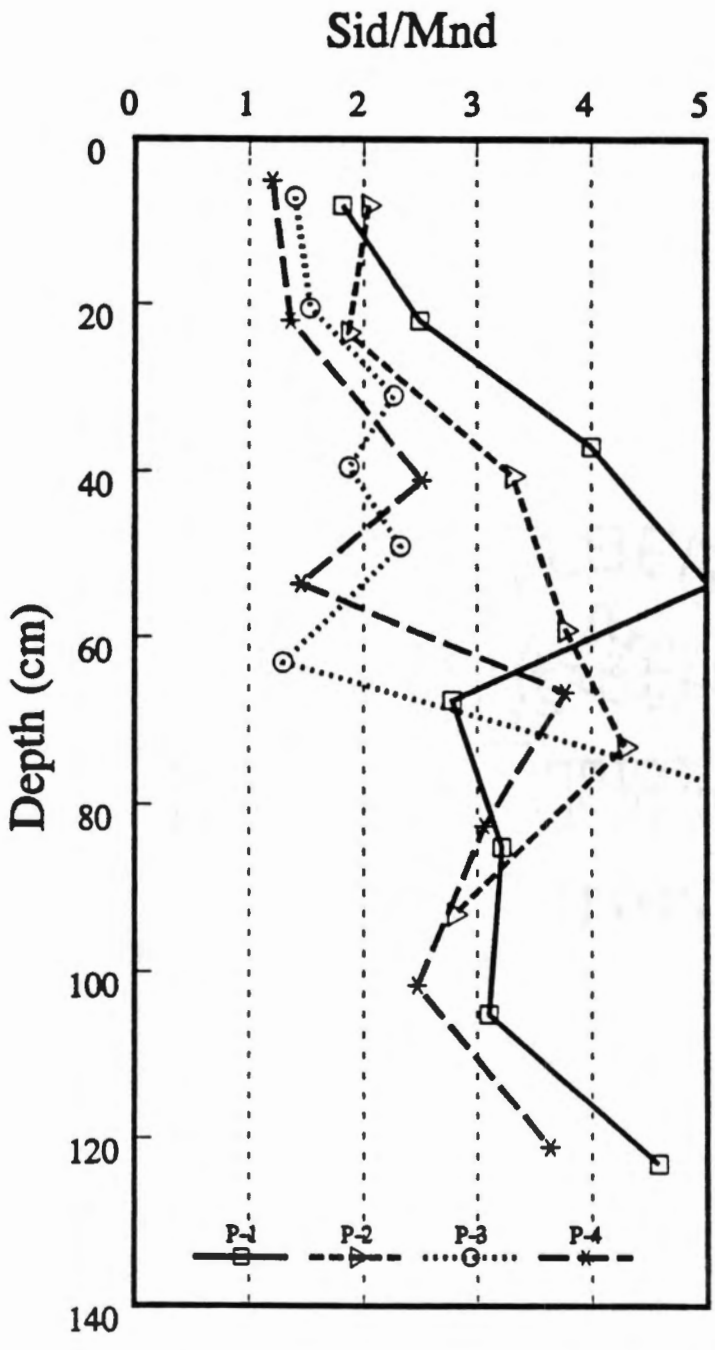


Figure 11. Dithionite extractable silica as a fraction of dithionite extractable manganese in the four soils studied.

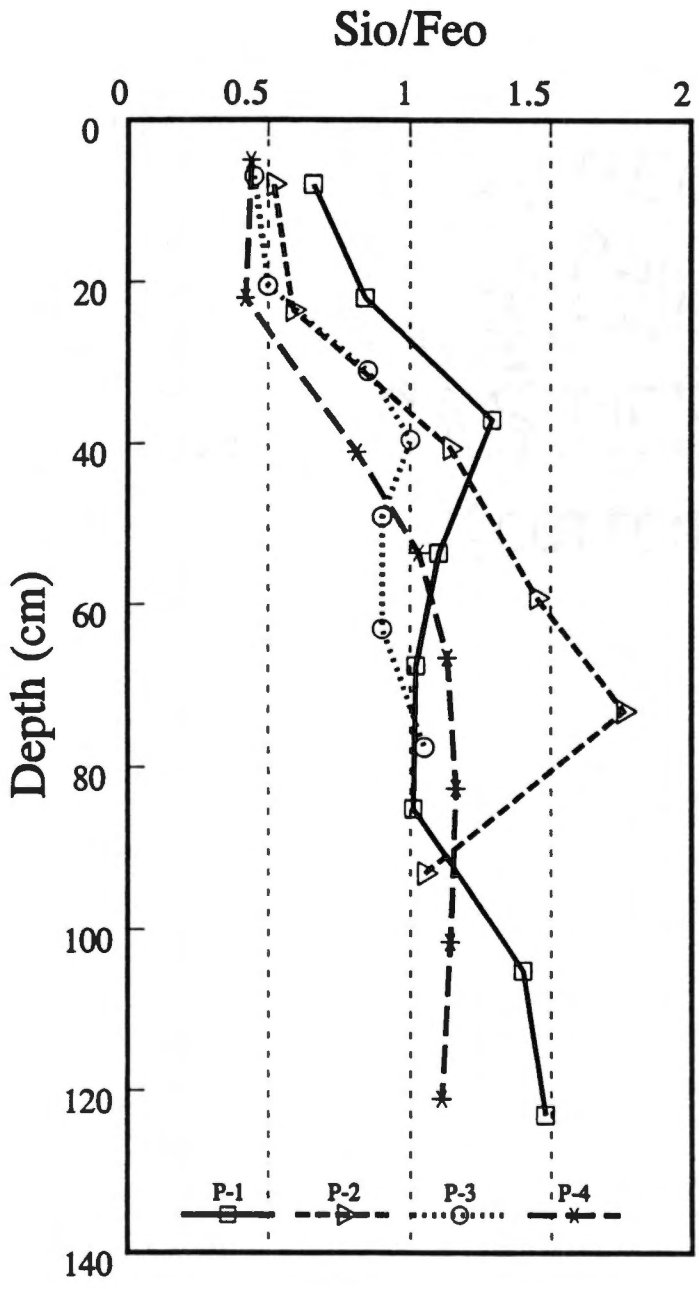


Figure 12. Ratio of oxalate extractable silica to oxalate extractable iron as a function of depth in Profiles 1 through 4.

investigated, silica sorbed to carbonate surfaces may represent a substantial portion of the extractable silica.

It was demonstrated earlier that hydroxylamine extractable Mn is not closely associated with the secondary iron species in this group of soils; thus, it should provide a measure of the association between the secondary manganese and silica species present. The ratio of these two fractions varied from about 0.3 to 0.7 (Figure 13). The variation in this ratio was much lower than that for the silica associated with the dithionite extractable Mn. This seems to imply that dithionite extracts silica from both the Fe and Mn compounds soluble in that extract. Because hydroxylamine is specific for secondary Mn compounds, the ratios of Si_h to Mn_h indicate that between 30 and 70 percent of the Mn-species in these soils could contain occluded or sorbed silica.

CONCLUSIONS

Iron contents from all extractions were highest in the surfaces and decreased with depth; generally as a function of dissolution and translocation of carbonates. Based on studies by Arduino et al. (1984 and 1986) silicate iron contents as a percentage of total iron in these soils suggested a maximum upper age limit of late Pleistocene to Holocene for the soils of the Cha River area. Dithionite to total iron ratios suggested a similar age range for these soils. Whole-profile averages of the various iron fractions were helpful in discriminating among landscape positions. The colluvial nature of Profile 2 reduced the effectiveness of this method for clearly separating it from the other two landscape positions. The ratio of oxalate to dithionite extractable iron was low in all four profiles. This suggested a relatively rapid conversion of reduced iron released by weathering of silicates into crystalline forms of secondary iron oxides.

The content of total Mn was comparable to the world-soil average of 850 mg kg^{-1}. Manganese contents were highest in the surface and decreased with depth for the same reasons outlined for the iron fraction. The ratio of silicate-Mn to total-Mn and that of dithionite to total manganese both indicated that manganese in these soils existed primarily as secondary oxides and organically bound species.

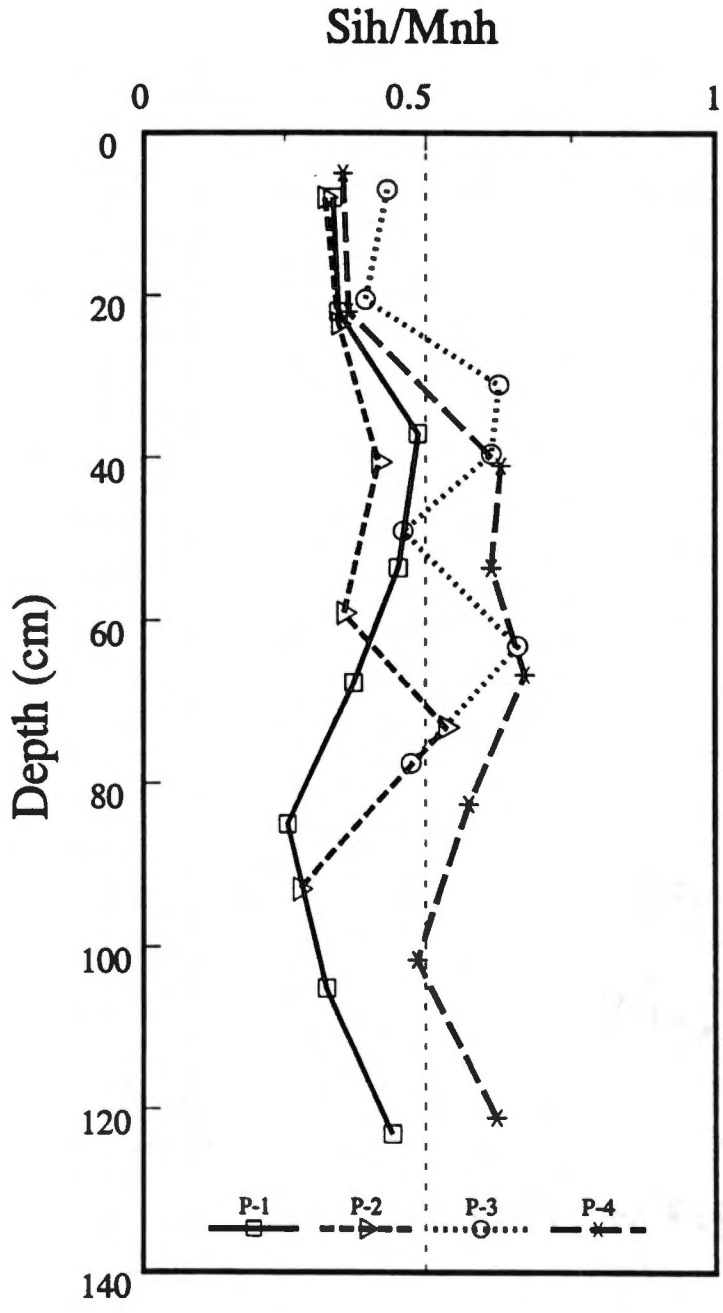


Figure 13. The relationship between hydroxylamine extractable silica and hydroxylamine extractable manganese in Profiles 1 through 4 plotted with depth.

Weighted profile Mn contents discriminated among landscape positions about as well as did the Fe-oxides. Acid ammonium oxalate extracted a wider range of Mn from these soils than did Na-dithionite. This suggested that for highly calcareous soils or soils containing Mn-bearing trioctahedral silicates, oxalate may not extract the same fraction of soil-Mn that dithionite does. Hydroxylamine extracted an average of 58.8 percent of the total Mn in these soils, while extracting only 0.05 to 4.1 percent of the total iron. This indicates that even in these highly calcareous soils, hydroxylamine-HCl at pH 2 was effective in removing the Mn-oxides not closely associated with the iron oxide components.

The content of all silica fractions was greatest in the surface horizons and generally decreased with depth primarily as a result of dissolution and translocation of carbonates. Extractable silica contents were probably associated with the iron and manganese oxides either as sorbed species or as occluded forms in these compounds. Additionally, some portion of these silica fractions could also have existed as components sorbed to carbonate surfaces and/or associated with sesquioxide-organic matter complexes.

There is a strong probability that some portion of the Fe and Si contents of these soils resulted from eolian additions. Studies by Nihlén and Solyom (1986) demonstrated that the dominant components of eolian dustfall on Crete were quartz and clay minerals. No data were given by Nihlén and Solyom (1986) regarding deposition rates or likely rates of accumulation of eolian sediments on Crete. Because no data of this sort were collected during the course of the present study, estimates of the contribution of dustfall to the Fe and Si content of the soils of the Cha River region would be approximate at best. The analysis of stable isotopes of quartz could yield more definitive information in this regard.

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PART 4. A MINERALOGICAL INVESTIGATION OF SOME SOILS FORMED IN CALCAREOUS GRAVELLY ALLUVIUM, EASTERN CRETE, GREECE

INTRODUCTION

Relatively little mineralogical information has been reported regarding the Quaternary sediments of northeastern Crete. Dermitzakis (1973) investigated the occurrence of Pleistocene deposits in the southeast Sitea district of eastern Crete. The same author discussed neotectonic activity and the existence of old Pleistocene strandlines throughout Crete (Dermitzakis, 1974).

A number of authors have investigated the mineralogical properties of soils with respect to parent materials and soil development through the Quaternary (Pedro et al., 1969; Wilson, 1973; Rostad et al., 1976; McFadden and Hendricks, 1982). Pedro et al. (1969) stated that the composition of the clay fraction appeared to be an important feature of the pedological evolution of Quaternary soils.

Several investigators have noted physical weathering and clay mineral inheritance as major processes in Quaternary soils from a number of locations. Wilson (1973) examined numerous soil profiles developed from Old Red Sandstone till in Scotland which exhibited significant variations in parent material, soil type and drainage to evaluate the effects of inheritance and pedogenesis on the composition of the soil clays. He reported that the clay minerals in soils developed from these tills were primarily derived from the parent rocks. Pedogenic influences on the clays included rapid degradation of expanding trioctahedral minerals and vermiculitization of dioctahedral micas in A-horizons. Where soil pH was above 6 the expanding minerals were often preserved. Chlorite and kaolinite in these soils were not greatly affected by weathering. Rostad et al. (1976) reported that a combination of inheritance and dissolution/concentration were responsible for increases in clay content in soils formed from Pleistocene calcareous gravels in Ohio. Bain (1977), in a study of chlorite weathering in Scottish soils, noted the persistence of trioctahedral chlorites throughout the soils he investigated. The chlorites, which were inherited from the parent materials, remained relatively unweathered irrespective of drainage class, soil texture, organic matter content, pH or other chemical/physical properties that were measured. In an investigation of soils that developed on Holocene and Pleistocene terraces and alluvial fans in southern California, McFadden and Hendricks (1982) reported systematic changes in clay-mineral composition with increasing soil age. The weakly developed late Holocene soils they examined

contained very little clay. The mineralogical composition of these clays was found to be primarily the result of inheritance from the parent sediments.

Because the nature and properties of soils formed from Quaternary deposits can hold information with respect to Quaternary paleoclimates and their resulting pedogenic effects, an investigation was undertaken to determine the mineralogical composition of a group of soils formed in Quaternary alluvium of the Cha River drainage. A close examination of the mineral weathering characteristics of these soils should allow a reconstruction of the chemical and physical weathering processes responsible for the suite of minerals observed and provide some insight into the stage of weathering and relative age of these soils.

MATERIALS AND METHODS

The study area was located at the northern end of the Isthmus of Ierapetra (Fig. 1). The profiles investigated represented three landscape positions; an upland shoulder (Profile 1), a lower backslope (Profile 2) and two profiles located in stable uplands (Profiles 3 and 4). The parent material consisted of coarse-textured dolostone alluvium which contained approximately one percent small phyllite gravels.

Soil separates were collected following routine particle-size analyses. The soils were dispersed using a combination of Na-hexametaphosphate and Na-carbonate (Gee and Bauder, 1986). Pretreatments consisted of H_2O_2 removal of organic matter from surface samples and citrate-dithionite (Holmgren, 1967) removal of iron oxides where necessary. Coarse (50-20 μm) and fine (20-2 μm) silts were separated by gravity sedimentation and decantation after particle-size analyses. The Na-saturated silts were oven-dried at 105° C and packed into aluminum sample holders for x-ray analysis.

Total (< 2 μm) and fine (< 0.2 μm) clay fractions were separated using centrifugation (Jackson, 1969). Clay samples were cation saturated using the appropriate chloride salt and washed free of excess salt with 95% ethanol. Slides were prepared using a filter-membrane peel technique (Drever,

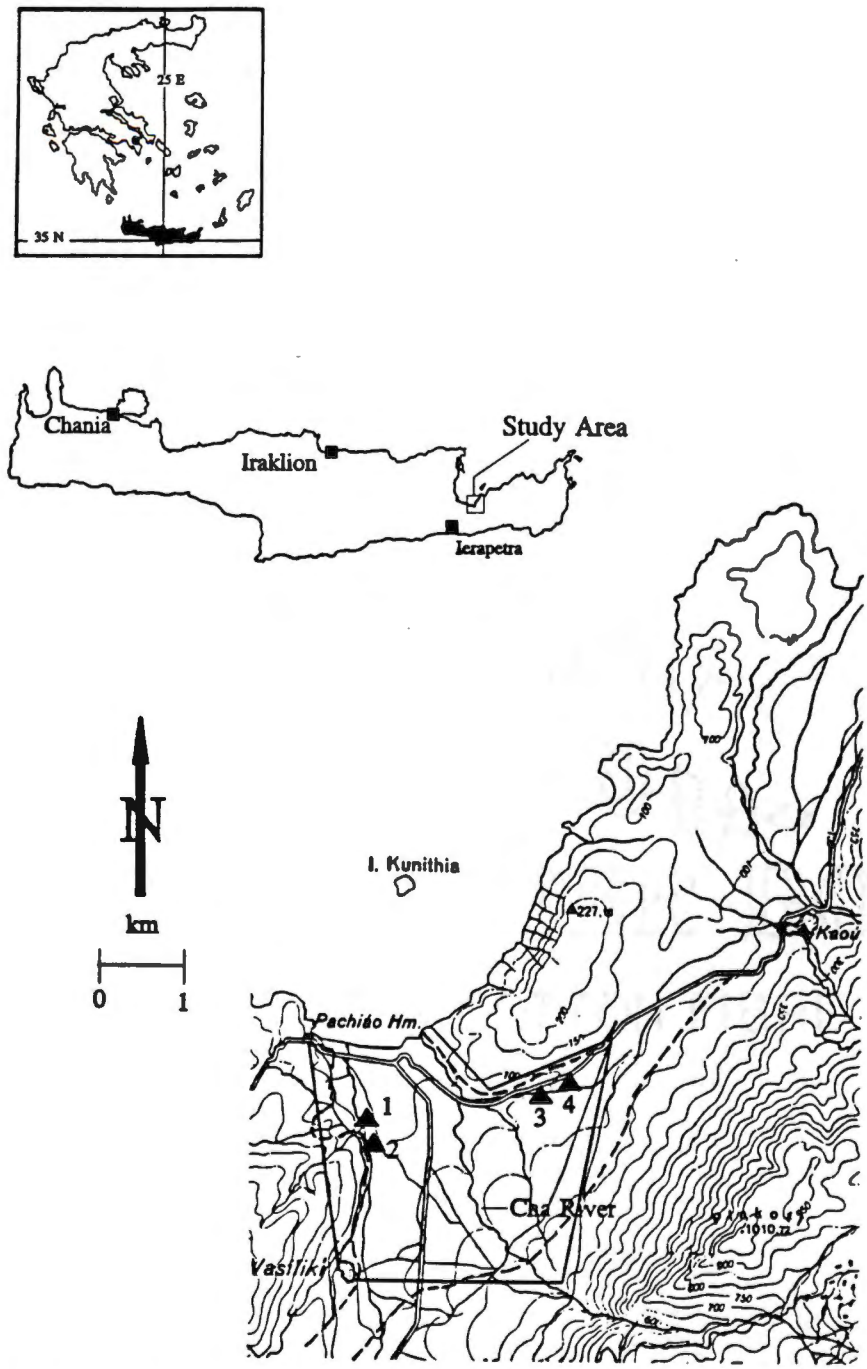


Figure 1. Map showing the location of the study area. Sampled profiles are illustrated with solid triangles. Solid line indicates the boundary of the study area. Dashed line illustrates the approximate extent of the Holocene alluvial deposits according to Papastamatioy et al. (1959). Scale is approximate. Elevation is in meters above sea-level.

1973). Total clays were mounted using 0.45 μm filters. Fine clays were mounted using 0.1 μm filter membranes.

Insoluble residues of the dolomite parent materials were collected using a modification of the method of Rabenhorst and Wilding (1984). A 0.25 M Na-acetate solution buffered at pH 3 was utilized to dissolve the carbonates. The following preparation scheme was used. Carbonate coarse fragments, collected during sample preparation, were selected from upper, middle and lower horizons from each profile. Individual horizons were treated as separate samples. Secondary carbonate accumulations on these gravels were removed by reacting them with approximately 0.5 M HCl for short periods (5-10 min.) followed by washing with distilled water. After 2-3 such treatments any remaining pendants were scrapped off with a steel straight-edge. One to two additional treatments with HCl were generally sufficient to finish the preparation. Gravels were rinsed with distilled water and then crushed lightly with a steel mortar and pestle. Three to four hundred ml of acetate buffer were added to the crushed materials and allowed to react for approximately 24 hr, at which point the solution was decanted and fresh buffer was added. Following the initial 24 hr replacement, new buffer was added only when visual evaluation suggested the reaction had slowed significantly or stopped completely. Samples were mixed several times daily. The samples were dissolved until the gravel-sized material disappeared and a residue covered the bottom of the beakers. Fresh buffer was added at this point and the residues remained in contact with the buffer for an additional two weeks. All samples were centrifuged at the end of this time and the supernatant was discarded. Deionized water was added to each beaker and the pH was adjusted to 5 ($\pm$ 0.1) by addition of solid Na_2CO_3. Silt-sized residues were separated by gravity sedimentation and the clays were collected from the decanted silt separations. Prior to x-ray analysis both size fractions were handled as outlined earlier.

Samples of unweathered phyllite residuum, from the nearby uplands, were crushed to approximately 2 mm with a steel mortar and pestle and dispersed by shaking overnight in a solution of Na-hexametaphosphate and Na-carbonate. Clay and silt fractions from these materials were treated in

the same manner as the soils. Samples from the soils and phyllite were treated with hot (≈ 75° C) 2 M HCl to remove the chlorites and investigate the occurrence of kaolinite.

Total clay fractions from the reddish-colored, clay-rich surface horizons were subjected to boiling 5 M NaOH treatments using the method of Norrish and Taylor (1961) to investigate the clay-sized iron oxides. The treated clay fractions were prepared as ethanol slurries on glass slides and scanned using conditions outlined below.

Diffractograms for both groups of separates were obtained at 35 kV and 15 mA using Cu-Kα radiation. The instrument is equipped with a diffracted beam graphite monochromator, a 1° divergence slit and a 1° receiving slit. The time constant for all scans was 2 s, and the scale factor was 500 or 1 000 counts. The scan rate was 2°/minute. Potassium saturated slides were scanned from 2-40° 2-θ following heat treatments at 300, and 550° C. Magnesium saturated slides were scanned following air-drying and ethylene glycol solvation. Glycol solvation was accomplished by vapor saturation at 25 C for 12 to 24 hours and/or by vapor saturation at 50° C for 12 to 24 hours. Silts were scanned from 4-62° 2-θ; only data for the region from 4-35° 2-θ are presented.

Cation exchange capacities were measured using a modification of the method of Bower et al. (1952). Index ion saturation and replacement were accomplished using a mechanical vacuum extractor (Holmgren et al., 1977). Sodium in the NH_4OAc extracts was determined by atomic emission spectrometry.

RESULTS AND DISCUSSION

Soils

The study covered an area of gently undulating topography approximately 4 km^2 in size. Slopes were generally 2 to 5 percent except on sideslopes of local drainageways. The soils were classified as Fluventic Xerochrepts and Calcixerollic Xerochrepts (Part 2, this dissertation). Surface horizons averaged 15 cm in depth. Surface textures consisted of clay loams, loams and sandy loams of varying gravel content (Table 1). Calcic horizons in each profile were a prominent feature of these

Table 1. Selected physical and chemical properties of the four soils studied.

Horizon	Coarse Frag.	Sand	Silt	Total Clay < 2 μm	Fine Clay < 0.2 μm	NaOAc CEC
	-- Vol. % --	g kg^{-1}				cmol (Na^+) kg^{-1}
Profile 1						
Ap	25	560	320	121	25	8.7
A/Bk	53	559	364	77	15	5.0
Bk1	40	597	374	29	8	2.1
Bk2	35	573	399	28	10	2.5
Bk3	65	727	202	72	14	4.7
Bk4m	73	659	268	73	16	4.6
Bk5	51	726	222	53	16	3.9
Bk6m	42	687	271	41	16	2.5
Bk7	ND	ND	ND	ND	ND	ND
Profile 2						
A	34	425	349	225	46	13.2
Bw	31	437	320	244	51	11.3
Bk1	63	661	232	108	16	4.5
Bk2	55	640	263	97	12	3.8
Bk3	47	626	261	113	19	3.4
Bk4	49	626	275	99	17	3.5
Bk5	ND	ND	ND	ND	ND	ND

Table 1 (continued)

Horizon	Coarse Frag.	Sand	Silt	Total Clay < 2 μm	Fine Clay < 0.2 μm	NaOAc CEC
	-- Vol. % --	g kg^{-1}				cmol (Na$^+$) kg^{-1}
Profile 3						
Ap	35	403	280	317	78	23.9
Bw	35	428	249	323	75	23.5
Bk1	52	826	79	96	26	6.4
Bk2	42	851	80	69	22	2.7
BCk1	41	825	106	69	22	2.2
BCk2	67	807	120	72	21	3.1
C	40	884	65	51	18	1.8
Profile 4						
Ap	27	394	321	285	88	16.3
Bw	34	408	298	294	73	15.3
Bk1	51	600	281	120	31	5.0
Bk2	57	641	287	72	17	3.1
Bk3	45	643	318	39	10	1.5
Bk4	50	679	292	29	10	1.3
Bk5	73	735	233	32	12	2.3
C	52	719	250	31	11	1.3

ND = not determined.

soils. Cation exchange capacities (CEC) ranged from 1 to 24 cmol (Na^+) kg^{-1}. The decrease in CEC with depth in all four profiles was related to the decrease in clay and organic carbon content.

Silt Mineralogy

The silt fractions of all four soils exhibited virtually identical mineral assemblages and depth distributions (Fig. 2). The silts consisted of quartz, dolomite, calcite, a feldspar component and minor amounts of chlorite, illite, and possibly kaolinite. Silt and sand-sized acid insoluble residues from the dolomitic parent material were composed primarily ($\approx$90 to 95 percent) of quartz. Silt fractions from the unweathered phyllite materials also contained abundant quartz. Thus, the quartz distribution with depth in these soils is readily explained by release of detrital quartz due to physical and chemical weathering of the dolostone and phyllite fragments. Eolian additions of quartz to the surface horizons are also probable (Chester et al., 1977; Rapp and Nihlén, 1986), although these could not be quantified.

The occurrence of dolomite in the silt fraction can also be attributed to simple physical weathering processes, as the parent material is primarily dolomite. The distribution of calcite in these soils likely stems from a combination of physical and chemical weathering processes. Dissolution and reprecipitation phenomena appear to be most responsible for the increase in calcite content with depth. Physical disintegration of pebble and sand-sized calcite inclusions in the dolomite and phyllite is also likely, although this process probably accounts for only a small portion of the calcite distribution in these soils.

The feldspar content decreases rapidly with depth in each of the soils examined. This can be explained by two possible mechanisms. The first is concentration of feldspars in the upper horizons by physical disintegration of the phyllite and dissolution of the carbonate parent material. Feldspars were identified by x-ray analysis of silt isolated from the unweathered phyllite material. The primary feldspar components of the phyllite were albite and orthoclase. Visual observation of the insoluble residues from the dolomite indicated that quartz was the dominant mineral phase present. X-ray diffraction analyses

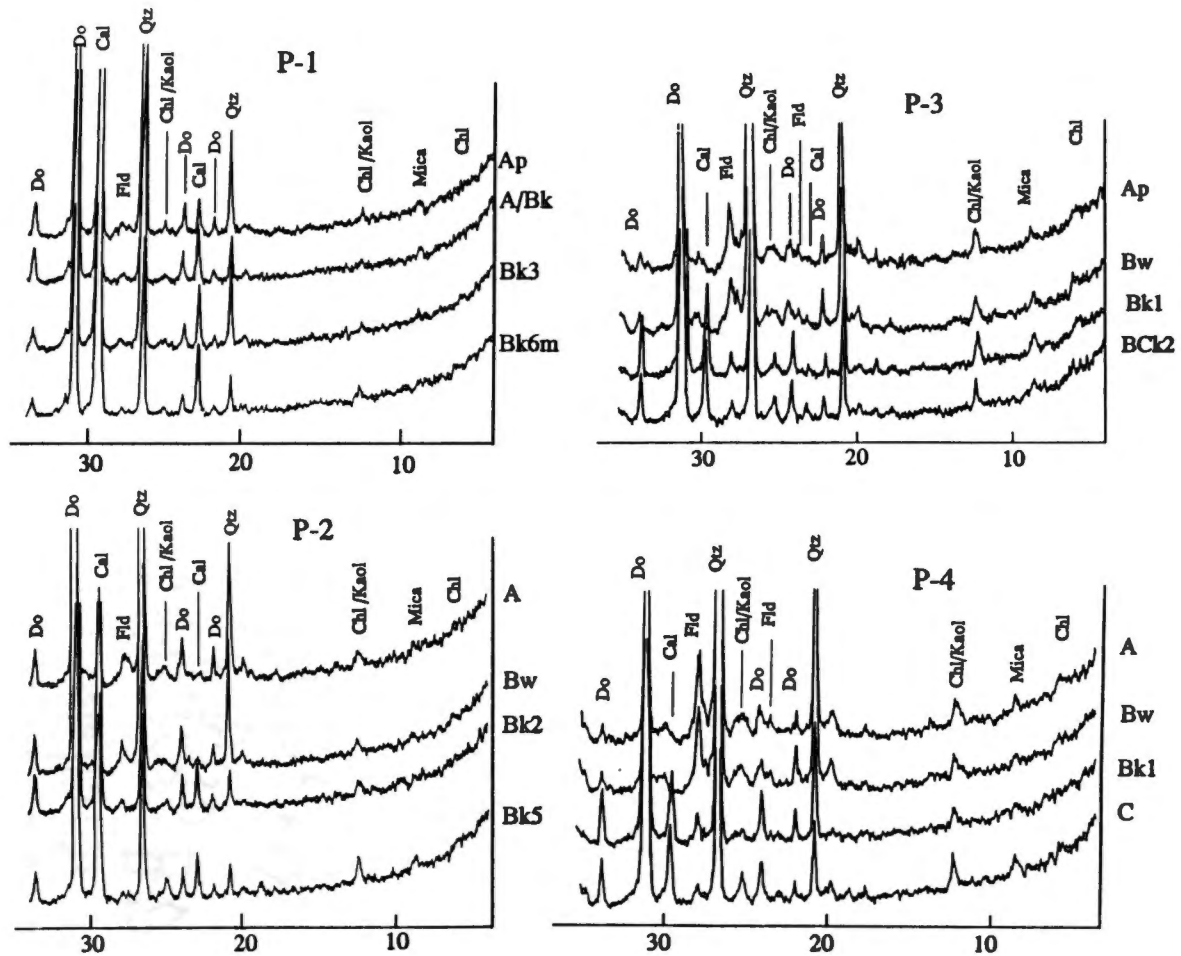


Figure 2. X-ray diffractograms of the fine silt (2-20 μm) fractions from all four Profiles. Cal = calcite; Chl = chlorite; Do = dolomite; Fld = feldspar; Kaol = kaolinite; Qtz =quartz.

indicated that a small proportion of the insoluble residues consisted of albite. The dominant feldspar component in the soils was albite; thus it appears that decomposition of the phyllite gravels and dissolution of the carbonates are liberating and concentrating the feldspars. The second mechanism of feldspar occurrence is eolian additions of silt-sized feldspars. Rapp and Nihlén (1986) reported quartz as the dominant mineral (>75%) in silt-sized eolian dusts collected in Crete. Feldspars and calcite were minor components of the same dust, although no quantitative data were presented for these two minerals. Based on the data of Rapp and Nihlén, and the low overall feldspar content in these soils, eolian additions are probably a minor source of feldspars in the soils investigated here.

The occurrence of clay minerals in the silt fraction of these soils could be the result of detrital phyllite fragments of silt size or an artifact of incomplete separation of the silt and clay fractions. The latter doesn't seem likely given the fact that the clays appear in both silt size fractions and exhibit similar abundances (based only on peak heights) with depth. Rapp and Nihlén (1986) demonstrated the occurrence of mica and chlorite in silt-sized dusts deposited in Crete; thus, the occurrence of these minerals in the surfaces of the soils studied here may also be the result of such deposition.

Clay Mineralogy

Figure 3 illustrates the mineralogical composition of the clay fractions from the alluvial soils. A comparison of the unweathered phyllite residuum collected from the uplands east of the study site (Fig. 4) with the clays from the alluvial soils demonstrates the similarity among the mineral assemblages. Clay-sized acid residues collected from the dolostone contained mica and a small proportion of kaolinite (which could have been an artifact of residue preparation). Dissolution of the carbonate parent material would release these clays and result in their concentration. The clay fraction from the phyllite sample was treated with 2 M HCl to remove the chlorite (Fig. 5). X-ray diffractograms of this material still contained first and second order peaks at 7.2 and 3.5 Å indicating the presence of a small quantity of kaolinite in the phyllites. Soil clays from all 4 profiles were also subjected to 2 M HCl treatments. The acid treatments confirmed the presence of kaolinite in these

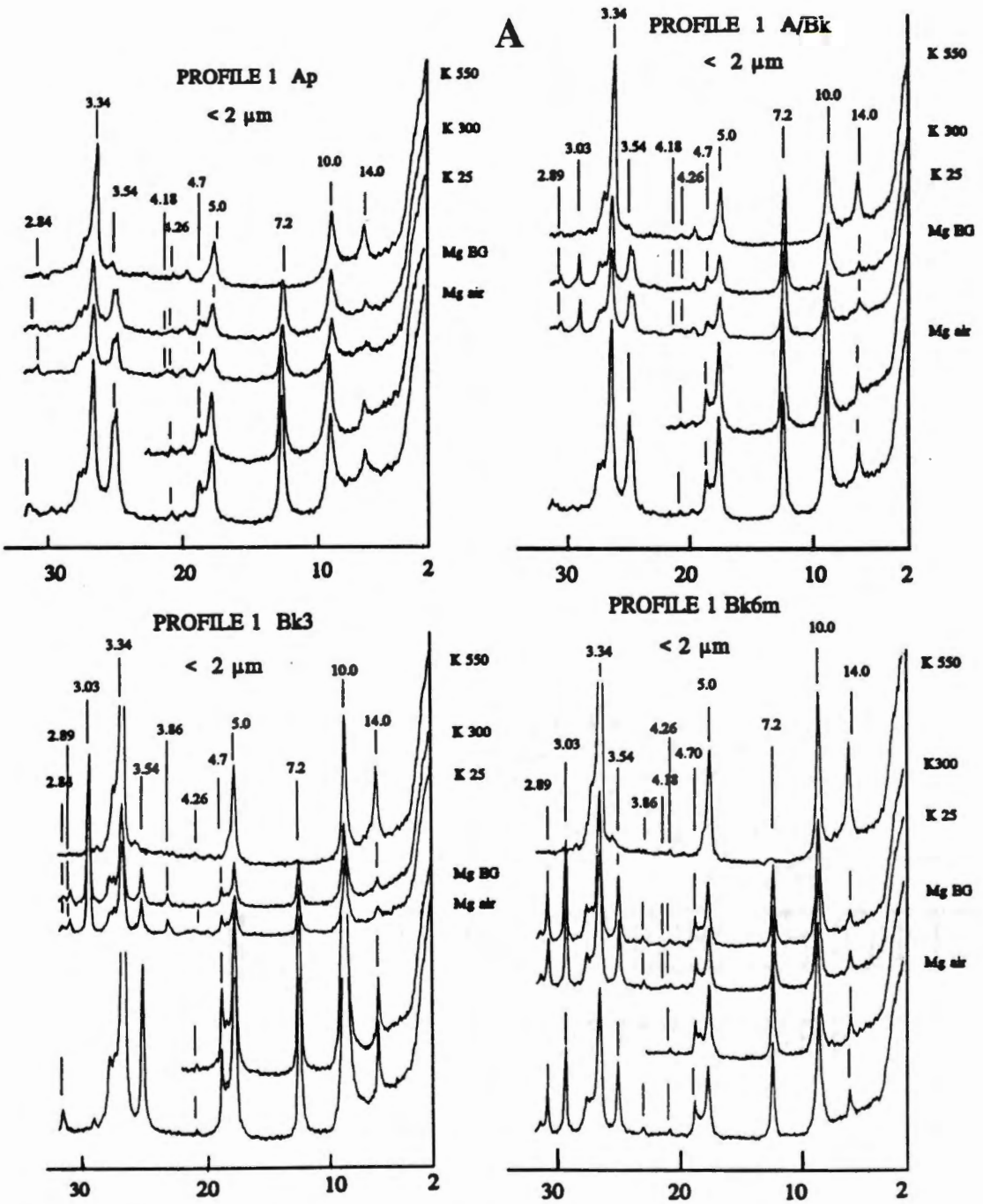


Figure 3. X-ray diffractograms of the total clay (<2 μm) fractions from Profile 1 (A) and Profile 4 (B).

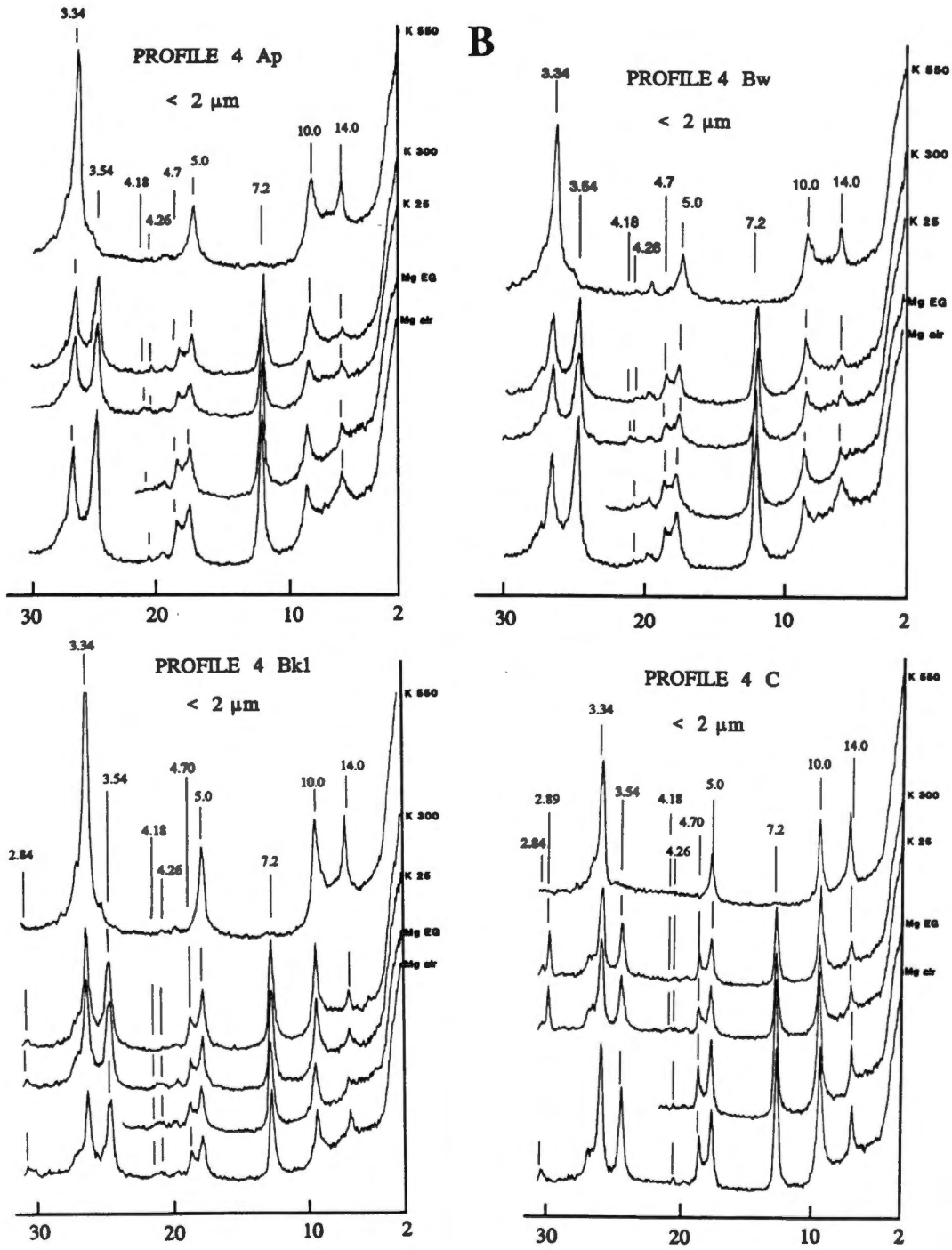


Figure 3 (continued).

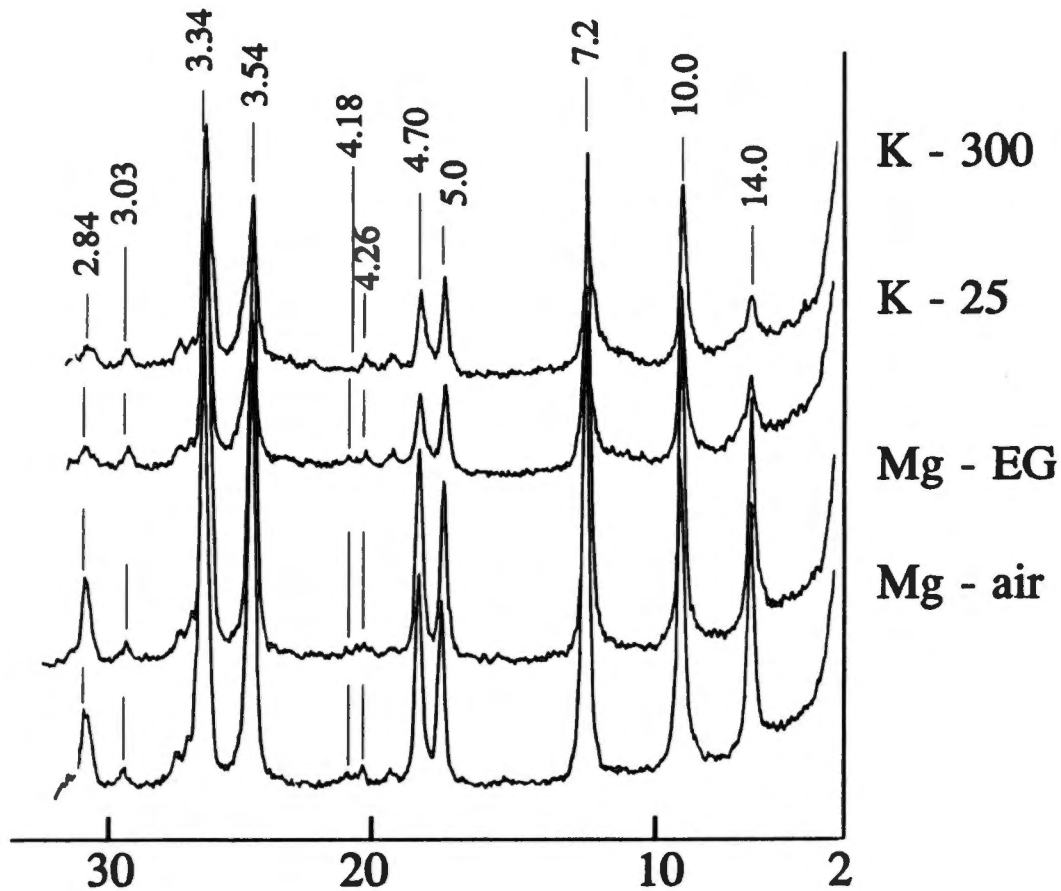


Figure 4. X-ray diffractograms of the total clay (< 2 μm) from the unweathered phyllite residuum. K_{sat} - 550 C not shown. Intensity differences between Mg- and K-saturated samples are the result of slide preparation and not the result of heat treatment or collapse upon potassification.

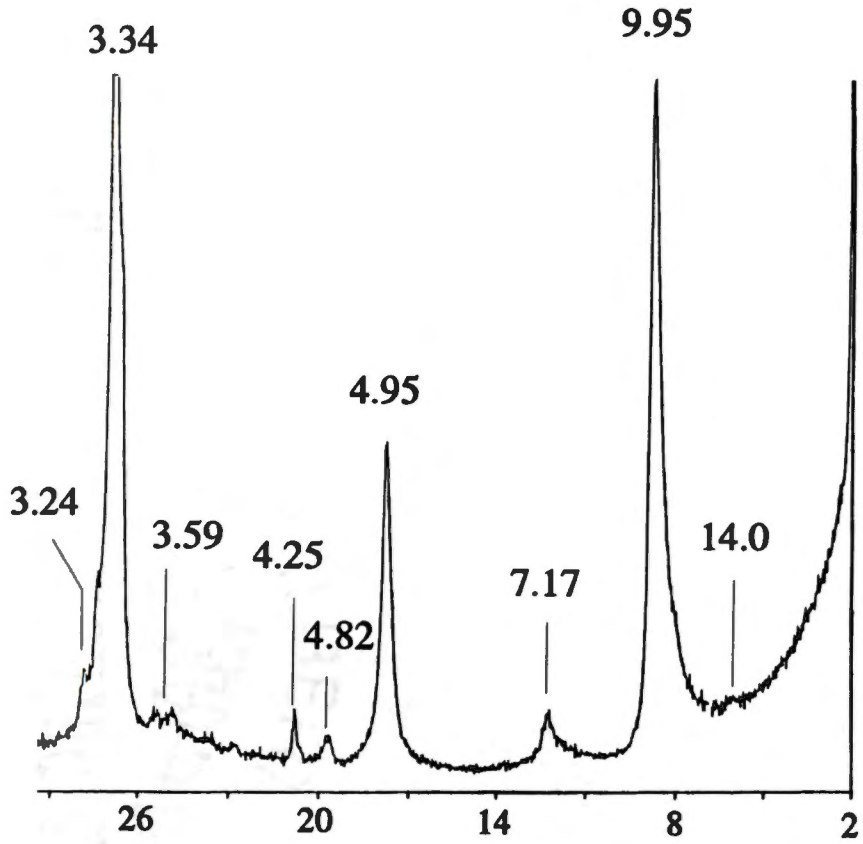


Figure 5. X-ray diffractogram of HCl-treated clay fraction (<2μm) from the phyllite. Scan was acquired at 40kV and 30 mA with Cu Kα_1 radiation. Sample was Mg-saturated and air dried (Rel. Humid. = 60%).

soils. Peak area measurements indicated that kaolinite contents were greatest in surface horizons and decreased with depth. The distribution pattern noted in these soils could be the result of three simultaneous processes. The first of these is eolian additions of kaolinite. Various authors have demonstrated that kaolinite is the dominant clay-mineral present in Mediterranean dusts (Chester et al., 1977; Rapp and Nihlén, 1986). The second is a simple concentration mechanism. Dissolution of the carbonate materials that form the bulk of the parent material would, given sufficient time, result in a significant increase in the content of kaolinite and other clay minerals in the surface horizons of these soils. The third process would be *in situ* weathering of other clays and feldspars to kaolinite.

Kaolinite formation as a result of modern (< 4,000 years) soil weathering processes can probably be ruled out. The limited degree of mica and chlorite weathering exhibited by these soils would argue against a large amount of authigenic kaolinite formation in the last 4-5000 years. Paleoclimatic conditions may have favored some degree of kaolinite formation. Once formed this mineral would probably remain stable in these soils. The two most likely explanations for the increase in kaolinite in the surface horizons of these soils were concentration and eolian depositon. Because these two processes are occurring simultaneously there is no way to determine which one dominates in these soils.

Total Clays

In the soil clays there was a general decrease in crystallinity exhibited by the mica and chlorite components as the soil surface was approached. These changes were the result of increased weathering in the pedogenically active portion of these soils. Similar weathering effects were noted by Yaalon et al. (1966) in some soils of Israel.

The 14 Å mineral in all of the soils contained a minor expanding component. Stephen and MacEwan (1950 and 1951) and Honeyborne (1951) reported a swelling chlorite in the clay fraction of soils developed from a Triassic marl in Britain. Bain and Russell (1981) identified a swelling chlorite developed from the weathering products of a basalt in Scotland. This mineral demonstrated expansion

to 18 Å on treatment with glycerol. Rich and Bonnet (1975) reported the occurrence of a swelling chlorite from a soil in the Dominican Republic. This mineral also demonstrated expansion to 18 Å upon glycerol solvation.

Because no clearly identifiable peak with a spacing larger than 14 Å appears in the x-ray scans of these soils, the expansion was probably the result of random removal of the hydroxide interlayers of the chlorite. Partial, random removal of the interlayer hydroxide sheet would allow expansion of the chlorite upon glycolation. Potassium saturation and heating to 550° C resulted in only slight collapse towards 10 Å (Fig. 3), further suggesting only a partial removal of the interlayer hydroxide sheet in these chlorites. Martin Vivaldi and MacEwan (1960) suggested that swelling chlorite contained incomplete "brucitic interlayers" which existed as "islands", with the remaining interlayer space being occupied by hydrated magnesium or other ions. They further suggested that this type of mineral could be formed from a "complete" chlorite structure by dissolution of the interlayer hydroxide sheet.

The dissolution of the chlorites by dilute HCl suggested that they were trioctahedral, ferrous chlorites (Ross, 1969 and Bailey, 1975). To further investigate the nature of this mineral, the composition of the tetrahedral and octahedral layers was estimated using x-ray intensity measurements. The content and distribution of heavy atoms (Fe, Mn, and Cr) in the octahedral sheets of chlorite can be estimated based on intensity ratios of the (00l) reflections (Brindley and Gillery, 1956; Petruk, 1964; Bailey, 1975; Moore and Reynolds, 1989). For structural reasons, x-rays scattered by the octahedral layers are exactly in phase for the even-ordered 00l reflections resulting in an increase in intensity for these reflections. If the number of heavy atoms in these sheets increases, through isomorphous substitution, the intensity of x-rays diffracted from these layers increases proportionally. X-rays diffracted from odd-ordered octahedral planes are out of phase and cancel each other. If the distribution of heavy atoms between the two sheets is symmetrical, the odd-ordered reflections due to the octahedra cancel completely. If the distribution of heavy atoms between the two sheets is asymmetrical, the octahedral reflections will not cancel each other. An asymmetrical distribution of heavy atoms in the octahedra therefore results in changes in the intensity of the odd-ordered reflections. Because of these

dual effects, a determination of the heavy atom content and degree of asymmetry is possible (Petruk, 1964; Bailey, 1975).

Based on data given in Bailey (1975) the approach outlined by Petruk (1964) was chosen to estimate the heavy atom content and degree of asymmetry in the octahedral layers of the chlorite identified in this study. The original research (Petruk, 1964) was conducted using basal (00l) reflections recorded from randomly oriented powder mounts. The data in this study were collected from oriented specimens. Whereas the original work was conducted using only basal reflections, it seemed acceptable to utilize the basal reflections obtained here because the method relies upon the ratio of two peak intensities and not the absolute intensity value. It was assumed that increases in intensity due to the preferred orientation would be equal for all basal reflections. Interference from the overlapping kaolinite peaks at 7 and 3.5 Å was deemed negligible based on the low intensities exhibited by this mineral in diffractograms of the HCl-treated clays (Fig. 5).

Results of the octahedral cation analyses suggested that iron in these layers is asymmetrically distributed, occurring in the interlayer hydroxide sheet. The chlorites contained an average of 0.40 moles of ferrous iron per half unit cell formula.

The aluminum plus chromium content of the chlorite was estimated using the approach of Albee (1962). These data resulted in Al + Cr contents of 3.5/10 formula cations. This estimate assumed complete cation occupancy in both tetrahedral and octahedral positions.

Based on x-ray analyses of two separate samples of unweathered phyllite a chlorite composition was estimated assuming; (i) O^{2-} plus OH^- equaled 18, and (ii) the total number of cations, excluding H^+, was 10. The formula estimated has the following composition: $(Mg_{2.4}, Al_{2.5}, Fe^{2+}_{0.40})$ $(Si_3,Al)\ O_{10}\ (OH)_8$. Using the nomenclature of Bayliss (1975) this chlorite corresponds to an iron substituted clinochlore. Given the fact that the chlorite is derived from metamorphic sources its polytype is likely to be II_b (Bailey, 1975; Moore and Reynolds, 1989), although no direct measurements of this were made.

Fine Clays

In general, the mineral assemblages in the < 0.2 μm fraction of all 4 soils were the same as the total clay (data not shown). The lack of carbonate minerals in the fine clay fraction was probably the result of the sample preparation technique used. Repeated washings with various salt solutions to achieve cation saturation probably dissolved the carbonates. The large surface area and high reactivity of fine clay-sized carbonates would contribute to their rapid dissolution. Iron oxides were not identified in the fine clay fractions either. This suggests that these minerals existed as coarse clay-sized particles.

The fine clays exhibited broader and generally more ragged diffraction peaks. Some degree of line broadening can be expected due to the effect of smaller crystallites; however, weathering may contribute to some of the broadening observed. Both phenomena would contribute to a general broadening and a decrease in sharpness of the peaks.

Iron Oxides

Boiling 5 M NaOH treatments of the < 2 μm fractions of the surface horizons proved inconclusive in identifying geothite and hematite in these soils. Dithionite pretreatment of the total clay fractions from the four profiles indicated the presence of goethite in most horizons. Redness ratings and dithionite extracts of the bulk soils (Part 2, this dissertation) supported the presence of goethite and possibly hematite in the upper horizons (0-25 cm) of all four soils. Goethite in the lower soil horizons was probably the result of weathering and release of iron from the phyllite gravels.

Mineral Occurrence and Weathering

The mechanisms responsible for the suite of clay minerals observed in these soils were a combination of inheritance of physically weathered phyllite fragments and chemical dissolution and concentration of insoluble residues from the dolomitic gravels. Clay mineral inheritance in soils has been observed by others (Mitchell, 1955; Gal, 1966; McFadden and Hendricks, 1982). Mitchell (1955) noted that clay minerals in soils formed from sedimentary and metamorphic rocks in Scotland were

primarily inherited from the parent materials. McFadden and Hendricks (1982) observed that the clay minerals in late Holocene alluvial soils from California were the result of inheritance from the parent sediments. A similarity in the mineralogical composition of Terra Rossa soils and the insoluble residue of their carbonate parent materials was noted by Gal (1966). The major process in the development of those Terra Rossa soils was slow, prolonged dissolution of carbonates with concomitant concentration of insoluble residues. Ritchie et al. (1974) attributed *in situ* clay gains in the soils they studied to disaggregation of shale lithorelicts. Rostad et al. (1976), in a study of soils formed from calcareous gravels, proposed that increases in all particle-size fractions were the result of disintegration of noncarbonate lithorelicts in the alluvial sediments. Dissolution of coarse carbonate clasts was also deemed important to clay accumulation in their soils due to the concentration effect and the liberation of clays entrained in the carbonate rocks.

Hayes (1970) presented the following weathering sequence for II_b chlorites: II_b Chlorite --> regularly interstratified Chlorite-Vermiculite --> randomly interstratified Chlorite-Vermiculite --> I_a Vermiculite. Coffman and Fanning (1975) suggested a similar sequence, but modified it to include the transformation of vermiculite to kaolinite. Under acid, oxidizing conditions, Ross and Kodama (1974, 1976) have demonstrated the laboratory transformation of chlorite to interstratified chlorite-vermiculite and/or direct transformation to vermiculite. Recently, Argast (1991) noted the weathering of a high-iron chlorite directly to vermiculite. This transformation occurred under acid, oxidizing conditions in some late Pleistocene dune sands in Indiana. Ross and Kodama (1976) suggested that the iron content of the parent chlorite influences the weathering sequence. High-iron chlorites appear to transform directly to vermiculites. Chlorites of intermediate iron content appear to weather to interstratified chlorite-vermiculite. Conversely, low-iron chlorites exhibited only limited vermiculitization.

The nature of the chemical system in the soils examined here was probably responsible for the limited weathering exhibited by the clays. The alkaline reaction of the soils (pH 7.5-8.5) would limit hydrolysis, preventing large-scale removal of the interlayer hydroxide sheets of the chlorites and minimizing the removal of interlayer potassium from the mica. It appears that micro-site acid attack of

the interlayers has occurred at some time and may still be continuing; thus the partial expansion of the 14 Å minerals upon glycol treatment. The low iron content of the chlorites in these soils probably played a role in the lack of vermiculitization observed. Because of the Mediterranean climatic conditions, the soils experience moisture conditions conducive to substantial weathering only during periods of cool temperatures. This would tend to slow the rate of weathering and impede the chemical transformation of the parent clays. Paquet and Millot (1972) suggested that mean annual precipitation needed to approach 1000 mm for vermiculitization to occur in Mediterranean regions. Mean annual rainfall in the study area averages 350-400 mm; thus, the chemical transformation of chlorite and/or mica to vermiculite should not be favored in these soils. Additionally, the activity of Mg^{2+} and K^{+} in the soil solution is probably maintained at sufficient levels to delay the hydrolitic decomposition of the chlorite and mica phases in these soils. Yaalon et al. (1966) suggested that the availability of Mg^{2+} in soils derived from dolomite retarded the formation of kaolinite in some of the soils they investigated.

CONCLUSIONS

The soils studied formed from alluvial sediments associated with the Cha River drainage in eastern Crete. The silt fractions contained quartz, calcite, dolomite, and a minor feldspar and clay mineral component. Physical weathering processes were primarily responsible for the suite of minerals observed in the silt fraction of these soils. The clay mineral assemblage consisted of chlorite, mica and minor amounts of quartz, goethite and kaolinite. The fine clay (< 0.2 μm) fraction was nearly identical to the total (< 2 μm) clay component. This indicated that physical comminution was the dominant process of weathering in these soils. A combination of disintegration of the phyllite component in the alluvium, release of detrital clays contained in the dolostone parent materials and minor eolian additions accounted for the occurrence of the phyllosilicates observed in this group of soils.

The mineralogical characteristics of these soils indicated that they were relatively young. The extent of clay mineral inheritance, the limited expansion of the chlorites and the lack of a chlorite or

mica weathering product (vermiculite), as well as the presence of carbonates in the clay fractions all four soils suggested that they were still in the initial stages of weathering and soil development.

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APPENDICES

APPENDIX A. SOIL DESCRIPTIONS FOR THE SOILS INVESTIGATED.

Soil Description for Pacheia Ammos 1
1989 Field Season

The profile was described August 7, 1989 by M.E. Timpson. Profile is located approximately 240 feet south of the northern margin of the terrace excavation at the summit/shoulder of the east side of the western stream valley. The native vegetation consisted of olives (Olea europaea) and native grasses (undescribed). The parent material was alluvial sediments. The profile occupied an upper shoulder to summit position. Elevation was estimated at less than 50 m, slope was 2% north, aspect was west. Soil drainage class was well drained.

C	17-0 cm overthrust road debris, not sampled.
Ap	0-16 cm 7.5 YR 4/4 (moist) 7.5 YR 6/4 (dry) gravelly sandy loam; weak medium subangular blocky structure; friable (moist) hard (dry); many fine roots; 25% coarse fragments; clear wavy boundary.
A/Bk	16-28 cm (A) 7.5YR 4/4 (moist) 7.5 YR 6/4 (dry); (Bk) 7.5 YR 5/4 (moist) 10YR 6/3 (dry) very gravelly sandy loam; weak medium and fine subangular blocky structure; friable (moist) hard (dry); common fine and few medium roots; 53% coarse fragments; clear wavy boundary.
Bk1	28-46 cm 7.5YR 7/4 (moist) 10YR 7/3 and 2.5Y 8/2 (dry) very gravelly sandy loam; structureless, massive; firm (moist) very hard (dry) few fine roots; 40% coarse fragments; clear wavy boundary.
Bk2	46-61 cm 10YR 7/3 (moist) 10YR 7/3 and 8/2 (dry);gravelly sandy loam; structureless, massive; firm (moist) hard (dry); 35% coarse fragments; few fine and medium roots; clear wavy boundary.
Bk3	61-74 cm 10YR 7/3 (moist) 10YR 7/3 and 8/2 (dry); extremely gravelly sandy loam; strucureless single grained; firm (moist) loose (dry); 65% coarse fragments; common fine and few medium roots; abrupt wavy boundary.
Bk4m	74-96 cm 10YR 7/3 (moist) 10YR 7/3 and 8/2 (dry); extremely gravelly sandy loam; structureless single grained; extremely firm (in place) (moist), loose (dry) (in hand); 73% coarse fragments; few fine roots, most along parting planes; abrupt wavy boundary.
Bk5	96-114 cm 10YR 7/3 (moist) 10YR 8/2 and some 7/3 (dry); very gravelly sandy loam; structureless, massive; extremely firm (in place) loose (in hand) hard (dry); 51% coarse fragments; no roots; clear wavy boundary.
Bk6m	114-132 cm 10YR 7/3 (moist) 10YR 8/2 (dry); very gravelly sandy loam; structureless massive; extremely firm (in place) loose (in hand), hard (dry); 42% coarse fragments; no roots; abrupt wavy boundary.
Bk7m	132+ cm 10YR 7/3 (moist) 10YR 8/2 (dry); no field texture; structureless massive; extremely firm (moist) extremely hard (dry); 70-80% coarse fragments; no roots. (Horizon not sampled).

Additional Notes:

The Bk4 is approximately 90% cemented. The Bk6 is approximately 60% cemented. The Bk7 is 95-98% cemented and was not sampled. Horizons Bk1 and Bk2 were box sampled on 8/7/89. I packed loose soil material around the blocks to cushion the intact sample. When these are opened in the lab, remember the loose material was added.

Micromorphology samples collected from Bk1, Bk2 and Bk4m and part of the Bk5.

Soil Description for Pacheia Ammos 2
1989 Field Season

The profile was described August 8, 1989 by M. E. Timpson. Profile is located downslope of the first high tension tower located on the terrace sediments (approximately 1 km south of Pacheia Ammos). The profile is located in the lower 1/3 of the backslope position on the west facing side of the Pacheia Ammos drainage. Native vegetation consisted of thyme (Thymus capitatus), Small Spiny Broom (Calycotome villosa), Lentisc (Pistacia lentiscus) and other garigue vegetation. The parent materials are alluvial sediments presumably of fluvial origin, overlain by a thin smear of colluvial sediments derived from upslope. Elevation was estimated at 25 m, slope was 33%. Aspect was west. Soil drainage class was well drained.

A	0-16 cm 7.5YR 3/4 (moist) 7.5YR 5/4 (dry) {5/3 looked better in places} gravelly loam; moderate fine subangular blocky structure; friable (moist), hard (dry);common fine and few medium roots; 34% coarse fragments; clear wavy boundary.
Bw	16-31 cm 5YR 3/4 (moist) 7.5YR 5/4 (dry) gravelly loam; weak to moderate fine subangular blocky structure; friable (moist), hard (dry); common fine and few medium roots; common ant holes and channels; 31% coarse fragments; abrupt wavy boundary.
Bk1	31-50 cm 7.5YR 5/4 and 5/6 (moist) 7.5YR 6/4 (dry); extremely gravelly sandy loam; structureless, massive; loose (moist), hard (dry); common fine and few medium roots; 63% coarse fragments; clear wavy boundary.
Bk2	50-68 cm 7.5YR 6/6 (moist) 7.5YR 7/4 (dry) very gravelly sandy loam; structureless, single grained; loose (moist), hard (dry); common fine and few medium roots; 55% coarse fragments; clear wavy boundary.
Bk3	68-78 cm 7.5YR 6/4 (moist) 7.5YR 7/4 (dry) very gravelly sandy loam; structureless, single grained; loose (moist), hard (dry); few medium roots; 47% coarse fragments; clear wavy boundary.
Bk4	78-108 cm 7.5YR 6/4 (moist) 7.5YR 7/4 (dry) very gravelly sandy loam; structureless, single grained; loose (moist), hard (dry); common fine roots; 49% coarse fragments; clear wavy boundary.
Bk5	108 + cm same as horizon above except for texture (gravelly sand). Not sampled.

Additional Notes:

The micromorphology sample from the Bk2 horizon is only intact from about 70-77 cm. The remainder of the material is fill. Three samples of the Bk1 horizon were collected for micromorphology.

Soil Description for Pacheia Ammos 3
1989 Field Season

The profile was described August 8, 1989 by M. E. Timpson. Profile is located on T1 of the modern floodplain of the Pacheia Ammos drainage approximately 1/4 - 1/2 mile north of Vasiliki. Native vegetation consisted of Olive (Olea europaea), Thyme (Thymus capitatus), Lentisc (Pistacia lentiscus) three lobed sage (Salvia triloba), Oregano (Origaanum heracleoticum) and two grasses (Piptatherum miliaceum and Bromus hordeaceous). The parent materials were recent Holocene fluvial sediments presumably derived from the Pliocene Makrilia Frm. Elevation was estimated at 3 m, slope is 0% at the pedon and 0-2% for this mapping unit. Aspect was 0. Soil drainage class was well drained in summer and probably poorly to somewhat poorly during the wet season.

A 0-12 cm 10YR 4/3 (moist) 10YR6/3 (dry) Loam; weak medium subangular blocky structure; very friable (moist), slightly hard (dry); common fine and medium roots; clear smooth boundary.

C1 12-24 cm 10YR 5/3 (moist) 10YR 6/3 (dry) Loam; structureless, massive; very friable (moist), hard (dry); common fine and medium roots; clear smooth boundary.

C2 24-41 cm. 10YR 5/4 (moist) 10YR 7/3 (dry) Loam; structureless, massive; friable (moist), extremely hard (dry); abrupt wavy boundary.

C3 41-75 cm. Cobbly fill from an old agricultural terrace, scraped off by channel stabilization activities. Not sampled.

2C4 75 cm. + Cemented terrace sediments in the channel bottom. Not sampled.

Additional Notes:

Walking south along the channelized section of the stream bed the soils represented by this profile ranged from 0.6 to 1.8 m in thickness. All consisted of similar particle size composition. All contained very few coarse fragments.

Soil Description for Pacheia Ammos 4
1989 Field Season

The profile was described August 9, 1989 by M. E. Timpson. It was located 24.38 m southeast of the southeast corner of the small stone chapel located 1.95 km east of the Pacheia Ammos village sign and 0.1 km west of P.A. 5. Native vegetation consisted of Olive (Olea europaea) and mixed grasses (undescribed). The parent materials were Pleistocene or Holocene alluvial sediments presumably of fluvial origin. The soil was located in a stable upland summit. Elevation was estimated at less than 50 m, slope was 2% east southeast at the pedon. Aspect was west northwest. Soil drainage class was well drained.

Ap	0-14 cm. 5YR 3/4 (moist) 5YR 5/4 (dry) gravelly clay loam; moderate medium subangular blocky structure; friable (moist), slightly hard (dry); very slight reaction to dilute acid; common fine and medium roots; 35% coarse fragments; clear smooth boundary.
Bw	14-27 cm. 2.5YR 3/4 (moist) 5YR 5/4 (dry) gravelly clay loam; moderate medium subangular blocky structure; friable (moist), slightly hard (dry); slight reaction to dilute acid; common fine and medium roots; 35% coarse fragments; clear wavy boundary.
Bk1	27-35 cm. 5YR 5/6 (moist) 5YR 6/6 (dry) very gravelly loamy sand; structureless, single grained; friable (moist), hard (dry); strong reaction to dilute acid; few fine roots; 52% coarse fragments; clear smooth boundary.
Bk2	35-44 cm. 5YR 5/6 and 4/6 (moist) 7.5YR 6/4 (dry);very gravelly loamy sand; structureless, massive; slightly hard (moist), very hard (dry); strong reaction to dilute acid; few fine roots; 42% coarse fragments; clear smooth boundary.
BCk1	44-54 cm. 10YR 6/4 and 4/6 (moist) 10YR 6/4 (dry) colors in this horizon were the result of individual sand grains and some iron stains. very gravelly loamy sand; structureless, single grained; friable (moist) loose (dry); violent reaction to dilute acid; no roots; 41% coarse fragments; clear wavy boundary.
BCk2	54-72 cm. colors were the result of coated and uncoated sand grains and iron stains; extremely gravelly to cobbly loamy sand; structureless, single grained; loose (moist), loose (dry); violent reaction to dilute acid; no roots; 67% coarse fragments; abrupt wavy boundary.
C	72-83 cm. colors were not recorded for this horizon as they consisted of individual sand grains and limestone/dolomite fragments; very gravelly sand/loamy sand; structuureless, single grained; loose (moist), loose (dry); violent reaction to dilute acid; no roots; 40% coarse fragments.

Additional Notes:

* colors represent regions where there was sufficient fine material to obtain a color reading.

Bk1 contains mostly 1-3 cm gravels with fines weakly cemented by carbonates. Many of these cemented fines are in pendants below gravels and as interstitial grain contact cements. Some fine

materials are moderately well cemented to stone bottoms. Moderate finger pressure would not remove the particles.

I collected some pendant coated gravels from the BCk2 (54-72cm).

Micromorphology samples were collected from the Bk1 and Bk2 horizons.

Soil Description for Pacheia Ammos 5
1989 Field Season

The profile was described August 10, 1989 by M. E. Timpson. The profile is located 2.05 km east of the Pacheia Ammos village sign and 0.1 km east of P.A. 4. Native vegetation consisted of plantation Olive (Olea europaea) and mixed grasses (undescribed). The parent materials were Pleistocene or Holocene alluvial sediments presumably of fluvial origin. The soil was located in a stable upland summit. Elevation was estimated at between 25 and 50 m, slope was 2% east- west, and 2% north-south. Aspect was 0. Soil drainage class was well drained.

Ap	0-10 cm. 5YR 4/4 (moist) 5YR 3/4 (mashed), 5YR 5/4 (dry) gravelly clay loam; weak and moderate fine subangular blocky structure; friable (moist), slightly hard (dry); many fine and common medium roots; 27% coarse fragments; very slight reaction to dilute acid; clear smooth boundary.
Bw	10-34 cm. 5YR 3/4 (moist) ped faces were 2.5YR 3/4 (moist), 5YR 4/4 (dry) gravelly clay loam; moderate medium and fine subangular blocky structure; friable (moist), hard (dry); common fine and medium roots; 34% coarse fragments; slight reaction to dilute acid; clear smooth boundary.
Bk1	34-48 cm. 5YR 4/6 and 2.5YR 4/6 and 4/8 (moist)" 5YR 4/6 and 5/6 very gravelly sandy loam; strucutreless, single grained; firm (in place), loose (dry); few medium and common fine roots; 51% coarse fragments; strong reaction to dilute acid;clear smooth boundary.
Bk2	48-59 cm. colors were only the result of loose sand grains and iron stains on the former (unrecorded) very gravelly sandy loam; structureless, massive; firm (moist, in place), loose (dry, in hand); few fine roots; 57% coarse fragments; violent reaction to dilute acid; abrupt smooth boundary.
Bk3	59-74 cm. colors were only the result of loose sand grains and iron stains on the former (unrecorded), very gravelly sandy loam; structureless, single grain; firm (moist, in place), loose (dry, in hand); few fine roots; 45% coarse fragments; violent reaction to dilute acid; abrupt smooth boundary.
Bk4	74-91 cm. colors were only the result of loose sand grains and iron stains on the former (unrecorded), very gravelly sandy loam; structureless, single grained; firm (moist, in place), hard (dry, in hand); few fine roots; 50% coarse fragments; violent reaction to dilute acid; clear wavy boundary.
Bk5	91-112 cm. colors were only the result of loose sand grains and iron stains on the former (unrecorded), extremely gravelly loamy sand; structureless, massive; firm (moist, in place), hard (dry, in hand); no roots; 73% coarse fragments; violent reaction to dilute acid; clear wavy boundary.
C	112-130 cm. colors were only the result of loose sand grains and iron stains on the former (unrecorded), very gravelly sandy loam; structureless, single grained; firm (moist, in place), loose (dry, in hand); no roots; 52% coarse fragments; strong reaction to dilute acid.

Additional Notes:

* the color of the Bk1 and Bk2 horizons are for in place soil only. When removed, the loose single grains did not allow determination of soil color.

iron stains and ferrans were noted on numerous pea-sized gravels in the Bk1 and Bk2 horizons.

Between 90 and 105 cm in the Bk5 I noted what appeared to be coprecipitates of iron and carbonates primarily coating the bottoms of some medium sized gravels. I collected some of these for analysis.

Micromorphology samples were collected from the following depths:

38-42 cm. and approx. 34-42 cm. with part of the weathering front contact.

74-78 cm CO_3 cemented layer, collected 2 boxes from this zone.

83-91 cm. CO_3 cemented layer.

109-114 cm. minor CO_3 cementation.

small cobble near 110 cm. this was broken with the hammer and sampled.

APPENDIX B. PARTICLE-SIZE DATA FOR PROFILES 1 THROUGH 4.

Table B-1. Particle-size distributions of the four soils studied. FC/CC data are the ratio of fine clay to coarse clay.

Horizon	Lower Depth	Co.Frag.	Total Sand	Total Silt	Coarse Silt	Fine Silt	Total Clay	Fine Clay	FC/CC
	- cm -	- Vol. % -	g kg^{-1}						
			Profile 1						
Ap	16	25	560	320	165	154	121	25	0.26
A/Bk	28	53	559	364	202	162	77	15	0.24
Bk1	46	40	597	374	222	152	29	8	0.38
Bk2	61	35	573	399	245	155	28	10	0.56
Bk3	74	65	727	202	91	110	72	14	0.24
Bk4m	96	73	659	268	134	134	73	16	0.28
Bk5	114	51	726	222	120	101	53	16	0.43
Bk6m	132	42	687	271	184	87	41	16	0.64
Bk7m	132+	ND	ND	ND	ND	ND	ND	ND	ND
			Profile 2						
A	16	34	425	349	162	187	225	46	0.26
Bw	31	31	437	320	148	172	244	51	0.26
Bk1	50	63	661	232	104	128	108	16	0.17
Bk2	68	55	640	263	119	144	97	12	0.14
Bk3	78	47	626	261	117	144	113	19	0.20
Bk4	108	49	626	275	128	147	99	17	0.21
Bk5	108+	ND	ND	ND	ND	ND	ND	ND	ND

Horizon	Lower Depth	Co.Frag.	Total Sand	Total Silt	Coarse Silt	Fine Silt	Total Clay	Fine Clay	FC/CC
	- cm -	- Vol. % -	---------- g kg^{-1} ----------						
			Profile 3						
Ap	14	35	403	280	114	166	317	78	0.33
Bw	27	35	428	249	107	143	323	75	0.30
Bk1	35	52	826	79	41	38	96	26	0.37
Bk2	44	42	851	80	44	36	69	22	0.47
BCk1	54	41	825	106	63	44	69	22	0.47
BCk2	72	67	807	120	69	51	72	21	0.41
C	83	40	884	65	38	26	51	18	0.55
			Profile 4						
Ap	10	27	394	321	141	180	285	88	0.45
Bw	34	34	408	298	115	184	294	73	0.33
Bk1	48	51	799	81	32	49	120	31	0.35
Bk2	59	57	851	77	42	35	72	17	0.31
Bk3	74	45	904	57	40	17	39	10	0.34
Bk4	91	50	928	44	28	16	29	10	0.53
Bk5	112	73	905	64	37	27	32	12	0.60
C	130	52	923	46	24	22	31	11	0.55

ND = Not Determined.

Table B-2. Distribution of sand-sized separates for the four soils studied.

Horizon	Lower Depth	Co.Frag.	Total Sand	Sand Fractions+				
				VCOS	COS	MS	FS	VFS
	- cm -	- Vol. % -	g kg^{-1}					
			Profile 1					
Ap	16	25	560	176	122	59	120	82
A/Bk	28	53	559	200	129	59	88	83
Bk1	46	40	597	232	167	54	72	73
Bk2	61	35	573	195	159	55	80	83
Bk3	74	65	727	422	150	52	69	33
Bk4m	96	73	659	331	132	50	90	56
Bk5	114	51	726	354	176	66	89	40
Bk6m	132	42	687	331	170	62	78	47
Bk7m	132+	ND	ND	ND	ND	ND	ND	ND
			Profile 2					
A	16	34	425	131	69	36	101	89
Bw	31	31	437	110	71	39	115	103
Bk1	50	63	661	302	127	58	108	65
Bk2	68	55	640	222	150	63	121	84
Bk3	78	47	626	258	135	58	104	71
Bk4	108	49	626	275	132	48	95	75
Bk5	108+	ND	ND	ND	ND	ND	ND	ND

Horizon	Lower Depth	Co.Frag.	Total Sand	Sand Fractions+				
				VCOS	COS	MS	FS	VFS
	- cm -	- Vol. % -	g kg^{-1}					
			Profile 3					
Ap	14	35	403	153	85	39	73	52
Bw	27	35	428	174	93	39	77	45
Bk1	35	52	826	478	228	56	48	15
Bk2	44	42	851	338	266	117	109	22
BCk1	54	41	825	359	250	101	90	25
BCk2	72	67	807	280	221	120	141	46
C	83	40	884	405	237	104	118	20
			Profile 4					
Ap	10	27	394	151	73	38	75	57
Bw	34	34	408	143	86	42	86	52
Bk1	48	51	799	351	225	98	100	25
Bk2	59	57	851	429	233	81	84	24
Bk3	74	45	904	376	286	115	102	25
Bk4	91	50	928	448	260	114	94	11
Bk5	112	73	905	558	187	67	75	18
C	130	52	923	563	220	60	62	17

+ Sand Abbreviations are as follows: VCOS = very coarse sand; COS = coarse sand; MS = medium sand; FS = fine sand; VFS = very fine sand.
ND = Not Determined.

APPENDIX C. PHYSICAL AND CHEMICAL DATA FOR PROFILE PACHEIA AMMOS 3.

Soil Number: PA-3
Soil Series:
Soil Classification: Fine Loamy, Mixed, Thermic Typic Ierofluvents
Location: Recent Floodplain near Vasiliki
Date Sampled: August 8, 1989

Sample Identification				Particle Size Distribution										
				Size Class and Particle Diameter (microns)										
Horiz.	Increment			USDA	VCOS	COS	MS	FS	VFS	SAND	SILT	CLAY	FINE	FSi	COSi
	BT	DB	MIDP	TEXT.	2000-	1000-	500-	250-	100-	2000-	50-	< 2	CLAY	20-	50-
			cm	CLASS	1000	500	250	100	50	50	2		<0.2	2	20
					(PERCENT)										
A	0	12	6.0	Loam	3.2	5.3	5.5	17.3	16.2	47.5	31.7	20.7	5.4	16.2	15.5
C1	12	24	18.0	Loam	2.5	7.9	6.1	14.6	14.4	45.6	34.5	20.0	5.0	19.1	15.4
C2	24	41	32.5	Loam	0.9	4.4	5.4	15.2	15.4	41.4	36.8	21.8	5.8	19.7	17.1

Horiz.	Increment					CRS FRAG. Wt. %				CRS FRAG	Based on
	BT	DB	MIDP	FC/TC	FC/(TC-FC)				%passing	VOL. %	0Z> 3"
			cm	RATIO	RATIO	>2 < 4.	>4.75	TOTAL	#10 sieve	TOTAL	BD = 1.5 g/cc
A	0	12	6.0	0.26	0.35	0.0	0.0	0.0	100	0	
C1	12	24	18.0	0.25	0.33	2.4	0.0	2.4	99		
C2	24	41	32.5	0.27	0.36	0.0	0.0	0.0	100	0	

Horiz.	Increment			CEC	CEC	Exchangeable Cations				CEC	BASE	ESP	SAR
	BT	DB	MIDP	(NaOAc)	(CLAY)	Ca	Mg	Na	K	SUMM.	SAT.	-%-	
			cm	cmol(p+)kg-1							-%-		
A	0	12	6.0	8.9		12.9	1.2	0.5	0.6	15.2	171.0	5.7	3.8
C1	12	24	18.0	7.6		17.0	1.2	0.9	0.3	19.4	256.0	12.3	4.5
C2	24	41	32.5	8.9		16.7	1.1	0.6	0.4	18.9	212.0	7.3	4.7

Horiz.	Increment			Saturation Extract Data											
	BT	DB	MIDP	pH	EC	CO3	HCO3	Cl	SO4	NO3	Ca	Mg	Na	K	SAR	TDS
			cm		dS*m-1	mmol(+/-)*L-1										mG/L
A	0	12	6.0	7.8	0.72	0.00	0.35	10.55	1.04	2.35	2.81	0.58	4.99	0.44	3.84	619
C1	12	24	18.0	7.7	1.75	0.00	0.26	12.52	7.04	8.53	8.35	1.57	9.95	0.19	4.47	1205
C2	24	41	32.5	7.9	0.74	0.00	0.41	8.59	2.14	3.77	2.44	0.39	5.61	0.16	4.71	596

Soil Number: PA-3
Soil Series:
Soil Classification: Fine Loamy, Mixed, Thermic Typic Xerofluvents
Location: Recent Floodplain near Vasiliki
Date Sampled: August 8, 1989

Sample Identification

Horiz.	Increment DT	Increment DB	MIDP cm	TOTAL CARBON %	CaCO3 Equiv. %	INORG. CARBON %	ORGANIC CARBON %	Calcite %	Dolomite %	pH 1:1 H2O	pH .01M CaCl2
A	0	12	6.0	5.3	42.3	5.1	0.3	21.90	20.41	8.25	7.88
C1	12	24	18.0	5.6	44.7	5.4	0.2	22.83	21.84	8.15	7.98
C2	24	41	32.5	5.6	42.6	5.1	0.5	21.21	21.38	8.40	7.98

Horiz.	Increment DT	Increment DB	MIDP cm	Dithionite Extractable Fe ug/g	Mn ug/g	Si ug/g	Fe %	Fe2O3 %	SiO2 %	H4SiO4 %
A	0	12	6.0	7820	403.7	630.0	0.8	1.1	0.14	0.22
C1	12	24	18.0	8372	244.3	838.9	0.8	1.2	0.18	0.29
C2	24	41	32.5	7655	249.2	1098.8	0.8	1.1	0.23	0.38

Horiz.	Increment DT	Increment DB	MIDP cm	Oxalate Extractable Fe ug/g	Mn ug/g	Si ug/g	Fe %	Fe2O3 %	SiO2 %	H4SiO4 %
A	0	12	6.0	1317	287.9	422.4	0.1	0.2	0.09	0.14
C1	12	24	18.0	927	50.3	369.5	0.1	0.1	0.08	0.13
C2	24	41	32.5	1218	91.6	407.3	0.1	0.2	0.09	0.14

Horiz.	Increment DT	Increment DB	MIDP cm	Hydroxylamine Extractable Fe ug/g	Mn ug/g	Si ug/g	Fe %	Fe2O3 %	SiO2 %	H4SiO4 %
A	0	12	6.0	26.0	214.9	66.6	0.003	0.004	0.02	0.03
C1	12	24	18.0	17.0	58.8	50.5	0.002	0.003	0.01	0.02
C2	24	41	32.5	24.0	90.3	71.2	0.002	0.004	0.02	0.03

Horiz.	Increment DT	Increment DB	MIDP cm	TOTAL ANALYSES Al2O3 %	Ba ug/g	Fe2O3 %	K2O %	Mn ug/g	Na2O %	P ug/g	Pb ug/g	SiO2 %	Sr ug/g	TiO2 %	ZrO2 %
A	0	12	6.0	7.03	163.71	3.52	1.10	529.9	0.833	76.31	24.18	50.4	245.3	0.131	tr
C1	12	24	18.0	6.72	150.48	3.46	1.05	369.6	0.818	0.01	28.55	48.3	266.8	0.121	tr
C2	24	41	32.5	7.27	161.59	3.71	1.15	393.5	0.861	0.01	35.39	44.3	250.0	0.133	tr

APPENDIX D. MAP UNIT DESCRIPTIONS FOR THE SOIL MAP OF THE STUDY AREA.

MAP UNIT DESCRIPTIONS

Map Unit	Description
1	Recent Alluvium - This unit was confined to the major drainages. It consisted primarily of Typic Xerofluvents.
2	Terrace Deposits - This unit consisted of soils developed on first and second terraces along the major drainages. The soils consisted primarily of Fluventic Xerochrepts and Typic Xerorthents. Slopes were generally 0 to 3 percent.
3	Colluvium - Agricultural Terrace Complex - This unit was confined to the western portion of the study area. The soils formed in colluvium from Neogene limestones and marls. The soils were predominantly Lithic and Typic Xerochrepts and Xerorthents. Agricultural terraces comprised 40 to 60 percent of the landscape. Slopes averaged 25 to 35 percent.
4	Rock Outcrop - Residual Soils - This unit was located on the northern edge of the study area. Soils consisted of Lithic Haploxeralfs and Xerochrepts derived from Cretaceous limestones and Triassic dolostones. Rock outcrop comprises approximately 60 percent of the unit. Slopes ranged from 5 to 50 percent.
4a	Local alluvium from Map Unit 4.
5	Residual and colluvial soils from Neogene Marls - This unit is located primarily on the western edge of the study area. The soils consisted of Typic and Lithic Xerochrepts and Lithic Xerorthents. Agricultural terraces comprised 40 to 50 percent of the unit. Slopes ranged from 10 to 35 percent.
5a	Local alluvium from Map Unit 5.
6	Colluvium and Alluvium from the Prina Complex Conglomerates - This unit was restricted to the western edge of the study area. The soils consisted of Typic Xerochrepts and Xerorthents, the subsoils are very cobbly. Agricultural terraces comprised 60 percent or more of the unit. Slopes ranged from 25 to 40 percent.
7	Fluventic and Calcixerollic Xerochrepts - These soils occupied shoulder and middle backslope positions in the uplands and around local drainages. The soils were highly to severely eroded. Slopes ranged from 30 to 70 percent. Agricultural terraces comprised 40 to 100 percent of this unit.

Map Unit	Description
7a	Local alluvium from Map Unit 7.
8	Fluventic and Calcixerollic Xerochrepts - These soils occupied stable upland positions. Slopes ranged from 2 to 10 percent.
9	Beach Deposits - Recent littoral deposits. Cobbly Psamments composed predominantly of limestone and dolomite.
10	Talus - The unit was restricted to the eastern margins of the study area. It consisted of debris fans and colluvial fans associated with the Ierapetra Fault scarp.
11	Colluvium from talus of the Ierapetra Fault Scarp. The soils were very cobbly and gravelly. They were primarily Typic Xerorthents.
Q	Rock and gravel quarries.
R	Rock Outcrops.
SC	"Scalped" - Areas that have had the upper soil horizons removed for use as greenhouse soil. This unit was of localized and limited extent.
S1...S5	Location of sampled profiles. S1, S2, S4, S5 correspond with Profiles 1 through 4, respectively.

APPENDIX E. GEOLOGY AND LANDFORM RELATIONSHIPS OF THE STUDY AREA.

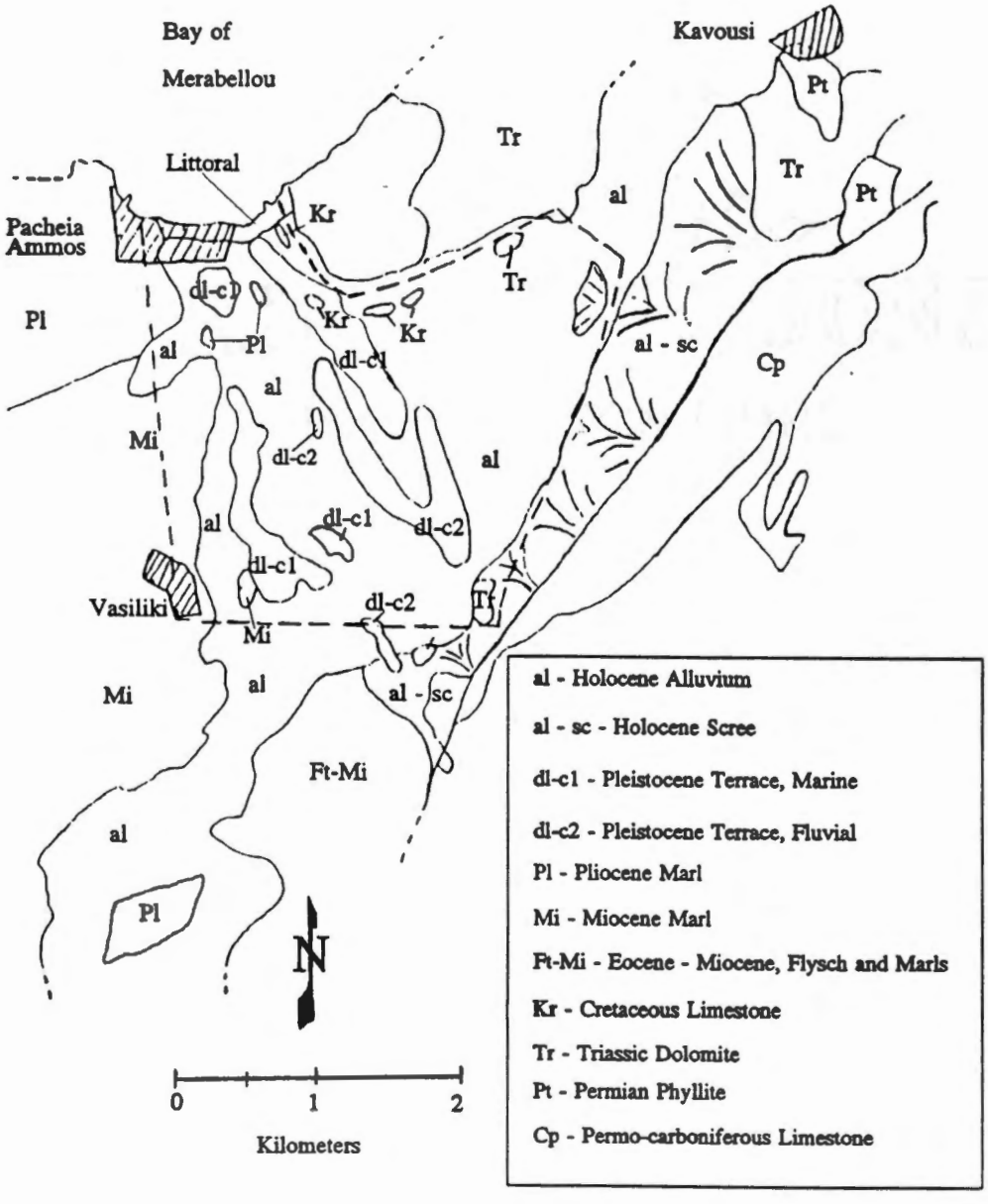


Figure E-1. Generalized geologic map of the study area. Dashed line indicates the boundary of the study area. Scale is 1:50,000. Modified from Papastamatioy et al., 1959. Geologic Map of Greece, Ierapetra Sheet. Inst. for Geol. and Subsurface Res. Athens, Greece.

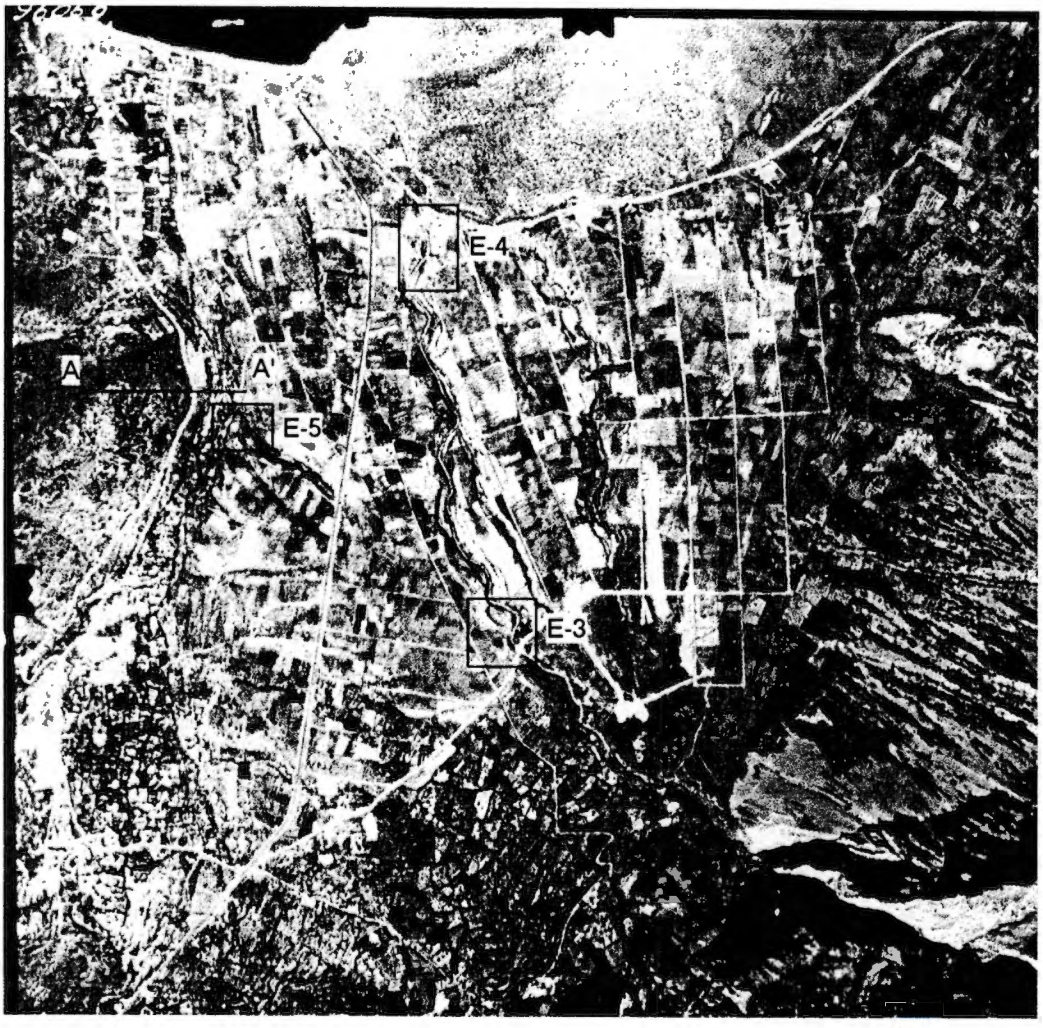
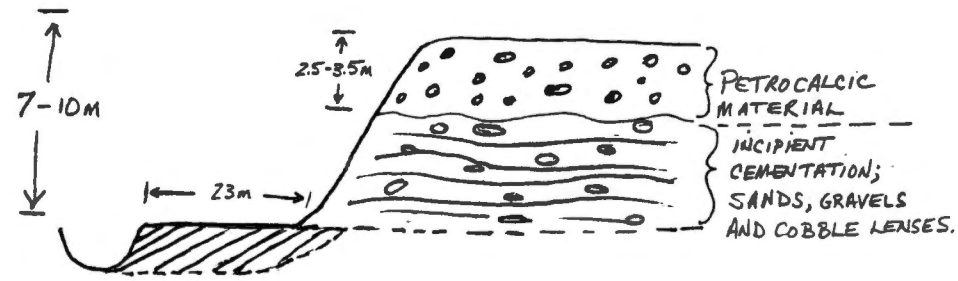
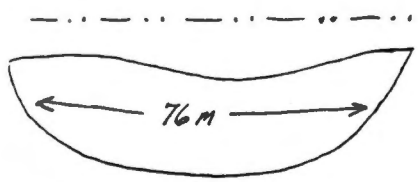


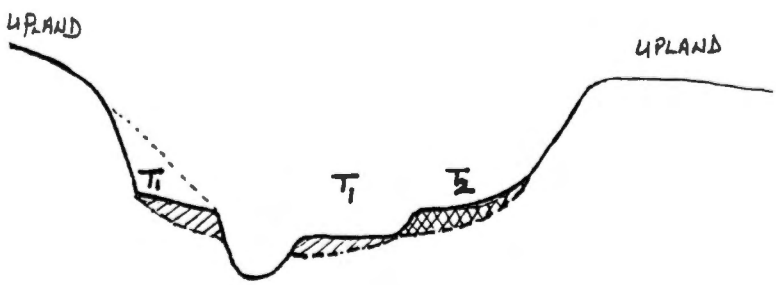
Figure E-2. Aerial photograph of the study area indicating the location of the landform relationships given in Figures E-3 through E-6, on the following pages.



A. SIDE VIEW



B. PLAN VIEW OF TERRACE ILLUSTRATED IN "A" ABOVE



C. SIDE VIEW

Figure E-3. Relationship of the stream terraces and uplands located in the upper reach of the Cha River.

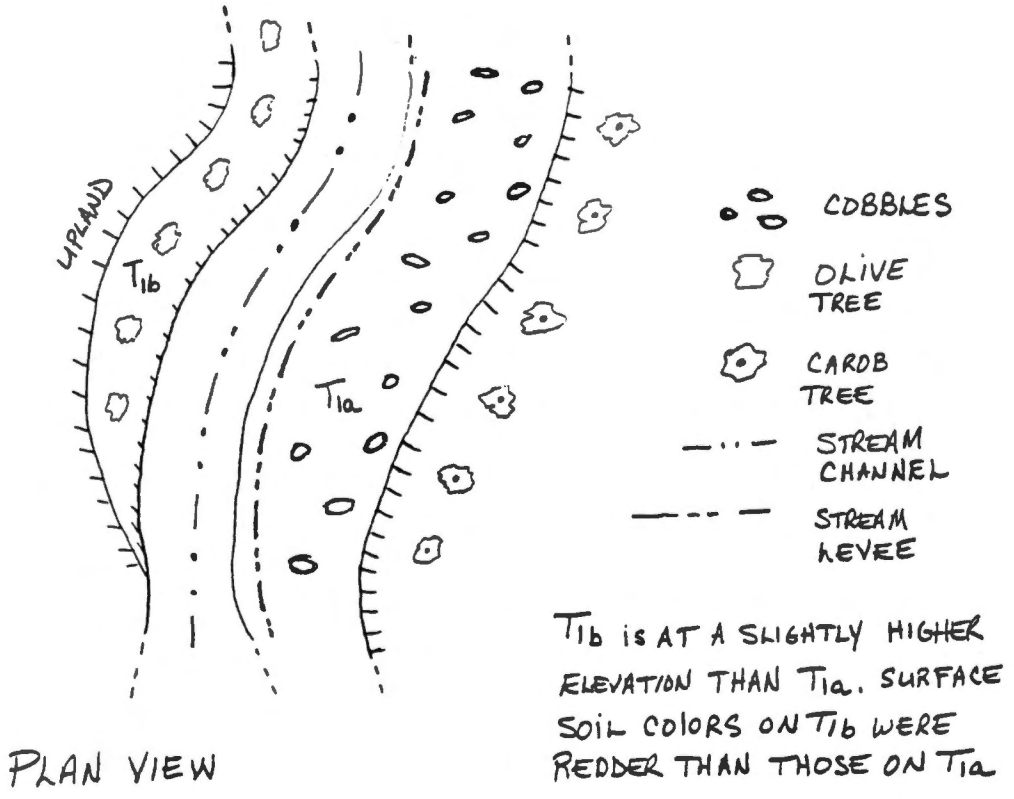


Figure E-4. Relationship between the stream terraces and the uplands in the lower reach of the Cha River.

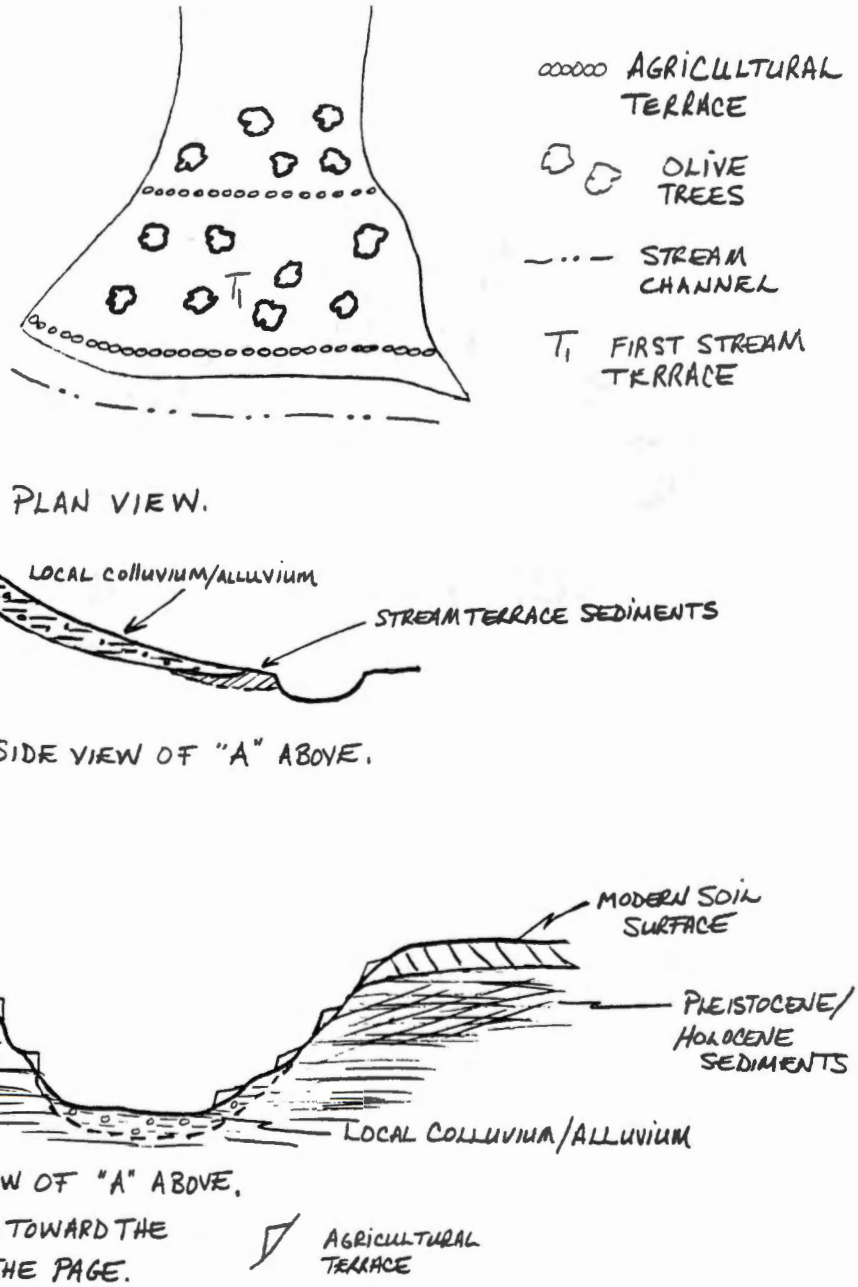


Figure E-5. Relationship of the stream terraces, alluvial sediments and uplands in the western portion of the study area.

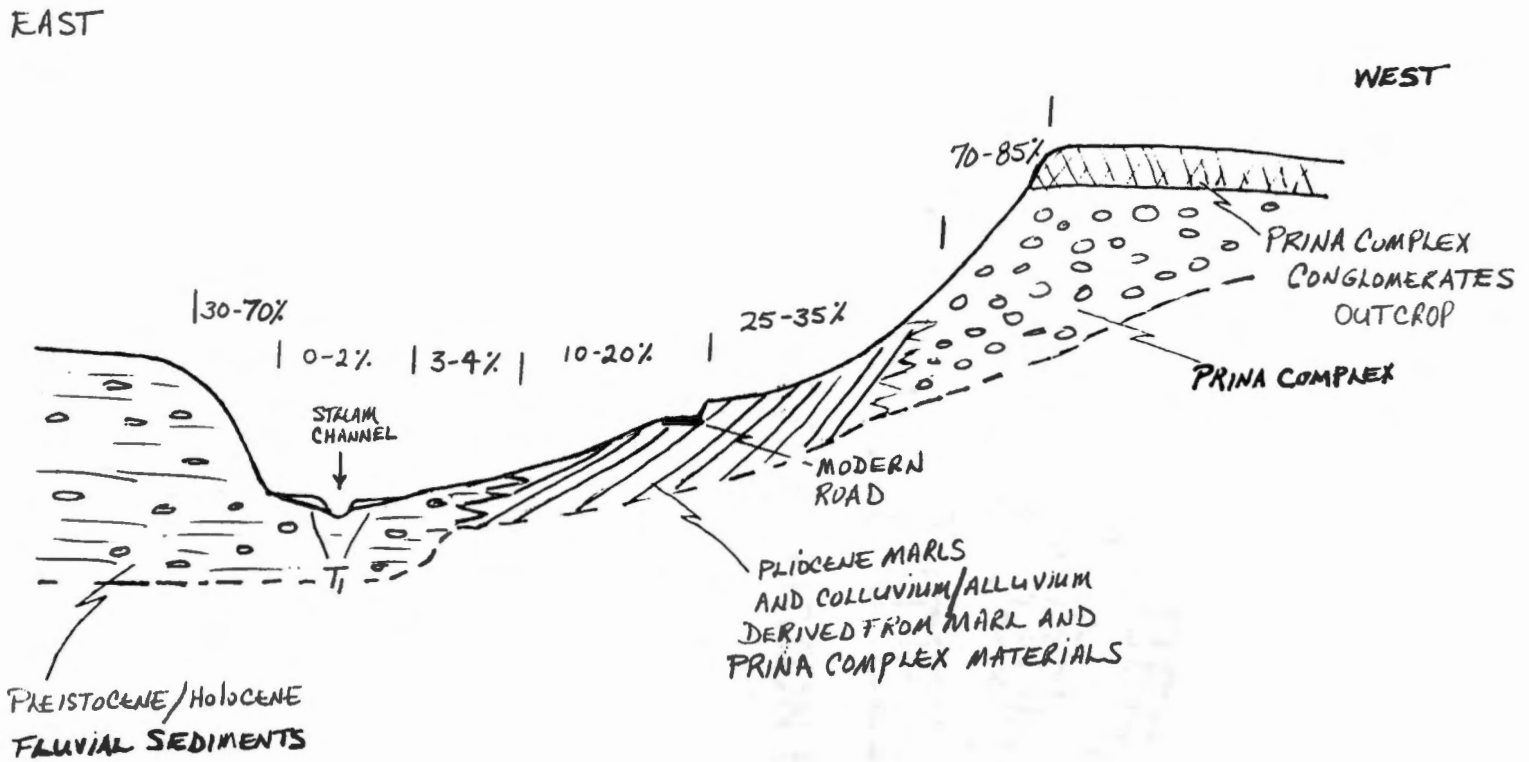


Figure E-6. Landform, geology and slope relationships in the western portion of the study area along line A to A' in Figure E-2. Dashed lines indicate infered geologic contacts.

VITA

The author grew up in Exeter, Rhode Island. After graduating from North Kingstown High School in 1977, he entered the University of Rhode Island. In 1982 he received a Bachelor of Science Degree in Natural Resources, with a concentration in soils and geology. During the summer of 1982 he worked for the U. S. National Park Service as a seasonal employee at Mesa Verde, National Park, CO. In the fall of 1982 he entered North Dakota State University as a Masters candidate. He received an M. S. Degree in Soil Science, with a minor in Geology, in 1985. After initiating a Ph. D. program at North Dakota, he transfered to the University of Tennessee in May of 1987 to take a position as Research Associate in charge of operating the Soil Characterization Laboratory in the Department of Plant and Soil Science. He received a Ph. D. in Plant and Soil Science with a concentration in Environmental Science in August of 1992.