2007

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Citation/Publisher Attribution

Muhs, D. R., J. R. Budahn, J. M. Prospero, and S. N. Carey (2007), Geochemical evidence for African dust inputs to soils of western Atlantic islands: Barbados, the Bahamas, and Florida, J. Geophys. Res., 112, F02009, doi:10.1029/2005JF000445
Available at: https://doi.org/10.1029/2005JF000445

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JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, F02009, doi:10.1029/2005JF000445, 2007

Geochemical evidence for African dust inputs to soils of western Atlantic islands: Barbados, the Bahamas, and Florida

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Received 22 November 2005; revised 27 August 2006; accepted 17 November 2006; published 24 April 2007.

[1] We studied soils on high-purity limestones of Quaternary age on the western Atlantic Ocean islands of Barbados, the Florida Keys, and the Bahamas. Potential soil parent materials in this region, external to the carbonate substrate, include volcanic ash from the island of St. Vincent (near Barbados), volcanic ash from the islands of Dominica and St. Lucia (somewhat farther from Barbados), the fine-grained component of distal loess from the lower Mississippi River Valley, and wind-transported dust from Africa. These four parent materials can be differentiated using trace elements (Sc, Cr, Th, and Zr) and rare earth elements that have minimal mobility in the soil-forming environment. Barbados soils have compositions that indicate a complex derivation. Volcanic ash from the island of St. Vincent appears to have been the most important influence, but African dust is a significant contributor, and even Mississippi River valley loess may be a very minor contributor to Barbados soils. Soils on the Florida Keys and islands in the Bahamas appear to have developed mostly from African dust, but Mississippi River valley loess may be a significant contributor. Our results indicate that inputs of African dust are more important to the genesis of soils on islands in the western Atlantic Ocean than previously supposed. We hypothesize that African dust may also be a major contributor to soils on other islands of the Caribbean and to soils in northern South America, central America, Mexico, and the southeastern United States. Dust inputs to subtropical and tropical soils in this region increase both nutrient-holding capacity and nutrient status and thus may be critical in sustaining vegetation.

Citation: Muhs, D. R., J. R. Budahn, J. M. Prospero, and S. N. Carey (2007), Geochemical evidence for African dust inputs to soils of western Atlantic islands: Barbados, the Bahamas, and Florida, *J. Geophys. Res.*, *112*, F02009, doi:10.1029/2005JF000445.

1. Introduction

[2] Interest in the long-range transport (LRT) of dust has increased over the past decade. The new interest in dust is in part a reflection of the recognition that dust can travel great distances [*Prospero and Lamb*, 2003; *Prospero et al.*, 2002], it can influence radiative transfer in the atmosphere and therefore affect climate [*Harrison et al.*, 2001; *Tegen*, 2003], and Fe-rich dust can fertilize the ocean's primary productivity [*Hutchins and Brunland*, 1998] and consequently impact the global carbon cycle [*Falkowski et al.*, 1998]. Another important effect of LRT dust is that it can form or at least influence the parent material for soils. It is now known, for example, that Asian dust plays an important role in the genesis of soils on many Pacific islands, including the Marianas [*Birkeland*, 1999, pp. 199–200] and Hawaii [*Jackson et al.*, 1971; *Vitousek et al.*, 1997; *Chadwick et al.*, 1999]. African dust influences the development of soils around many parts of the Mediterranean basin [*Yaalon and Ganor*, 1973].

[3] There have been few studies of the influence of dust on soils of islands in the Atlantic Ocean and Caribbean Sea. Yet, as early as the 19th century, Darwin, after observing an 1833 dust fall aboard the *Beagle* in the Cape Verde Islands, recognized that wind-blown dust from Africa might be a significant contributor to Atlantic Ocean deep-sea sediments [*Darwin*, 1846]. Detailed measurements conducted over four decades have shown regular delivery of clay-rich dust to the Caribbean region every year [*Prospero and Lamb*, 2003]. Clay-rich soils are present on many islands in the Caribbean–western Atlantic region, and carbonate terrains of exceptionally high purity host many of these soils [*Ahmad et al.*, 1966; *Ahmad and Jones*, 1969a, 1969b; *Scholten and Andriesse*, 1986; *Foos*, 1991; *Muhs*, 2001].

[4] There are at least four possible modes of origin for soils on carbonate islands, such as those found in much of the Caribbean region, summarized by *Muhs et al.* [1987]. One cited by many authors is the accumulation of insoluble residues produced by chemical weathering of the underlying carbonate rock. Another pedogenic pathway is fluvial transport of soil clays (derived from some noncarbonate parent material) from topographically higher terrains to lower-lying carbonate surfaces. Two other modes of origin

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Figure 1. Map of North America and the Caribbean basin with islands studied. Also shown are the distribution of loess (from compilation of *Muhs and Bettis* [2003]) and approximate extent of African dust in summer, based on 1983–1992 TOMS satellite data and studies by *Prospero and Carlson* [1972], *Prospero* [1999], *Perry et al.* [1997], and *Kallos et al.* [2006].

require the transport of particles from sources external to the insular environment. One is volcanic ash that has fallen on the carbonate surfaces and the other is fine-grained, wind-borne particles derived from distant regions.

[5] Most investigators of Caribbean and western Atlantic limestone-hosted soils have concluded that soils are formed by accumulation of residual particles as the carbonates dissolve over time. *Harrison and Anderson* [1919], *Vernon and Carroll* [1965] and *Ahmad and Jones* [1969a] either stated or implied that Barbados soils were derived primarily from insoluble residues in the coral reef limestone. Both *Ahmad et al.* [1966] and *Scholten and Andriesse* [1986] considered soils on limestone in Jamaica to be of residual origin. A similar interpretation was made for soils on limestone in the Bahamas and on the Cayman Islands [*Ahmad and Jones*, 1969b].

[6] A strong argument against a residual origin for many carbonate-island soils is that there are simply too few impurities in most island carbonates to account for the amount of observed soil. For example, given the typical insoluble residue contents of limestones on the Pacific Ocean island of Guam in the Marianas chain, *Tracey et al.* [1964] point out that dissolution of ~60 m of carbonate rock would be necessary to produce a soil profile ~0.3 m thick. For Rota Island, also in the Marianas chain, *Birkeland* [1999, p. 199–200] estimates that the entire island would have to have been dissolved in order to explain the observed soil thickness entirely by residual accumulation, a physical impossibility. *Muhs et al.* [1987] calculate the amount of reef carbonate dissolution that would generate measured soil profiles on the younger uplifted carbonate reefs on Barbados. Assuming a noncarbonate component of ~2%, 20–23 m of reef dissolution with no subsequent erosion would be required over the past 125–190 ka to produce soil profiles less than a meter thick. Recognition of upper reef crest facies in these terraces [*Mesolella*, 1967; *Mesolella et al.*, 1969] indicates that this amount of surface lowering by solution has not taken place.

[7] Other workers have suggested volcanic ash as a parent material for soils on Barbados. Barbados is adjacent to the active Lesser Antilles volcanic island arc. *Harrison and Anderson* [1919, p. 170] point out the external origin of

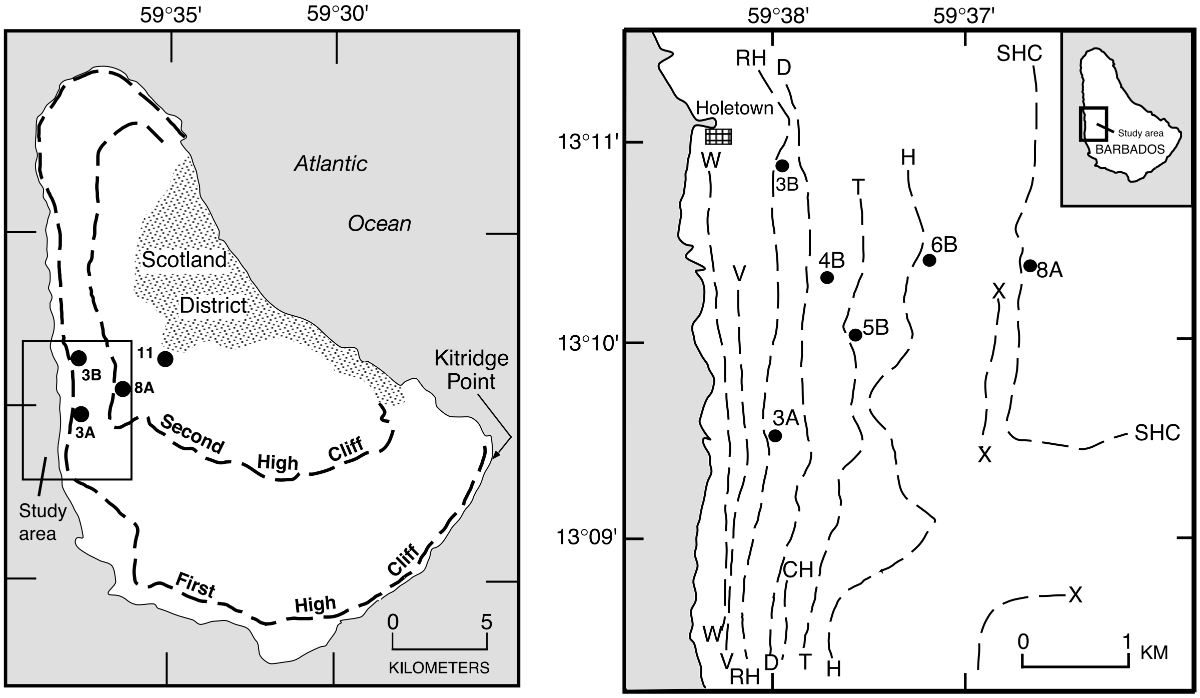

Figure 2. (left) Map of Barbados showing the two most prominent coral terraces (reef crests are shown by dashed lines). Tertiary sedimentary rocks crop out in the stippled area. Distribution of the ~125 ka First High Cliff (also called the Rendezvous Hill terrace) and ~460 ka Second High Cliff reef crests is taken from *Taylor and Mann* [1991]. Shown also is the Kitridge Point dust trap sampling locality of *Prospero* [1968]. (right) Detail of terrace reef crests (dashed lines) in the vicinity of Holetown, Barbados (redrawn from *Bender et al.* [1979]); numbered localities are soil profiles sampled. Terrace names are from *Bender et al.* [1979]: W, Worthing (~80 ka); V, Ventnor (~100 ka); RH, Rendezvous Hill (~125 ka, also called First High Cliff); D, Durants (~190 ka); CH, Cave Hill; T, Thorpe (~220 ka); H, Husbands (~320 ka); X, unnamed and undated terrace; SHC, Second High Cliff (~460 ka).

minerals in the soils not found in the island limestone, with an implication of possible volcanic ash additions. *Milne* [1940] and *Beaven and Dumbleton* [1966] conclude that soils on Barbados are derived mainly from volcanic ash. Despite their conclusion of a mainly residual origin, *Ahmad and Jones* [1969a] suggest the possibility of some volcanic ash influence on Barbados soils. *Borg and Banner* [1996] use Sr and Nd isotopes to study the possible origins of clay-rich soils on Barbados, using the same samples that had been collected by *Muhs et al.* [1990]. They conclude that volcanic ash is the dominant parent material for the soils, although they report a lesser (perhaps 30%) component of parent material from a continental crustal source.

[8] Finally, some workers emphasize the importance of LRT dust to the genesis of soils on limestone islands in the Caribbean Sea and western Atlantic Ocean. *Syers et al.* [1969], *Foos* [1991] and *Carew and Mylroie* [1991] suggest an African dust origin for clay-rich soils in the Bahamas. *Herwitz et al.* [1996] conclude that red, clay-rich soils on relatively pure carbonate eolianites of Bermuda are derived primarily from African dust. *Muhs et al.* [1990] suggest that soils on Barbados, Jamaica, the Bahamas, and the Florida Keys are derived primarily from African dust and, on Barbados, secondarily from volcanic ash. However, this latter study was limited because the geochemistry of African dust was not well characterized, volcanic ash samples studied were of limited number, LRT dust from North America was not considered, and only a few immobile elements were used in the analysis.

[9] In the present study, we test the conflicting hypotheses of origins of clay-rich soils hosted by limestone on islands of the Caribbean and western Atlantic Ocean (Figure 1). Numerous studies show that rare earth elements (REE) and other relatively immobile trace elements are powerful tools in eolian sediment provenance studies [*Olivarez et al.*, 1991; *Nakai et al.*, 1993; *Kurtz et al.*, 2000; *Sun*, 2002; *Muhs and Budahn*, 2006]. Here we present new data on the REE compositions of African dust samples, tephra samples from the Lesser Antilles island arc, and the fine-grained component of midcontinental North American loess. These data are compared to the trace element composition of carbonate island soils on Barbados, the Bahamas and the Florida Keys, in order to assess the relative importance of the possible parent materials. All geochemical data are in Table S1 of the auxiliary material.[1]

2. Study Areas

2.1. Barbados

[10] Barbados is situated in the western Atlantic Ocean approximately 145 km east of the Lesser Antilles island

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[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/jf/2005jf000445. Other auxiliary material files are in the HTML.

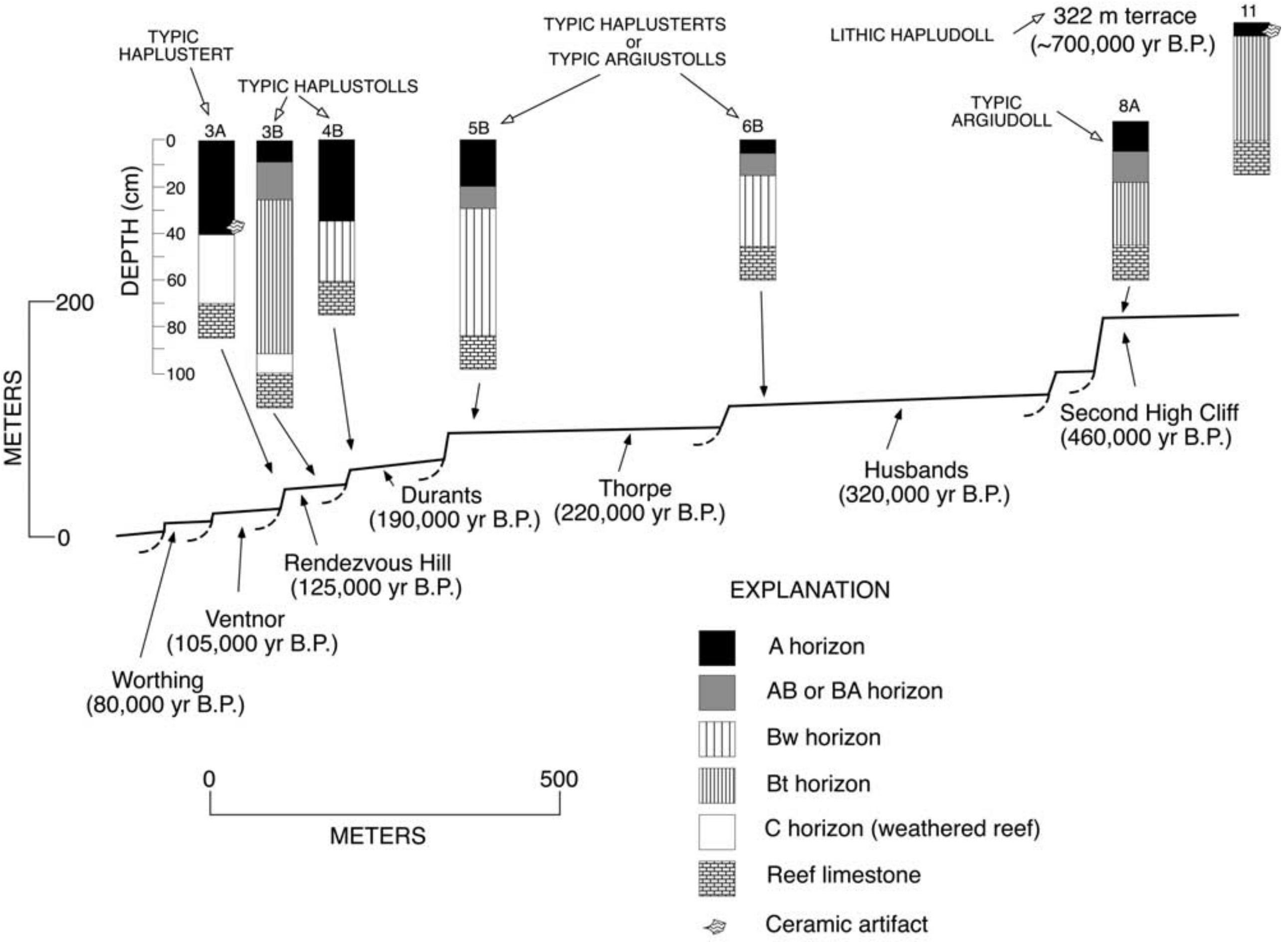


Figure 3. Topographic profile and ages of reef terraces in the Holetown area of Barbados and soil profiles studied. Modified from *Muhs* [2001].

arc (Figures 1 and 2). Unlike the volcanic rocks of that island chain, Barbados is the emergent portion of the Lesser Antilles forearc. Tertiary sedimentary rocks compose the core of most of the island, but are subaerially exposed only in a small area called the Scotland District (Figure 2). The majority of the exposed rocks of the island are Quaternary limestones that are tectonically uplifted coral reefs [*Mesolella*, 1967; *Mesolella et al.*, 1969]. *Borg and Banner* [1996] point out that most of the Tertiary sedimentary rocks of the Scotland District are situated in an erosional "window," or area of lower elevation than the highest reef terraces. Furthermore, streams in the Scotland District flow to the east, away from the coral reef cap portion of the island. Detailed study by *Acker and Stearn* [1990] shows that sediment from the Scotland District is transported to the offshore shelf to the east of the island. Thus fluvial delivery of Tertiary-rock-derived sediments from the Scotland District to the coral terraces to the west is probably minimal or nonexistent. Consequently, we do not consider the Tertiary rocks as a likely soil parent material.

[11] The soil chronosequence we studied on the emergent reefs of Barbados is in the Holetown area of western Barbados (Figures 2 and 3). Terraces in this region have been well mapped and range in age from ~80 ka to ~450 ka [*Mesolella et al.*, 1969; *Bender et al.*, 1979; *Radtke et al.*, 1988; *Gallup et al.*, 1994; *Edwards et al.*, 1997]. Soils sampled are on terraces dated to ~125 ka, ~190 ka, ~220 ka, ~320 ka, and ~450 ka. We also sampled a soil on a high terrace (site 11, Figures 2 and 3) that on the basis of an extrapolated uplift rate, may be ~700 ka. Details of the soils and sampling localities are given in *Muhs* [2001]; photographs of the reef terraces and soils in the field are in Figures S1 and S2.

2.2. Bahamas

[12] The Bahamas are islands composed primarily of carbonate reefs, carbonate oolitic marine sediments, and carbonate oolitic eolianites of Quaternary age (see Figure S1). Thin soils cap some of these deposits and are present as intercalated paleosols. Most of our soil samples are from New Providence Island, although we also have new samples from Norman's Pond Cay and Pigeon Cay, both of which are in the southern Exuma Cays (Figure 4). Soils from New Providence Island are on oolitic eolianites that are dated to ~125 ka, ~200 ka, and ~300 ka (Figure 5). On the basis of preliminary U series ages [*Halley et al.*, 1991], the reefs and oolitic eolianites on many of the southern Exuma Cays appear to be ~125 ka (Figure 5). We generated U series ages of aragonite corals

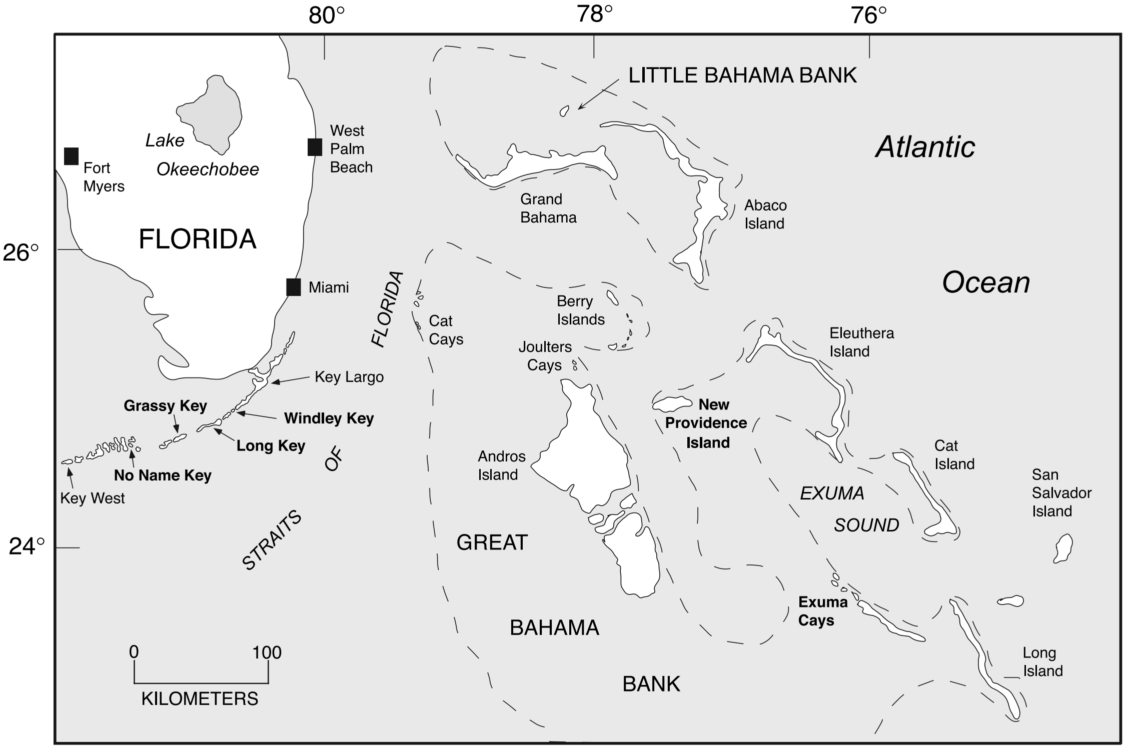


Figure 4. Map showing the Florida Keys and Bahamas area; islands in bold type are localities where soils were sampled.

and oolites from the Bahamas; these ages, along with supporting isotopic data, are given in Table S2.

2.3. Florida Keys

[13] The upper Florida Keys (Figure 4) are composed of the Key Largo Limestone, a reef-facies carbonate rock similar to those that form the reef terraces of Barbados. Recent U series ages indicate that the Key Largo Limestone dates to ~125 ka [*Fruijtier et al.*, 2000]. However, a coral from Long Key dates to ~200 ka [*Muhs et al.*, 2004], and records the penultimate interglacial high sea stand. Soils are thin or absent on most of the Florida Keys, probably the result of erosion from hurricanes or tropical storms due to the low (1–5 m) elevations of these islands. In places, however, there are thin, patchy occurrences of reddish brown, clay-rich soils, underlain by laminar calcretes, on reef limestone. These thin, clay-rich soils were sampled on Windley Key, Grassy Key, and No Name Key (all dated, or assumed to be ~125 ka), as well as Long Key (~200 ka).

3. Potential Soil Parent Materials on High-Purity Island Limestones in the Caribbean and Western Atlantic Ocean

3.1. Volcanic Ash (Tephra)

[14] Given the amount and longevity of volcanic activity in the Lesser Antilles island arc [*Briden et al.*, 1979], volcanic ash is clearly a potential parent material for soils in the region. One might expect that ash is important for Barbados soils because of its proximity to the active volcanic chain. Nevertheless, the year-round dominance of the northeast trade winds in the region does not favor transport of ash to the island except under breaks in the flow (e.g., with the passage of tropical cyclones) or via transport in the middle and upper troposphere that might occur during very explosive eruptions. Nevertheless, studies of offshore cores by *Sigurdsson et al.* [1980], *Carey and Sigurdsson* [1980], *Sigurdsson and Carey* [1981], and *Reid et al.* [1996] demonstrate that a significant amount of tephra is dispersed to the east of the Lesser Antilles island arc (Figure 6). Historical accounts of eruptions on the island of St. Vincent, situated immediately to the west of Barbados (Figure 6), report tephra falls to the east toward Barbados [*Anderson and Flett*, 1903; *Carey and Sigurdsson*, 1978; *Sigurdsson*, 1982]. Modern, offshore, carbonate-dominated sediments on the west coast of Barbados contain a small amount (<10%) of noncarbonate components, with volcanic minerals that are interpreted to be derived from St. Vincent eruptions [*Macintyre*, 1970]. Stratigraphic studies of cores indicate that volcanic eruptions in this area have occurred over much of the Quaternary (Figure 7).

3.2. Loess From Central North America

[15] Another potential source, at least in the past, is the fine-grained (<20 μm) component of loess from North America (Figures 1 and 8). During the last glacial period, loess-transporting winds over midcontinental North America were dominantly from the west or northwest [*Muhs and Bettis*, 2003]. Although much loess is coarse-grained silt and is deposited within a few tens to hundreds of kilometers from its source, a large component of loess

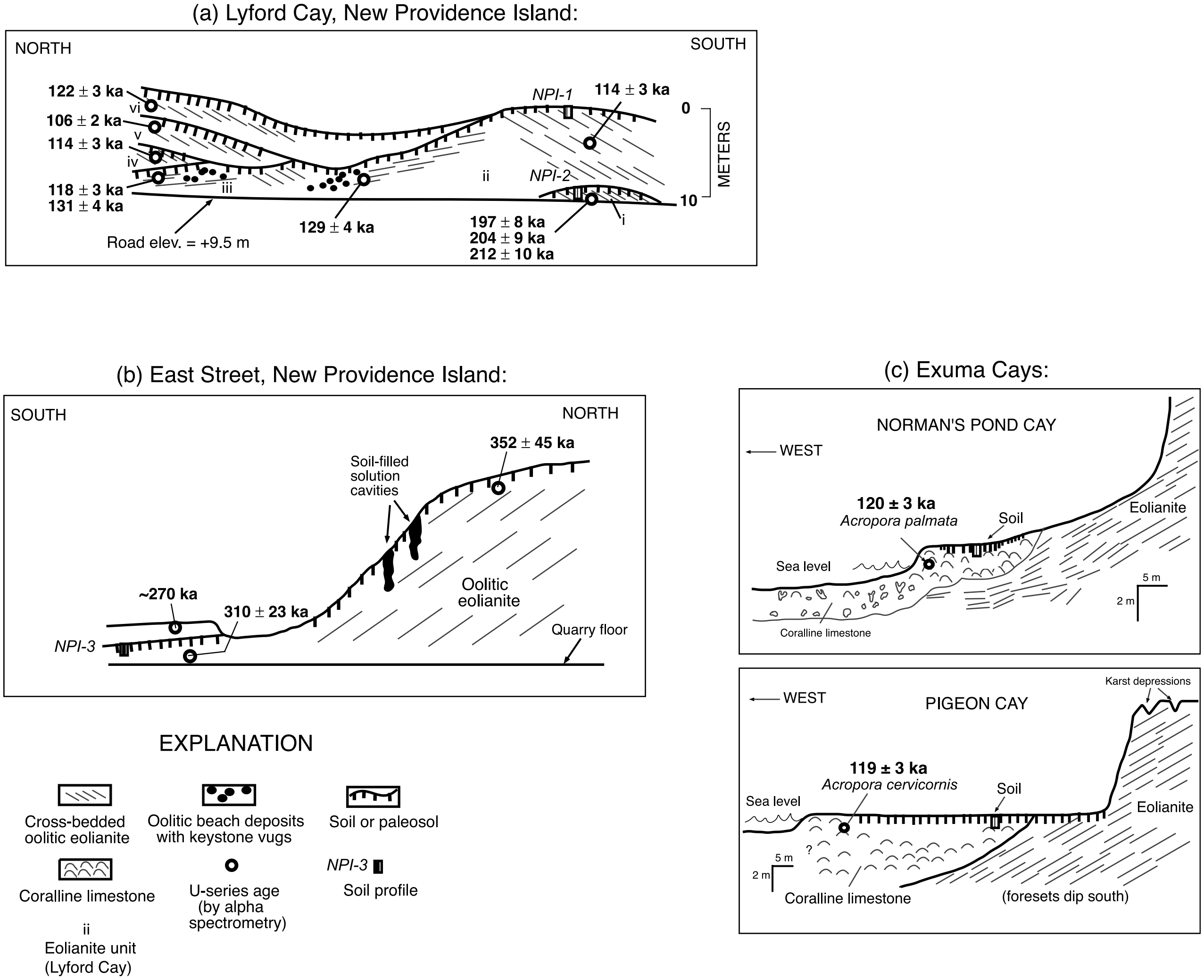


Figure 5. Stratigraphy and ages of eolianite and paleosol sections studied on (a and b) New Providence Island and (c) the Exumas Cays, Bahamas. Stratigraphy of the Lyford Cay section is modified from *Garrett and Gould* [1984]; stratigraphy of other sections is from this study. U series ages are from *Muhs et al.* [1990] and *Halley et al.* [1991]; all ages are on aragonitic ooids on New Providence Island and aragonitic corals for the Exuma Cays (see Table S2).

has particles with diameters finer than 20 μm and a significant component (as much as 30%) has particles with diameters less than 2 μm. *Mahowald et al.* [2006], using model results, show that the fine-grained component of North American loess was capable of LRT during the last glacial period. Because last glacial mass accumulation rates of loess in the North American midcontinent were among the highest in the world [*Bettis et al.*, 2003], even a small percentage of the total mass could yield a potentially significant LRT component to the Caribbean Sea–western Atlantic Ocean region. Mississippi River valley loess has a silt mineralogy dominated by quartz, feldspars, mica, calcite, and dolomite, and a clay mineralogy dominated by smectite, with lesser amounts of mica, kaolinite, and quartz.

3.3. African Dust

[16] A third potential source of soil parent material in the study region is African dust, carried west across the Atlantic Ocean (Figures 1 and 9). The dust-bearing "Saharan Air Layer," near its sources in Africa, can reach altitudes as high as 5–7 km. Farther west, dust concentrations are greatest at altitudes of 1.5–3.7 km, within the zone of the northeasterly trade winds. Dust outbreaks can reach Barbados within about a week after departure from the western African coast [*Prospero et al.*, 1970, 1981; *Prospero and Carlson*, 1972]. Aerosol filter studies conducted over four decades show that fine-grained eolian sediment from Africa reaches the western Atlantic Ocean and Caribbean Sea in varying amounts every year [*Prospero and Lamb*, 2003]. On the basis of analyses of satellite imagery, aerosol sampling networks, and back-trajectory calculations, the sources of this eolian dust are the Sahara and Sahel regions of Africa [*Prospero et al.*, 1970, 1981, 2002; *Prospero and Nees*, 1986; *Goudie and Middleton*, 2001; *Caquineau et al.*, 2002]. In summer, dust from Africa is transported at least as far north as Florida [*Prospero and Nees*, 1987; *Prospero*, 1999] and probably into the central and eastern United States [*Perry et al.*, 1997; *Kallos et al.*, 2006]. In winter,

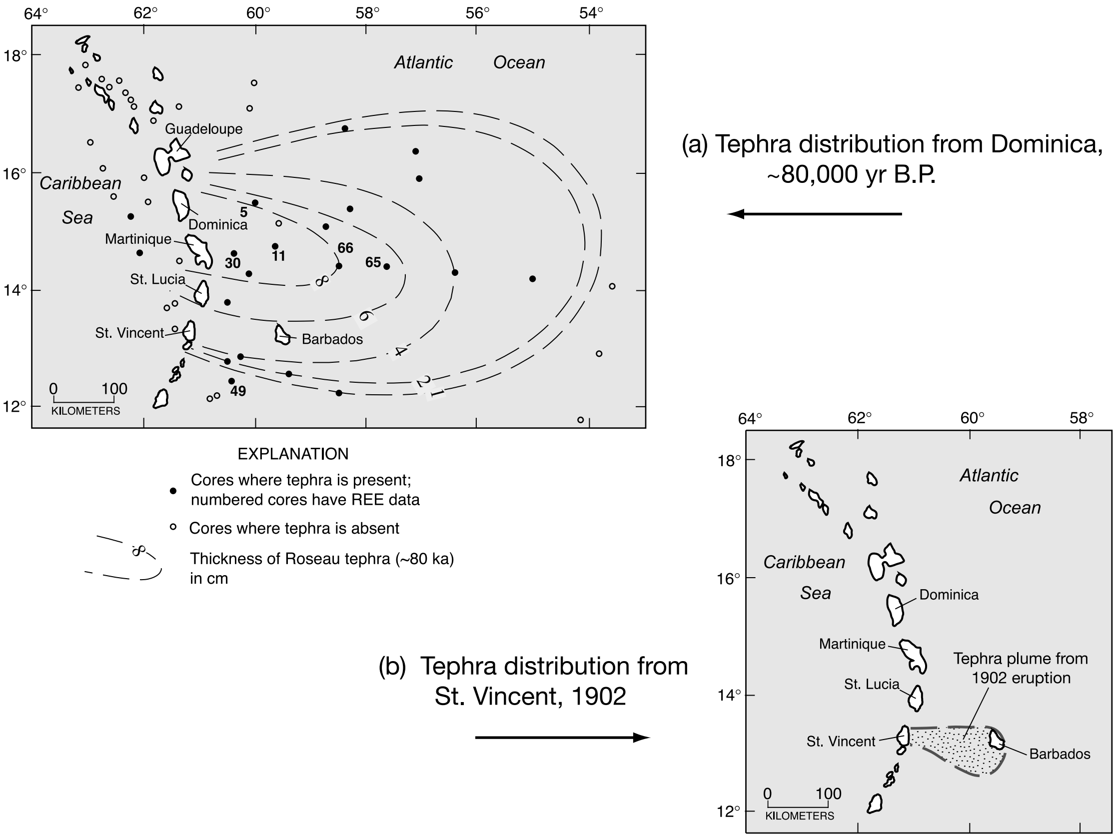


Figure 6. (a) Map of the Lesser Antilles volcanic island arc and Barbados, showing locations of piston cores studied by other workers (solid circles, cores with tephras; open circles, cores without tephras), thickness of the ~80 ka Roseau tephra, and locations of cores (EN and GS prefixes omitted for map clarity) with tephras from this study (numbered solid circles). (b) Map of the Lesser Antilles volcanic island arc and Barbados, showing tephra plume from the 1902 eruption of St. Vincent. Maps redrawn from *Carey and Sigurdsson* [1978, 1980].

dust from Africa is transported at least as far south as northern South America [*Prospero et al.*, 1981; *Swap et al.*, 1992].

[17] Airborne dust from Africa that reaches the western Atlantic Ocean is composed mostly of particles less than 20 μm in diameter, and about 30–50% of this is clay-sized material less than about 2.5 μm in diameter [*Prospero et al.*, 1970, 2001]. The mass median diameter of the particles is in the range 2.5 μm to 5.0 μm [*Li-Jones and Prospero*, 1998]. Studies by *Delany et al.* [1967] and *Glaccum and Prospero* [1980] have shown that quartz is the most important mineral in the silt-sized fraction and that mica dominates the clay-sized fraction. Kaolinite, chlorite, microcline, plagioclase, calcite and gypsum are also present in smaller quantities. *Caquineau et al.* [2002] showed that the relative amounts of mica and kaolinite in the clay fraction are a function of source areas within the Sahara and Sahel regions. Several studies of deep-sea cores from the Atlantic Ocean demonstrate that the flux of dust from the Sahara and Sahel regions is greater during glacial periods than during interglacial periods [*Bowles*, 1975; *Kolla et al.*, 1979; *deMenocal et al.*, 1993], observations that are consistent with recent modeling results [*Mahowald et al.*, 2006]. Greater flux during glacial periods may have occurred because the source regions were expanded and drier, and because of cooler sea surface temperatures, trade wind speeds may have been enhanced.

4. Methods

[18] Soils on Barbados, the Florida Keys and the Bahamas were sampled by horizon from hand-dug pits, road cuts, or quarry exposures. Most samples have been analyzed previously for other elements [*Muhs et al.*, 1990]; detailed soil descriptions and other analytical data for soils on Barbados are given by *Muhs* [2001]. All soil samples were analyzed in bulk, i.e., as "whole rocks," without pretreatments, other than pulverization to a uniform particle size. We note, however, that soils on Barbados are dominantly composed of particles less than 2 μm in diameter [*Muhs*, 2001].

[19] African dust samples were collected at Kitridge Point, Barbados (latitude 13°10′N, longitude 59°30′W, Figure 2; see *Prospero and Nees* [1977] for sampling details) in 1967, 1968, and 1969. The protocol used in the early program of Barbados dust studies was based on sampling of aerosols by means of nylon monofilament screens suspended in the wind; four square meters of collector typically yield tens of grams of dust during the dusty summer season. With such large samples, it is

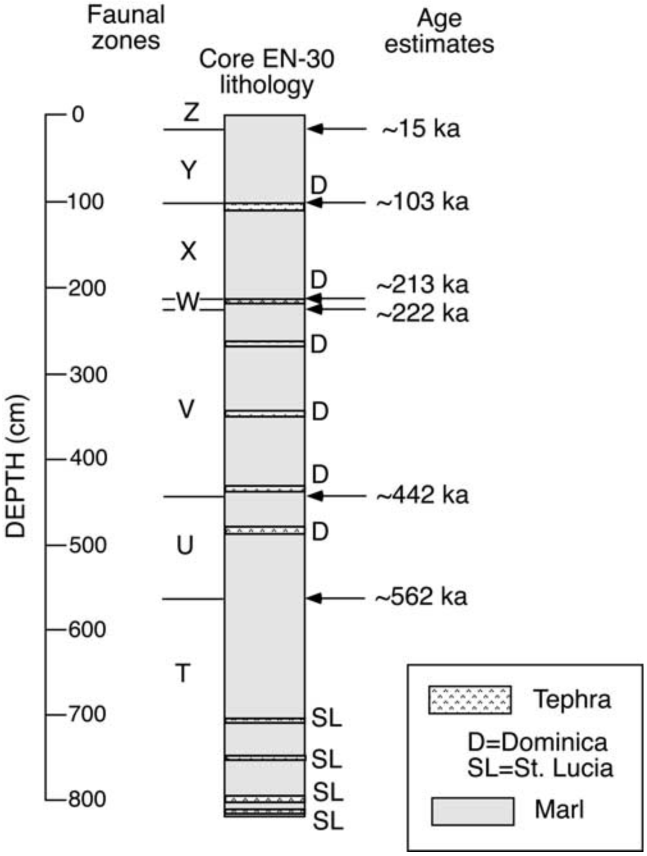


Figure 7. Stratigraphy of core EN-30 (see Figure 6 for location) showing many of the tephras analyzed in the present study. Core stratigraphy and faunal zones are from *Sigurdsson and Carey* [1981]; age estimates are from *Reid et al.* [1996].

possible to separate the mineral dust into size classes by settling in aqueous suspensions [*Prospero et al.*, 1970]. The size cuts used in this study were >20 μm, 20–10 μm, 10–5 μm, 5–2 μm, and <2 μm.

[20] Tephra samples, considered to be primarily from Dominica and St. Lucia (Figure 6), were taken from deep-sea cores previously described by *Carey and Sigurdsson* [1980], *Sigurdsson and Carey* [1981], and *Reid et al.* [1996]. Because the tephra layers in these cores are thin, care was taken to sample only those portions of identified tephra bands that were clearly volcanic, in order to avoid the possibility of sampling subjacent and superjacent layers that may contain African dust. As an added precaution, the tephra samples were treated with Na pyrophosphate overnight and ultrasonicated. Following this procedure, fine-grained (<2 μm) material was removed three times by settling and decantation. The remaining material was wet sieved with a 37-μm sieve; grains >37 μm retained on the sieve were analyzed chemically. Volcanic materials of Quaternary age from St. Vincent, described by *Hay* [1959, 1960], and provided by him, were analyzed in bulk. Because of the limited number of samples available to us from St. Vincent, we also use geochemical data for Quaternary volcanic materials reported by *Turner et al.* [1996] and *Heath et al.* [1998].

[21] For North American loess samples, we wished to analyze only the LRT dust component most likely to be transported to the western Atlantic Ocean. We hypothesize that such sediments would be from the lower Mississippi River Valley, the most southerly loess source on the continent (Figures 1 and 8). Therefore loess samples taken from depths below the zone of pedogenesis were collected from localities in Tennessee, Mississippi and Louisiana, a transect from latitudes ~36°N to ~30°N (detailed locality data are given by *Muhs et al.* [2001]). We conducted particle size separations of the sediments to obtain the fine-grained (<20 μm) loess fraction, i.e., the component that could be carried great distances. Loess samples were first treated with hydrogen peroxide to remove organic matter. Sodium hexametaphosphate was then added as a dispersant and left overnight. To aid dispersion of clays, samples were then treated by ultrasonic shaking. Sands were removed by wet sieving (53 μm) and clays and fine silts were sampled by repeated settling and decantation. The resulting <20 μm silt-and-clay separate was then analyzed for geochemistry. We note that carbonates, if present, are retained by this process.

[22] Concentrations of rare earth elements (REE) and other trace elements were determined by instrumental neutron activation analysis (INAA), as described by *Budahn and Wandless* [2002]. For provenance studies, we utilized only those elements that are considered, on the basis of high ionic potential, to be immobile in low-temperature, near-surface environments (see discussion below). The suite of elements chosen includes Sc, Cr, Th and Zr as well as the REE, La to Lu. The most likely host minerals for Cr and Sc are micas, amphiboles and clay minerals. Th can be hosted

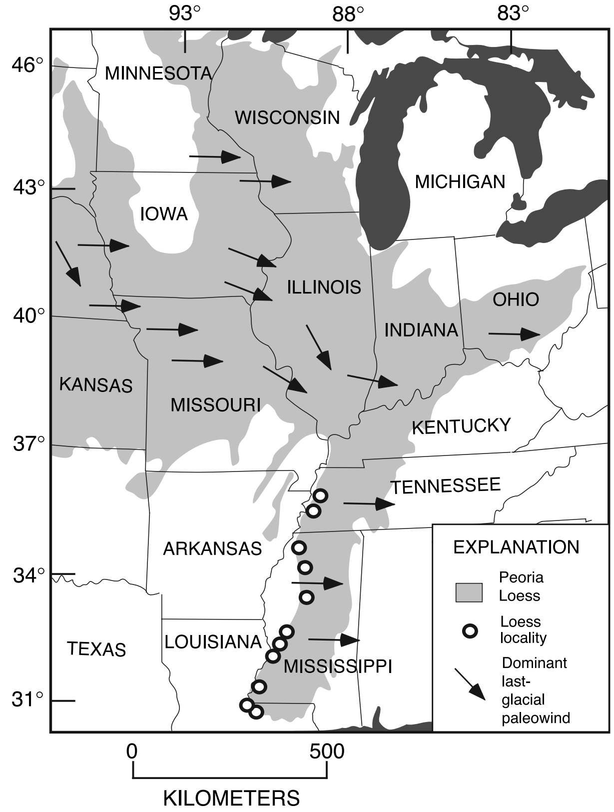


Figure 8. Map of the Mississippi River valley, showing distribution of loess and last glacial paleowinds (compiled by *Muhs and Bettis* [2003]) and locations of lower Mississippi River valley loess analyzed in this study. Samples are loesses from the C horizons of soils studied by *Muhs et al.* [2001].

by micas, amphiboles, zircon, sphene and clay minerals. Zr is found almost exclusively in zircon. The REE can be hosted by micas, chlorite, clay minerals, amphiboles, sphene, zircon, apatite and, in small amounts, feldspars.

[23] REE concentrations are typically normalized to chondritic meteorite compositions and we follow this protocol. In the discussions of REE patterns that follow, the terms "enriched" and "depleted" are used in descriptions and interpretations. Because all samples analyzed have higher concentrations of REE compared to chondrites, these terms refer to relative abundances of different parts of the REE suite compared to other parts, e.g., light REE compared to heavy REE.

5. Mobility of Elements With Intermediate Ionic Potential in Soils

5.1. Principles of Element Mobility as a Function of Ionic Potential

[24] The use of REE and other trace elements for provenance studies is dependent on an assumption of relatively low mobility during chemical weathering and pedogenesis. This assumption has a basis both in first principles and in empirical studies. The basic principle involved is ionic potential, which is ion charge divided by its radius. Soluble cations are formed by elements with very low ionic potential (Ca, Mg, Na, K, Rb, Sr, Ba) and soluble complex anions are formed by elements (B, C, P, N, S) with very high ionic potential [*Mason and Moore*, 1982]. However, elements with intermediate ionic potential (Sc, Y, Ga, Al, Th, Zr, Ti, Nb, Ta, V and the REE) tend to be precipitated by hydrolysis, i.e., they combine with hydroxyl groups from aqueous solution. Although some of these latter elements are found in highly resistant minerals in any case (such as Zr

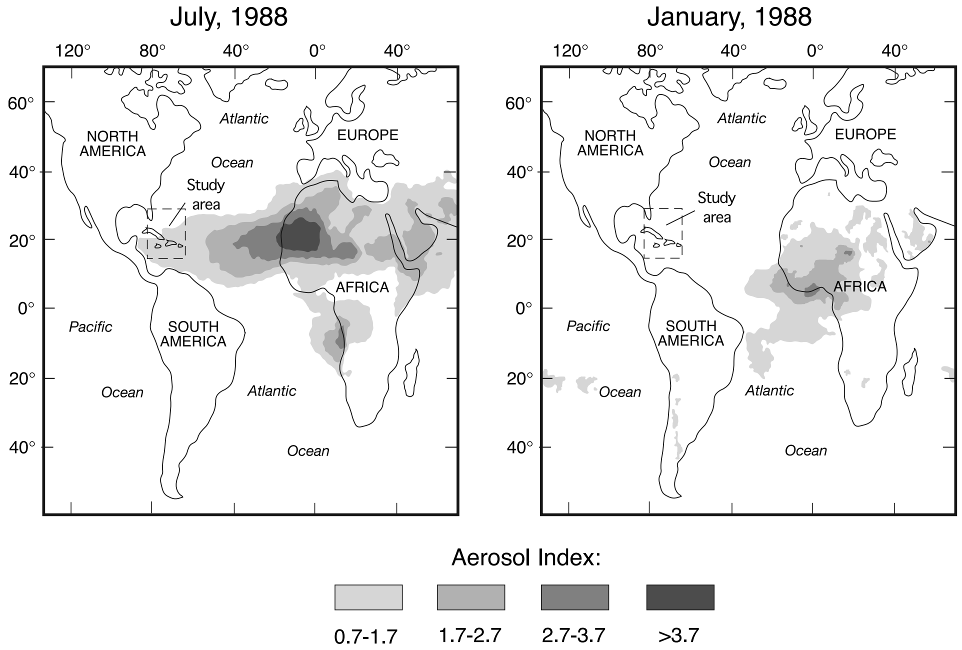


Figure 9. Aerosol index maps (compiled from Nimbus 7 satellite imagery, using the Total Ozone Mapping Spectrometer (TOMS)) for July and January 1988, showing seasonal shifts in the magnitude and location of African dust transport. Redrawn from data generated by the Ozone Processing Team at NASA's Goddard Space Flight Center.

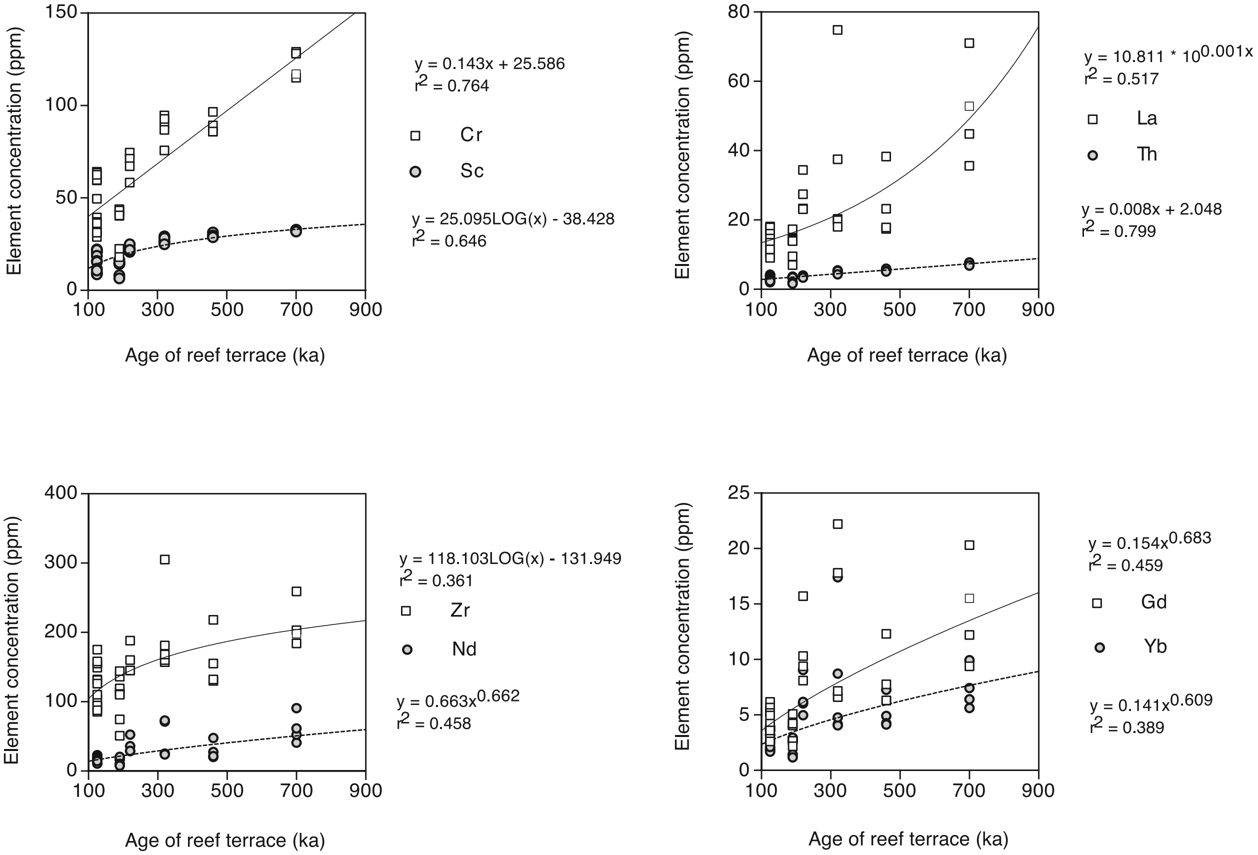


Figure 10. Chronofunctions of various element concentrations in individual soil horizons from Barbados along with best fit regression equations. See text for discussion of terrace ages.

in zircon), the principle of ionic potential predicts that even if the host mineral undergoes chemical weathering, elements of intermediate ionic potential will precipitate close to the site of release, such as adsorption onto nearby clay minerals. Low mobility of intermediate ionic potential elements is supported by the observation that they have low concentrations and short residence times in oceans [*Mason and Moore*, 1982] and river waters [*Goldstein and Jacobsen*, 1988].

[25] The use of intermediate ionic potential elements for provenance studies, based on an assumption of their relatively low mobility, has a long tradition. REE and other intermediate ionic potential elements (particularly Sc, Cr, Th, Ti, Y, Zr, and Hf) have been used in studies of the tectonic setting of volcanic rocks [*Pearce and Cann*, 1973], the origin of sedimentary rocks [*Cullers et al.*, 1979; *Bhatia and Crook*, 1986; *McLennan*, 1989], and the sources of dust and loess [*Olivarez et al.*, 1991; *Nakai et al.*, 1993; *Kurtz et al.*, 2000; *Sun*, 2002; *Muhs and Budahn*, 2006]. Indeed, many of these elements have been crucial in reconstructing the geologic history of the continental crust itself [*Taylor and McLennan*, 1985].

[26] Despite their widespread use in a variety of geologic applications, there have been, nevertheless, challenges to the assumption of immobility of intermediate ionic potential elements, based on both field and laboratory evidence [*Morey and Setterholm*, 1997; *Hill et al.*, 2000; *Kurtz et al.*, 2000; *Hodson*, 2002]. In some of these studies, however, it is not always clear whether the element "mobility" described is a function of true element dissolution in pore waters or whether the apparent mobility is due to mechanical translocation of clays (illuvation in soils, for example) wherein the elements in question are sorbed onto mechanically migrating clays.

5.2. Empirical Test of Element Mobility on Barbados

[27] We acknowledge that some intermediate ionic potential elements may be mobile in certain field settings, although we maintain that these elements are the *least* mobile constituents in soils. Nevertheless, the geologic setting of Barbados allows a simple test of this assumption. As described above, most Barbados soils rest on tectonically uplifted reef terraces. On a slowing uplifting coast such as Barbados, topographically higher terraces are older terraces. U series dating of Barbados reef corals, conducted over almost three decades, confirms this principle [*Mesolella et al.*, 1969; *Bender et al.*, 1979; *Radtke et al.*, 1988; *Gallup et al.*, 1994; *Edwards et al.*, 1997]. If the elements of interest in our study are the least mobile, whatever the ultimate source of the soils, then concentrations should increase progressively with terrace age as mobile elements are depleted by chemical weathering. An earlier study of Barbados soils reports that mobile major elements such as Si, Na, K, and P all show progressive losses with terrace age [*Muhs*, 2001].

[28] Concentrations of Sc, Th, and Cr all show increases with terrace age (Figure 10). The coefficients of determina-

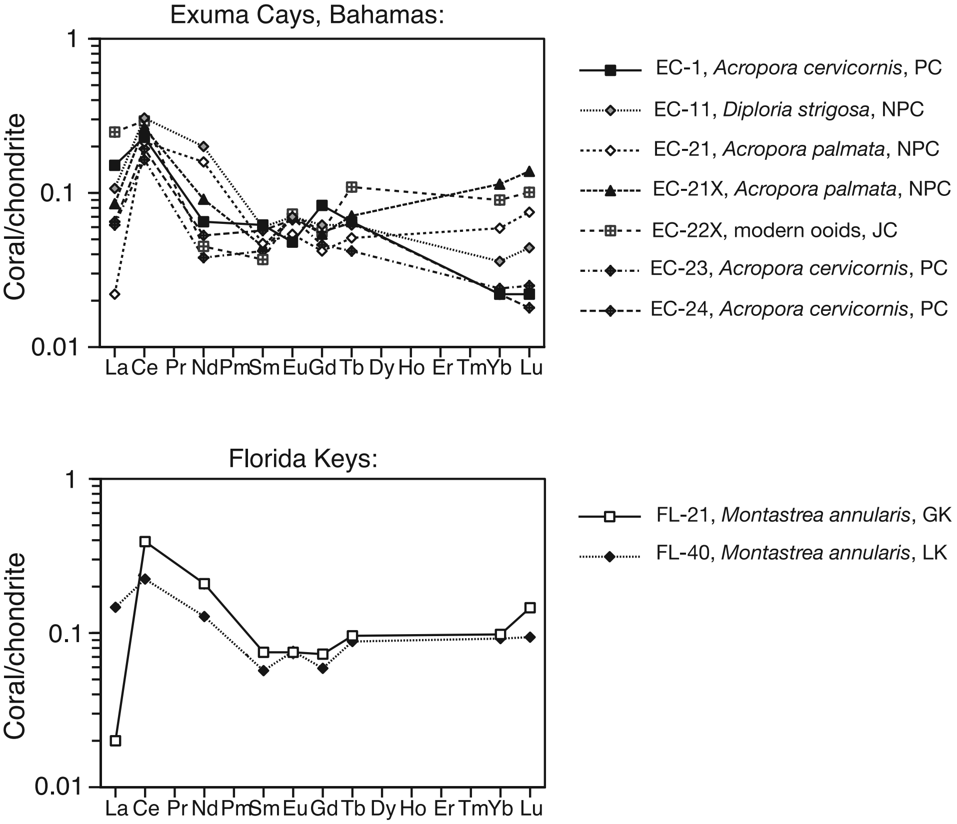


Figure 11. Chondrite-normalized REE plots of corals and ooids from the (top) Exuma Cays, Bahamas, and (bottom) Florida Keys. PC, Pigeon Cay; NPC, Norman's Pond Cay; JC, Joulters Cays (Bahamas); GK, Grassy Key (Florida); LK, Long Key (Florida).

tion for these elements versus terrace age are very high, with ~65–80% of the variation explained by terrace age (all significant at the 99.9% level). We interpret these data to indicate that Sc, Th, and Cr are accumulating in the soils as more soluble elements are lost through leaching. Similar plots of Zr and selected REE (La, Nd, Gd, Yb) also show increases in concentrations with terrace age, although the amount of variation explained by terrace age is lower (all are significant at the 95–99% level, however). We conclude from this simple test that at least in this environment, the elements of interest to us (Sc, Th, Cr, Zr, and the REE) likely have at least minimal mobility and can be used, with caution, as provenance indicators.

6. Results: Trace Element Geochemistry of Parent Materials and Soils

6.1. Reef Corals

[29] Carbonates in coral terraces of Barbados have low amounts of detrital, noncarbonate impurities (see reviews by *Muhs et al.* [1987, 1990]), reflective of the same low, detrital mineral content in modern carbonate sediments offshore western Barbados [*Macintyre*, 1970]. Indeed, we suspect that many of the impurities found in reef carbonate are actually particles derived from the same external sources (volcanic ash, eolian silts and clays) that we hypothesize for the island soils. Nevertheless, uncertainties remain about the REE and other trace element concentrations in the aragonite matrices of corals themselves. Studies by *Scherer and Seitz* [1980], *Sholkovitz and Shen* [1995], and *Webb and Kamber* [2000] all show that there are low but measurable amounts of REE in corals from the Bahamas, Florida, Bermuda, and Australia. However, these studies were limited in the number of corals analyzed, in the purity of the coral aragonite, or in the number of REE that were permitted by the analytical methods used. We therefore analyzed a series of last interglacial (~125 ka) corals from our study areas in the Exuma Cays (Bahamas) and the Florida Keys. These same species of corals are also the most common forms found in the reef terraces of Barbados [*Mesolella*, 1967; *Mesolella et al.*, 1969; *Bender et al.*, 1979]. With one exception (FL-21), X-ray diffraction analyses indicate that all corals analyzed are 99–100% aragonite; FL-21 is ~95% aragonite.

[30] Results of our INAA analyses for the more commonly studied major and trace elements in corals (see Table S1) are in good agreement with data from other studies. The only exception to this generalization is FL-21, which has ~5% calcite (by X-ray diffraction), and ~35% Ca (by INAA). For the other corals, Ca ranges from 37 to 38%, Sr ranges from 7700 to 8900 ppm, Ba is 16–24 ppm, and Rb is 0.5–0.97 ppm. These concentrations are in good agreement with those from other studies, summarized by *Allison* [1996]. INAA analyses are sufficiently precise that well-established but subtle intergeneric coral differences in U content can be detected, where *Acropora* consistently has between 3 and 4 ppm U, and *Diploria* and *Montastrea* have between 2 and 3 ppm U (see comparable data on U content

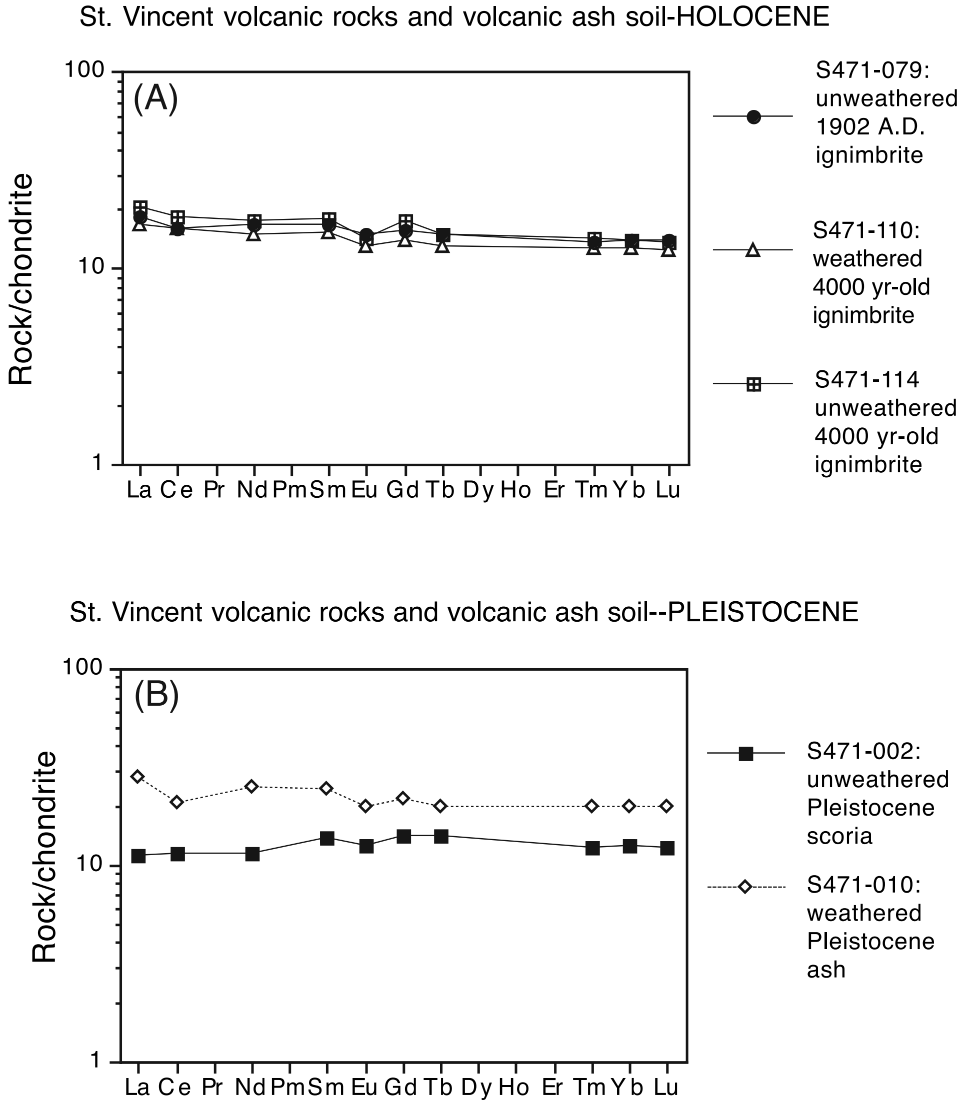


Figure 12. Chondrite-normalized REE plots of unweathered and weathered ignimbrites, scoria, and ash from the island of St. Vincent. For geologic setting of samples, see *Hay* [1959, 1960].

by *Mesolella et al.* [1969], *Bender et al.* [1979], and *Gallup et al.* [1994]). These results give us confidence that INAA analyses can yield accurate and precise data for major and trace elements in a carbonate matrix.

[31] Concentrations of REE in Florida and Bahamas corals are in the single- to double-digit ppb range for all elements except Ce, where concentrations are in the triple-digit ppb range. Our values are higher than those for Bermuda corals reported by *Sholkovitz and Shen* [1995] but lower than those reported for Bahamas corals by *Scherer and Seitz* [1980], when only their unrecrystallized specimens are considered. Thus all coral REE values we report are well below chondrite concentrations, but all have a very pronounced positive Ce anomaly when chondrite-normalized (Figure 11). *Sholkovitz and Shen* [1995] report both positive and negative Ce anomalies in the corals they analyzed. *Webb and Kamber* [2000] point out that REE in corals have low concentrations, unpredictable differences in fractionation between taxa, and nonproportional incorporation into the aragonite lattice. Our results seem to support their summary, particularly when our data are compared to those of other workers. In any case, for the purpose of the present study, the important findings are that overall, concentrations are extremely low and all samples show a distinct positive Ce anomaly. For other trace elements of interest, Florida and Bahamas corals have Th and Sc concentrations of <0.1 ppm, Cr concentrations of 0.3–1.0 ppm, and Zr concentrations of 1–5 ppm.

6.2. Volcanic Ash

[32] Analyses of fresh and weathered Pleistocene, Holocene, and historic ignimbrites and scoria from St. Vincent Island show similar REE patterns (Figure 12). All St. Vincent samples analyzed show relatively low REE contents (relative to loess or African dust: see below) and none shows light REE enrichment. All show a very minor negative Eu anomaly. Overall, the St. Vincent samples show a relatively "flat" REE pattern over the entire suite of elements. These results are similar to those reported by

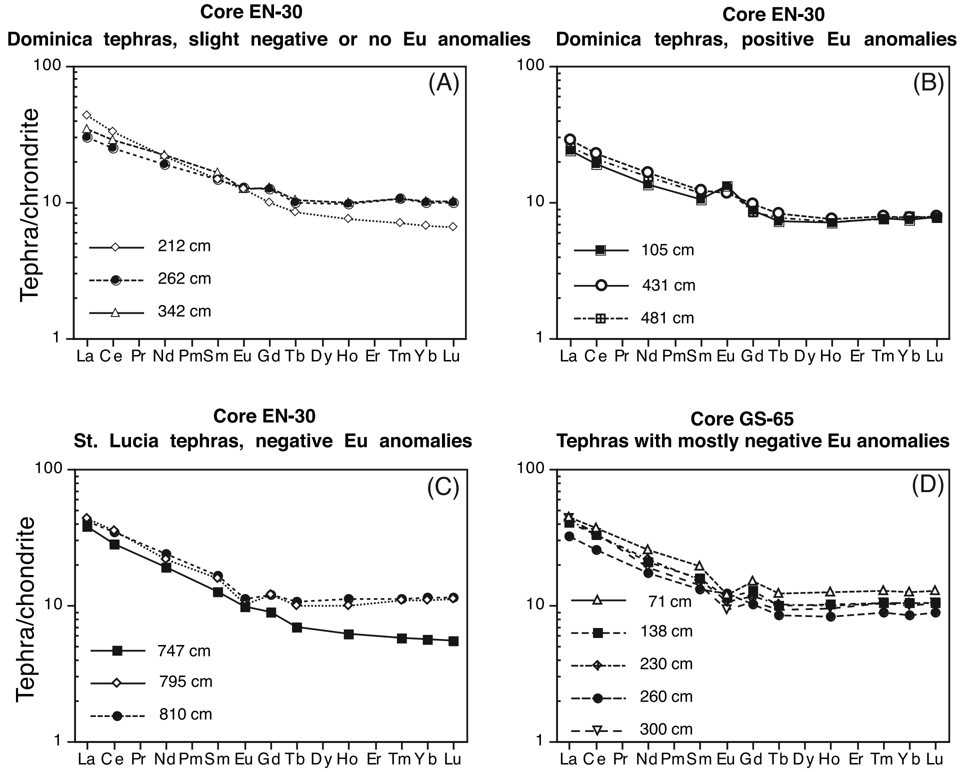


Figure 13. Chondrite-normalized REE plots of Dominica-derived and St. Lucia–derived tephras from various depths of core EN-30 (see Figures 6 and 7).

White and Patchett [1984] and *Heath et al.* [1998] for volcanic rocks from St. Vincent.

[33] Tephras from the islands of Dominica and St. Lucia, collected from deep-sea cores, show a wide variety of REE compositions (Figure 13). Tephras from St. Lucia, which seem to be dominant in sediments estimated to be older than ~560 ka (Figure 7), show a pronounced light REE enrichment (La_N is 30–50 times chondrite values; note that an "N" subscript denotes chondrite-normalized concentrations of an element), slight negative Eu anomalies, and depleted heavy REE (Figure 13c). Deep-sea core faunal and oxygen isotope stratigraphy indicates that eruptions from Dominica are most common during the past ~560 ka in this part of the Lesser Antilles island arc (Figure 7). Dominica tephras from intermediate depths (200–400 cm in core EN-30) show a REE pattern similar to those in tephras from St. Lucia, except for a less pronounced negative Eu anomaly (Figure 13a). In contrast, Dominica tephras from shallow (<200 cm) and greater (>400 cm) depths in core EN-30 show a slight light REE enrichment, (La_N is 20–30 times chondrite values), positive Eu anomalies, and depleted heavy REE (Figure 13b). Tephras from core GS-65 are closest to those from St. Lucia found in core EN-30: they are characterized by enriched light REE, depleted heavy REE, and, with one exception at 260 cm, negative Eu anomalies (Figure 13d).

6.3. Lower Mississippi River Valley Loess

[34] The clay and fine-silt fractions (<20 μm) of lower Mississippi River valley loess have REE patterns with little variability compared to volcanic materials from the Lesser Antilles island arc (Figure 14). All samples, from Tennessee to Louisiana, show enriched light REE values (La_N is 85–225 times chondrite values), strongly negative Eu anomalies, and depleted heavy REE. Overall, the loess samples have a REE pattern that is very typical of upper crustal rocks and sediments, including loesses from other regions, such as central Alaska [*Muhs and Budahn*, 2006].

6.4. African Dust

[35] African dust, like lower Mississippi River valley loess, also shows much more uniform REE patterns than volcanic materials from the Lesser Antilles island arc (Figure 15). All African dust samples analyzed have enriched light REE (La_N is >100 times chondrite values), a pronounced negative Eu anomaly and depleted heavy REE. Differences in the REE patterns reflect particle sizes in African dust. Light REE (La through Gd) have their highest chrondrite-normalized values in the clay (<2 μm) fraction, whereas heavy REE are more abundant in the fine silt (2–20 μm) fractions compared to the clay fractions. The compositions of dust samples collected from different years, or from different months of the same year, have no detectably significant differences.

6.5. Soils on Barbados, the Florida Keys, and the Bahamas

[36] Soils on terraces of Barbados show age-related differences in REE compositions (Figures 16 and 17). Soils on the ~125 ka and ~190 ka terraces, both those on reef and lagoonal facies, are enriched in light REE, have a pronounced negative Eu anomaly, and are depleted in heavy REE. Soils on the ~220 ka, ~320 ka, ~460 ka, and ~700 ka terraces have two other properties, in addition to these characteristics: (1) chondrite-normalized values for all REE

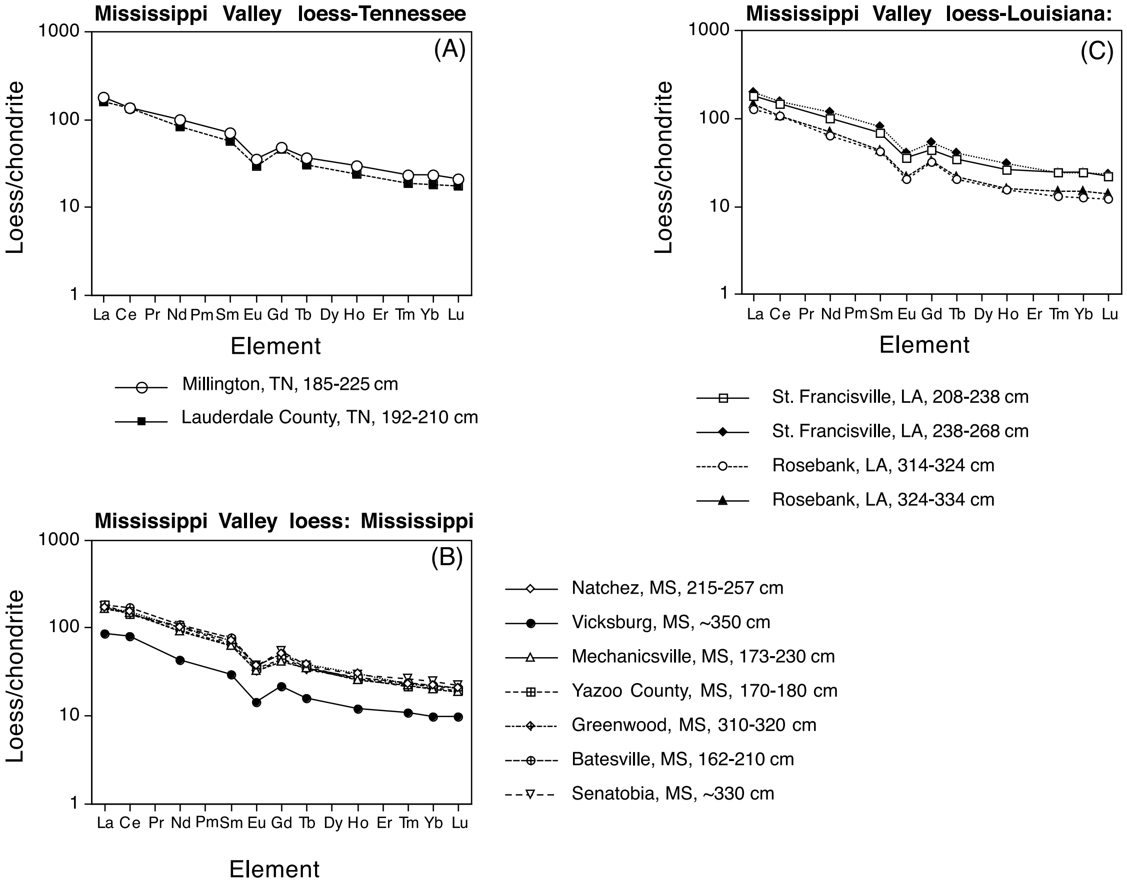


Figure 14. Chondrite-normalized REE plots of the <20 μm fraction of Mississippi River Valley loess from (a) Tennessee, (b) Mississippi, and (c) Louisiana.

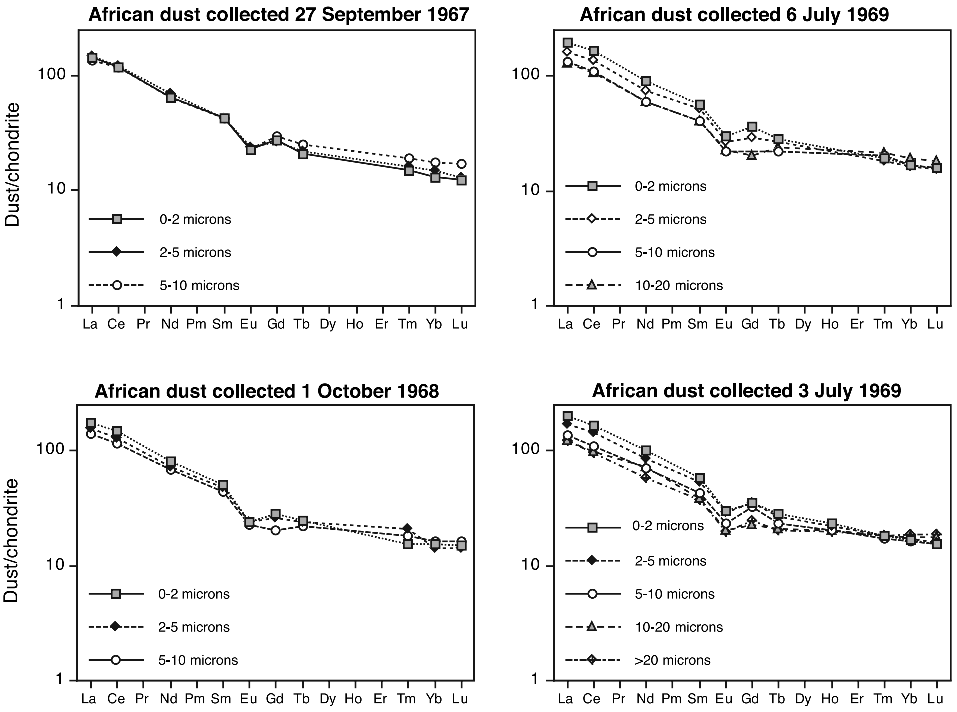
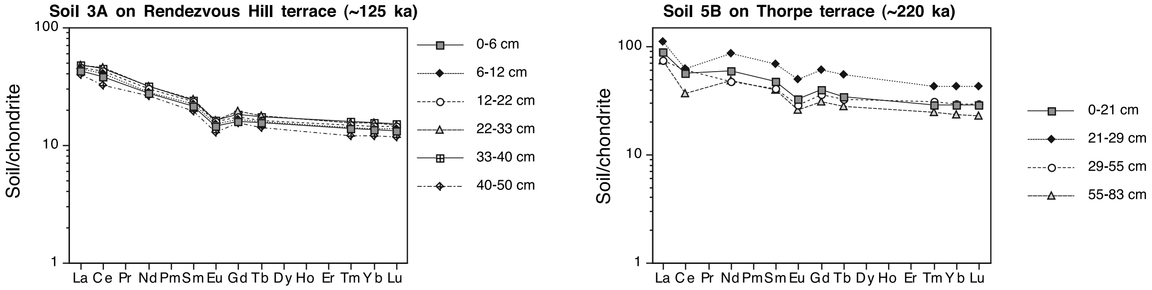


Figure 15. Chondrite-normalized rare earth element (REE) plots of various size fractions of African dust collected during three different years (1967, 1968, and 1969).

(a) Soils on reef crest facies



(b) Soils on lagoonal facies

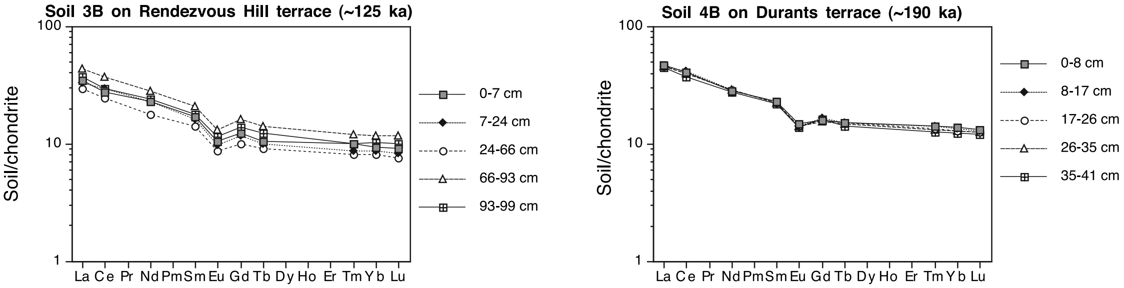


Figure 16. Chondrite-normalized REE plots of soils from lower (younger) terraces on Barbados.

in these older soils are generally higher, and concentrations increase with terrace age; and (2) almost all the soils from these older terraces show negative Ce anomalies. The exceptions to this are three horizons from the soil on the ~320 ka terrace, in which there are positive Ce anomalies.

[37] As with Barbados, soils on the Florida Keys and the Bahamas show enrichments in light REE, distinct negative Eu anomalies and depleted heavy REE (Figure 18). Concentrations of REE in soils of the Florida Keys and Bahamas show a wide range of values, and seem to be inversely proportional to the detrital carbonate contents of the soils, based on physical appearance. Unlike Barbados, none of the soils on the Florida Keys and Bahamas has a negative or positive Ce anomaly.

6.6. Overall Measures of REE Composition to Discriminate Parent Materials

[38] Certain parameters have been developed that reduce REE data and facilitate comparisons in provenance studies. The degree of Eu anomaly can be quantified by the Eu/Eu* value, where "Eu" is the chondrite-normalized Eu concentration (Eu_N), and "Eu*" is $(Sm_N \times Gd_N)^{0.5}$. Eu/Eu* less than 1.0 indicate negative Eu anomalies; values greater than 1.0 indicate positive Eu anomalies. Oceanic basalts, without a significant upper continental crustal component, will have no Eu anomaly. Archean sedimentary rocks usually have positive Eu anomalies, but post-Archean sedimentary rocks typically have negative Eu anomalies, with Eu/Eu* ranging from 0.6 to just under 1.0 [*McLennan*, 1989; *Taylor and McLennan*, 1985, 1995]. These differences reflect the fact that Archean and post-Archean continental crusts have significant differences in composition, possibly related to different mantle sources or mechanisms of crustal differentiation. Chinese and Alaskan loess of Quaternary age have Eu/Eu* that range from 0.59 to 0.68, very typical of post-Archean sedimentary rocks [*Gallet et al.*, 1996; *Jahn et al.*, 2001; *Muhs and Budahn*, 2006].

[39] Two other measures of REE composition reflect differences in the abundances of light to heavy REE. La_N/Yb_N is a measure of the overall abundance of light REE to heavy REE; higher La_N/Yb_N indicate light REE enrichment. Oceanic basalts have low La_N/Yb_N. Typical post-Archean sedimentary rocks have REE compositions that yield higher La_N/Yb_N, but less than about 15 [*McLennan*, 1989; *Taylor and McLennan*, 1985, 1995]. Chinese and Alaskan loess have, for example, La_N/Yb_N that range from about 7 to 10 [*Gallet et al.*, 1996; *Jahn et al.*, 2001; *Muhs and Budahn*, 2006]. Gd_N/Yb_N is a measure of heavy REE depletion, where high Gd_N/Yb_N indicates significant heavy REE depletion. Plots of Eu/Eu* versus La_N/Yb_N and Eu/Eu* versus Gd_N/Yb_N provide the potential for defining REE compositional fields that are distinctive for the various soil parent materials. This approach was used by *Nakai et al.* [1993] in studying the origin of eolian dust in deep-sea sediments of the Pacific Ocean and by *Sun* [2002] in ascertaining the sources of loess in China.

[40] Values of Eu/Eu*, La_N/Yb_N and Gd_N/Yb_N are distinct for the some of the soil parent materials considered here. Volcanic materials from St. Vincent occupy a Eu/Eu* versus La_N/Yb_N field distinct from that of tephras from Dominica and St. Lucia (Figure 19, top). In contrast, Eu/Eu* versus Gd_N/Yb_N for the two volcanic groups overlap (Figure 19, bottom). Because of the wide range of Eu/Eu* values, tephras from Dominica and St. Lucia define large fields for both plots. African dust and lower Mississippi River Valley loess have Eu/Eu* that occupy a

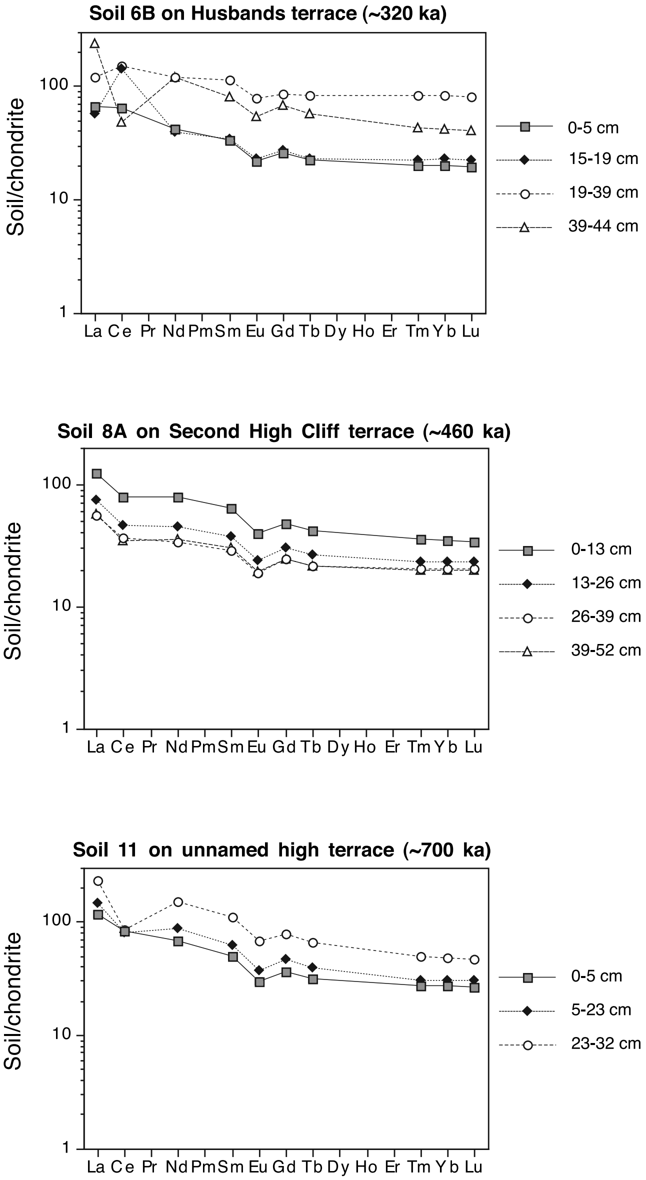


Figure 17. Chondrite-normalized REE plots of soils from higher (older) terraces on Barbados.

narrow range and overlap only the lowest range of values of tephras from Dominica and St. Lucia. Similarly, African dust has a wide range of La_N/Yb_N but only a small part of the field for dust overlaps the range of values for Dominica and St. Lucia tephras. Lower Mississippi River valley loess has La_N/Yb_N and Gd_N/Yb_N that do not overlap those of the volcanic materials at all.

[41] Soils on Barbados have Eu/Eu* that are higher than Mississippi Valley loess but (with one exception) are lower than St. Vincent volcanic materials (Figure 19). The soils on this island also have no overlap with La_N/Yb_N and Gd_N/Yb_N from Mississippi Valley loess. Most Barbados soils have La_N/Yb_N that are lower than African dust but overlap the field defined for tephras from Dominica and St. Lucia. One interpretation of this plot, therefore is that Barbados soils are derived mostly from tephras from Dominica and St. Lucia. An alternative interpretation, however, is that Barbados soils are derived from a mix of St. Vincent tephras and African dust. This interpretation is consistent with the fact that Barbados soils overlap only a small part of the Eu/Eu* versus La_N/Yb_N field defined by Dominica-St. Lucia tephras. In addition, in the Eu/Eu* versus Gd_N/Yb_N plot, many of the Barbados soils do not overlap the range of Dominica-St. Lucia tephras, but all overlap the range of African dust samples.

[42] Soils on the Florida Keys and the Bahamas show significant differences when compared with soils on Barbados (Figures 19). Soils from these northerly islands have somewhat lower Eu/Eu* that overlap both African dust and Mississippi River valley loess, but have only a slight overlap with tephras from Dominica and St. Lucia. With one exception, La_N/Yb_N for soils from Florida and the Bahamas also have considerable overlap with both African dust and Mississippi Valley loess. However, soils from Florida and the Bahamas have Gd_N/Yb_N that overlap African dust but not Mississippi Valley loess.

6.7. Parent Material Discrimination Using Sc-Th-La, Sc-Th-Zr, and Cr-Th-Nd

[43] Other trace elements with relatively low mobility (Sc, Th, Zr, Cr) can be extremely useful in provenance studies. One of the most commonly used approaches is to plot concentrations of three geochemically distinct elements in ternary diagrams. An example of such an approach is the relative abundance of Sc, Th, and La [*Taylor and McLennan*, 1985; *Bhatia and Crook*, 1986; *Olivarez et al.*, 1991]. Oceanic basalts, or sediments derived from them, will plot near the Sc pole, whereas average upper continental crustal rocks or sediments will plot near the La pole. Island arc rocks usually fall between these two extremes. An alternative ternary plot, using Sc, Th, and Zr [*Bhatia and Crook*, 1986] can distinguish these same rock types, and in addition can discriminate between sediments generated at active and passive continental margins. In making these plots, we have used not only the data generated in our study, but also data on Quaternary volcanic materials from St. Vincent reported by *Turner et al.* [1996] and *Heath et al.* [1998].

[44] A ternary plot of Sc-Th-La easily distinguishes between the two volcanic sources and between both volcanic source materials and African dust/Mississippi loess (Figure 20). These three elements do not, however, distinguish African dust and Mississippi loess from each other, an expected result because both are derived from well-mixed upper continental crustal materials. Barbados soils fall mostly on the field defined by the Dominica-St. Lucia volcanics on a Sc-Th-La plot, although some samples trend upward, closer to the field defined by African dust and Mississippi loess. As with the Eu/Eu* versus La_N/Yb_N plot, this result can be interpreted in two ways: (1) derivation mostly from Dominica-St. Lucia volcanics, or (2) derivation from a mix of St. Vincent volcanics and African dust/Mississippi loess. Soils from the Florida Keys and Bahamas fall squarely on the field defined by African dust/Mississippi loess, indicating little or no influence from any volcanic source, which is consistent with the Eu/Eu* versus La_N/Yb_N data.

[45] Relative abundances of Sc-Th-Zr for soil parent materials and soils are consistent with Sc-Th-La data.

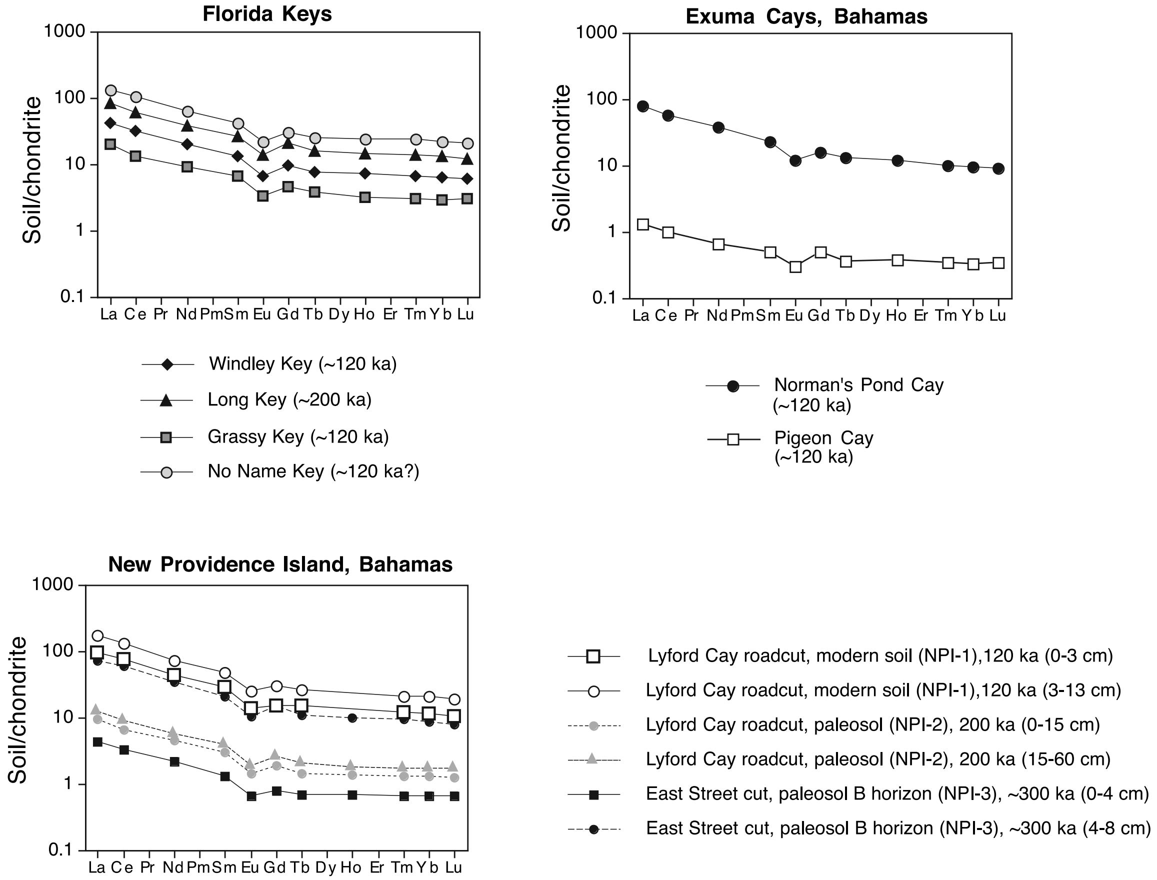


Figure 18. Chondrite-normalized REE plots of soils on the Florida Keys, New Providence Island, Bahamas, and two of the Exuma Cays, Bahamas.

Compositional fields for the two volcanic sources are easily distinguished from each other, and both are easily distinguished from African dust and Mississippi loess (Figure 21). African dust shows, however, a much larger compositional field, mainly a function of the range of Zr abundances. Concentrations of Zr vary with particle size; finer (<2 μm) fractions of dust have lower Zr contents than do coarser (20–10 μm) fractions. Barbados soils, as with the Sc-Th-La plot, show a compositional similarity to Dominica-St. Lucia volcanics. Again, two interpretations are possible: either sole derivation from this source, or a mix of St. Vincent volcanics and African dust or Mississippi loess. Soils from the Florida Keys and Bahamas again plot in the fields of African dust and Mississippi loess, and suggest little or no volcanic influence. However, in the Sc-Th-Zr plot, these soils are clustered only within the area where African dust and Mississippi loess overlap, suggesting little input from the coarser fractions of African dust.

[46] Because of the uncertainties in interpreting sources of Barbados soils using the ternary plots described above, we generated a third ternary plot, using Cr-Th-Nd. Relative abundances of Cr-Th-Nd show significant differences with the Sc-Th-La and Sc-Th-Zr plots (Figure 22). As with the other two plots, volcanic sources are distinguished from each other, but the low Th concentrations and high range of Cr variability are emphasized for St. Vincent. In addition, African dust and Mississippi loess show less overlap than for the other plots, primarily because of differences in Cr concentrations. Unlike the Sc-Th-La and Sc-Th-Zr plots, Barbados soils show no overlap with Dominica-St. Lucia volcanics with Cr-Th-Nd, but do fall between St. Vincent volcanics and African dust/Mississippi loess. Also unlike the previous plots, soils from the Florida Keys and Bahamas do not fall squarely on the fields of African dust and Mississippi loess. These soils fall partly on the field for African dust and appear to trend away from this field along a mixing line with some high-Cr source.

[47] Finally, we generated a bivariate plot of Ta/Th versus Sc/Th in order to discriminate African dust from Mississippi loess (Figure 23). The two source materials generate geochemical fields for Ta/Th versus Sc/Th with minimal overlap. Soils from Florida and the Bahamas, with one exception, fall between the two fields. In contrast, Barbados soils fall completely outside both fields, requiring input from a relatively high-Sc and high-Ta source.

6.8. Geochemical Modeling of Soil Parent Materials Using Multilinear Regression Analysis

[48] An alternative to the bivariate and ternary plots of immobile element ratios is to integrate a number of elements in a geochemical modeling approach. Utilizing several relatively immobile elements (Sc, Cr, Th, Ta, Zr, Hf, As, and Sb) and seven REE (La, Ce, Sm, Eu, Gd, Tb and Yb), we performed quantitative geochemical modeling to assess parent materials of the soils, using a least squares multi-

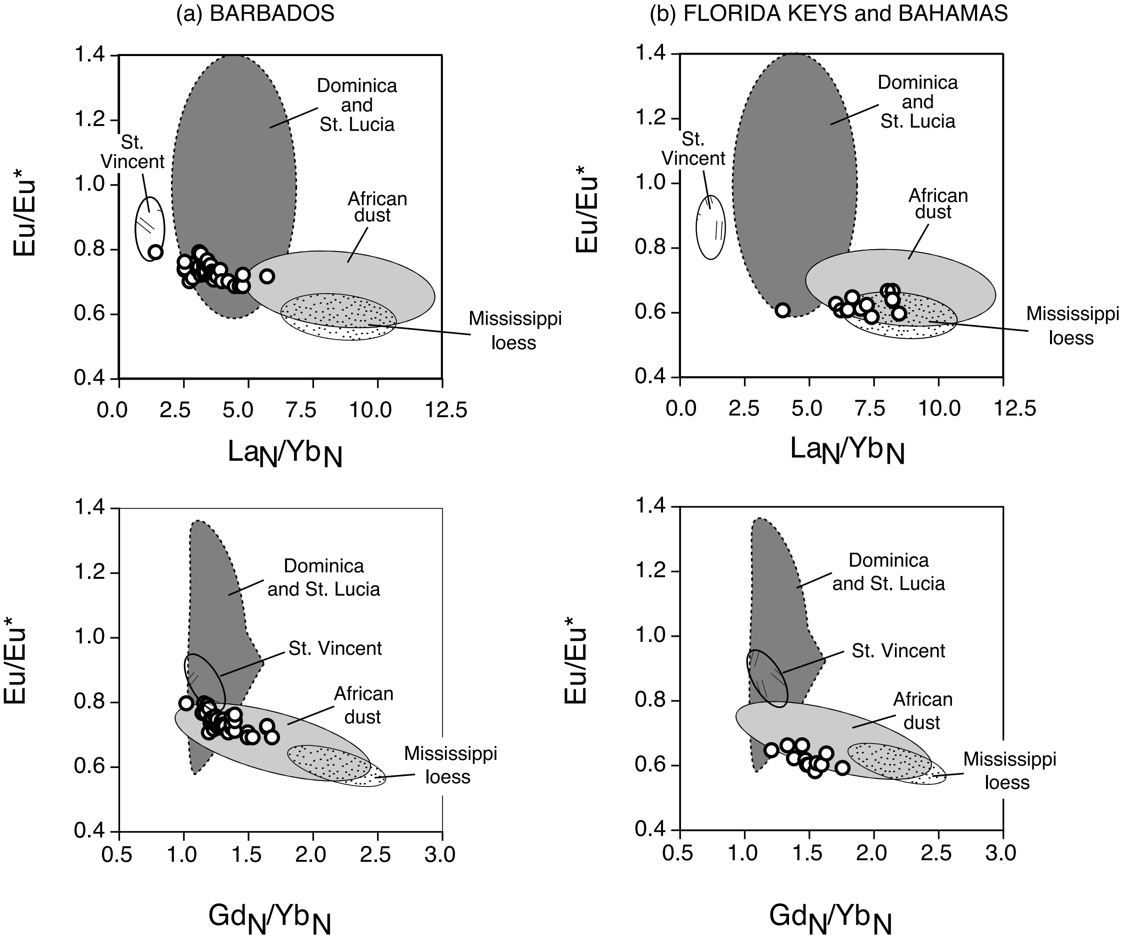


Figure 19. (top) Plots of Eu/Eu* versus La_N/Yb_N for island soils (shown as circles) and ranges of these values (shown as ellipses) for tephras from St. Vincent, Dominica, and St. Lucia, African dust, and lower Mississippi River Valley loess. (bottom) Plots of Eu/Eu* versus Gd_N/Yb_N for island soils (shown as circles) and ranges of these values (shown as ellipses or polygons) for tephras from St. Vincent, Dominica, and St. Lucia, African dust, and lower Mississippi River Valley loess.

linear regression analysis (MRA) approach described by *Budahn and Schmitt* [1985]. *Olivarez et al.* [1991] use a similar approach, utilizing many of the same elements, in ascertaining the sources of Pacific Ocean sediments. The method involves several steps, only summarized here, and the reader is referred to *Budahn and Schmitt* [1985] for details. The *Budahn and Schmitt* [1985] and *Olivarez et al.* [1991] methods yield similar results. We calculated source material contributions (upper continental crust versus oceanic crust) using the *Budahn and Schmitt* [1985] method for two samples (TT67476 and TT67477) studied by *Olivarez et al.* [1991]. Our results are in good agreement, within 5% of the results obtained by *Olivarez et al.* [1991].

[49] In the initial calculations, potential parent materials of the soils included the average compositions of the four African dust size fractions (0–2 μm, 2–5 μm, 5–10 μm, and 10–20 μm), St. Vincent volcanic materials, representative high-REE and low-REE tephras with negative Eu anomalies from Dominica and St. Lucia, and high-REE and low-REE loess from the Mississippi River valley. If large (>20%) negative contributions of a parent material are obtained in modeling, that component is removed in subsequent calculations. Ultimately, three end-members are able to account for the compositions of the soils: the average of all the fine-grained (<2 μm) fractions of African dust, a representative St. Vincent ignimbrite (S471-114, an ~4000-year-old Holocene ignimbrite), and a high-REE Mississippi River valley loess. The finest-grained (0–2 μm) component of African dust as a major contributor is reasonable, because this fraction accounts for a significant portion of the dust reaching the study area [*Prospero et al.*, 1970, 2001]. The ~4000-year-old ignimbrite has a composition that is very typical of both older and historic volcanic materials on St. Vincent Island [*Heath et al.*, 1998]. Finally, the high-REE Mississippi River valley loess is likely a high clay content loess, because REE in sediments generally have higher concentrations in the clay (<2 μm) fraction compared to the silt and sand fractions, although there are exceptions to this [*Cullers et al.*, 1979]. Interestingly, this approach suggests that ashes from Dominica and St. Lucia appear to have had little influence on the genesis of western Atlantic soils, even on Barbados, a point we discuss in more detail later.

[50] The MRA modeling requires calculation of potential source sediments in a carbonate-free soil. All of the Barbados soil profile 3B samples contain more than 12.5% Ca,

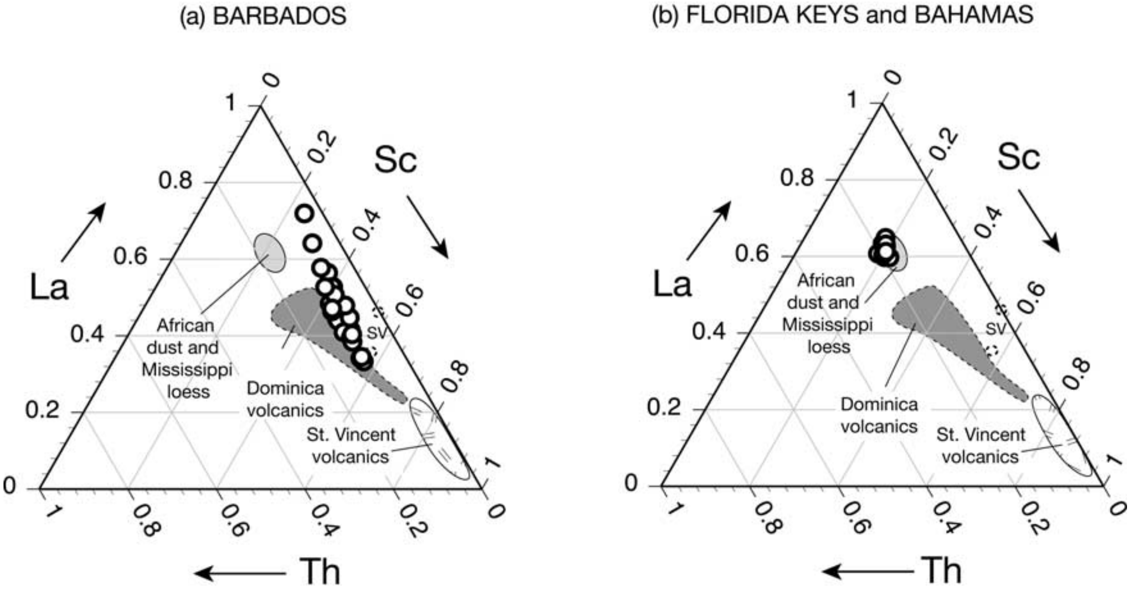


Figure 20. Ternary plots of relative abundances of Sc, Th, and La, showing fields defined by range of variability for various soil parent materials, and circles showing values for soils from (a) Barbados and (b) the Florida Keys and Bahamas. Data from St. Vincent are from this study and also *Turner et al.* [1996] and *Heath et al.* [1998].

which is strongly indicative of high carbonate contents, supported by carbonate data of *Muhs* [2001]. In order to model the samples from this soil profile, a carbonate-free composition was estimated by subtracting the carbonate contribution. A pure carbonate substrate was not sampled from Barbados, so we use the average composition of several Exuma Cays corals. For simplicity, it is assumed that all of the Ca in these soils is from the carbonate. The Barbados soil profile 3B used in modeling is the average of five estimated soil compositions taken from various depths. On the basis of the similarity in the MRA results between this composite sample and the other Barbados soils, this approach appears to be reasonable in obtaining a carbonate-free soil composition.

[51] Most of the Florida Keys, Exuma Cays, and New Providence Island soils have high carbonate content, containing >19% Ca. In fact, only one soil was modeled without any compositional adjustment. Although Ca abun-

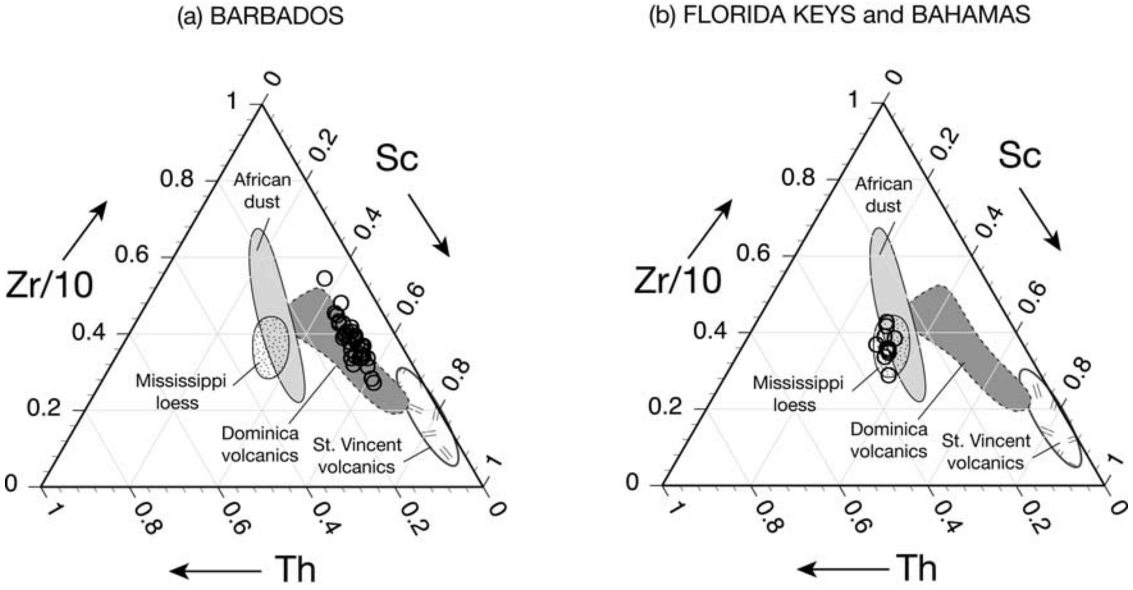


Figure 21. Ternary plots of relative abundances of Sc, Th, and Zr (divided by 10), showing fields defined by range of variability for various soil parent materials, and circles showing values for soils from (a) Barbados and (b) the Florida Keys and Bahamas. Data from St. Vincent are from this study and also *Turner et al.* [1996] and *Heath et al.* [1998].

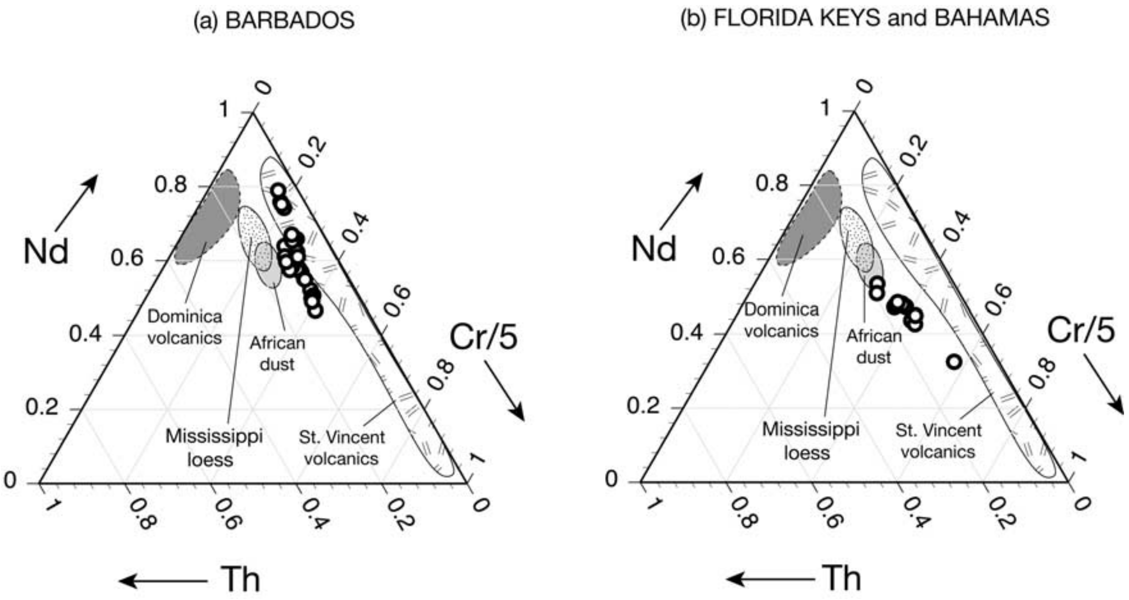


Figure 22. Ternary plots of relative abundances of Cr (divided by 5), Th, and Nd, showing fields defined by range of variability for various soil parent materials, and circles showing values for soils from (a) Barbados and (b) the Florida Keys and Bahamas. Data from St. Vincent are from this study and also *Turner et al.* [1996] and *Heath et al.* [1998]. Note that a single sample from Dominica falls within the range of African dust.

dances were not determined for one of the modern soils from New Providence Island (Lyford Cay, NPI-1, 3–13 cm depth), this sample appears be carbonate-free on the basis of its high Fe and trace element contents. Four samples have Ca contents <26% and carbonate-free compositions of these soils were estimated by subtracting the carbonate contribution following the method used for the Barbados 3B soil profile. The carbonate compositions used in these calculations were the average of several Florida Keys and Exuma Cays corals.

[52] We present the results of the MRA calculations for Barbados profile 3A (0–6 cm depth), because they are typical of model results for Barbados soil profiles 3A (at other depths), 3B, 4B and 6B (Figure 24). Figure 24 shows that modeled composition has a reasonable fit (±20%) to the observed composition for most elements, with the exception of Ta and As. In general, calculated Ta contents for the soils are about 50% higher than the observed contents, although in Barbados soil profile 4B, the calculated Ta values are about 80% lower. The sum of the components ranges from about 80% for profile 4B to 110% for profile 6B. In Figure 24, which shows normalized plots comparing the actual to calculated abundances of selected elements in the profile 3A (0–6 cm depth) sample, we note that REE, Zr and Hf contents are chondrite-normalized, whereas the other elements are arbitrarily multiplied by 10 (Th, As) or 100 (Sb) in order to fit the plot better.

[53] The MRA results from modeling the carbonate-free soil and the estimated soil compositions from the Florida Keys and Bahamas indicate that only two parent materials are needed to account for the composition of soils from these northerly islands: African dust and North American loess. Because most of the trace element contents in the carbonates are extremely low (see discussion above on

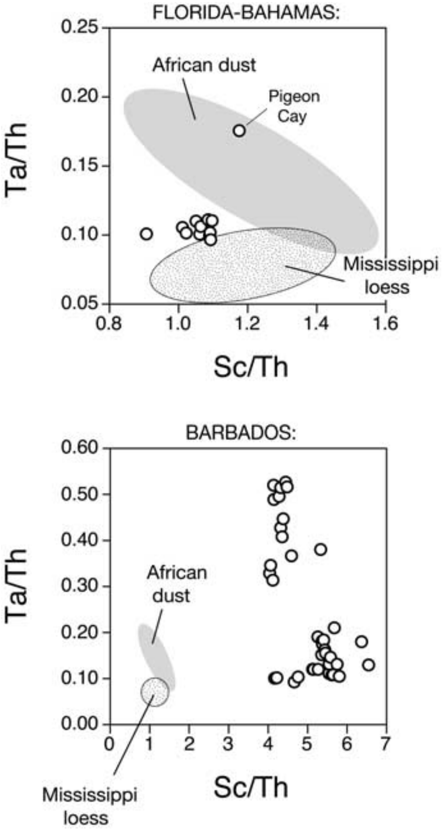


Figure 23. Bivariate plots of Ta/Th versus Sc/Th showing different compositions of African dust and Mississippi loess (ellipses) and compositions of (top) Florida-Bahamas soils and (bottom) Barbados soils. Note scale difference between Figures 23 (top) and 23 (bottom).

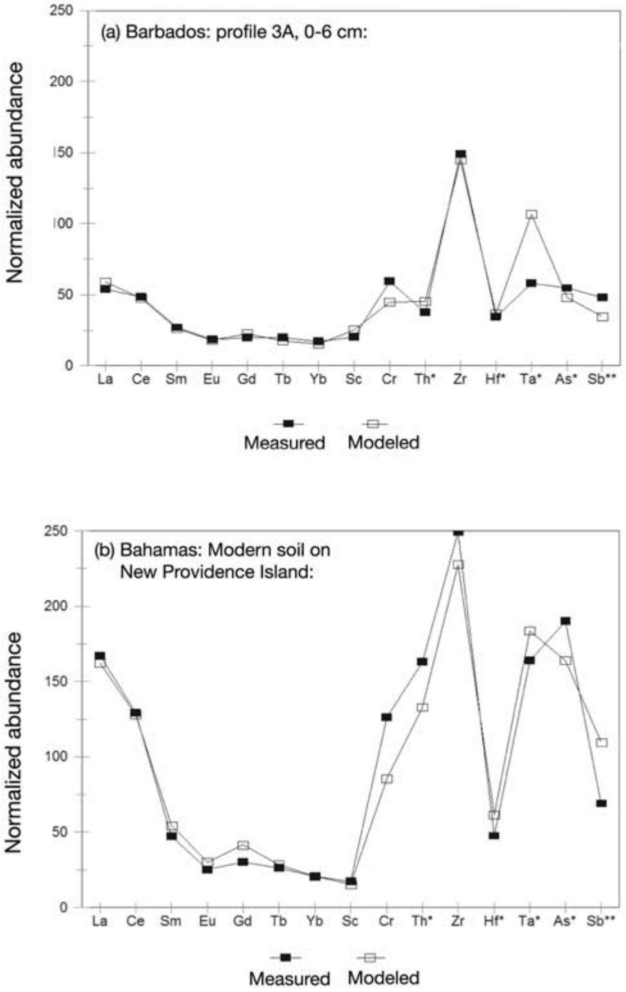


Figure 24. Plots comparing the measured and modeled abundances of REE and other immobile trace elements for two soils, (a) one from Barbados (uppermost horizon of profile 3A) and (b) one from New Providence Island, Bahamas (modern soil A horizon), demonstrating the good agreement between measured values and the MRA geochemically modeled values (see text for discussion).

composition of the reef carbonates), the addition of carbonate to the soil acts simply as dilution and thus has no appreciable effect on the relative abundances of other elements (analogous to the use of ternary plots above). Finally, the sums of the components in the estimated soil compositions are also near 100%, ranging from 90% to 120%, which further supports our method for estimating carbonate-free soils. The distinct trace element abundance patterns for the Barbados soil and the New Providence Island soil are striking in Figure 24.

[54] Using the approach described above, we also model the relative contributions of parent materials of selected soils from all localities (Figure 25). Using the carbonate-free horizons of three profiles, we model the source materials for three sample depths from profiles 3A and 4B and two sample depths of profile 6B on Barbados. Results show that the noncarbonate fractions of Barbados soils, at least on the lowest terraces, are derived from a mixture of $\sim$60–70% tephra from the island of St. Vincent, $\sim$25–40% African dust, and <10% loess from the Mississippi River valley. In contrast, soils on the Florida Keys are derived from a mixture of African dust ($\sim$60%) and Mississippi River valley loess ($\sim$40%). The same two parent materials dominate the soils of the Bahamas, although there are differences between islands. New Providence Island soils are $\sim$80% African dust and $\sim$20% Mississippi loess, whereas soils on the Exuma Cays are derived from about equal parts of the two source sediments (Figure 25).

7. Discussion

7.1. Reef Coral Residuum as a Soil Parent Material

[55] The new data on concentrations of REE and other trace elements in corals that occur commonly in Barbados reefs allow us to provide a rigorous test of the contribution of carbonate to REE in soils via residual accumulation after coral dissolution. *Acropora palmata*, *Acropora cervicornis*, and *Montastrea annularis* are the three most commonly occurring corals in the Pleistocene reefs of Barbados [*Mesolella*, 1967]. Concentrations of REE in all three coral species are very low and would require considerable reef dissolution to produce the observed concentrations of REE in Barbados soils. We did a quantitative estimate of the required dissolution for three REE, La, Nd, and Yb, using (1) the measured concentrations of La, Nd, and Yb in the soils and corals, (2) the amount of noncarbonate mineral material in a 1-cm^2 soil column in Barbados profile 3A (using carbonate content and bulk density data of *Muhs* [2001]), and (3) the measured porosity of Pleistocene corals on Barbados (reported by *Pittman* [1974]), along with the known density of coral aragonite (2.93 g cm^{-3}). Results of these calculations indicate that for the observed amount of La, Nd, and Yb in profile 3A, $\sim$309 m, $\sim$189 m, and $\sim$158 m, respectively, of carbonate dissolution would be required in $\sim$125 ka, the age of the host reef itself. This would require complete dissolution of the entire reef, plus dissolution to depths tens or hundreds of meters below sea level. This physical impossibility is analogous to *Birkeland*'s [1999] calculations for a residual origin for soils on Rota Island in the Marianas chain, requiring complete island dissolution. We conclude that reef dissolution plays, at most, a minor role in soil genesis on Barbados.

7.2. Origin of Soils on Barbados

[56] Barbados soils have the most variable REE patterns. In general, Barbados soils, with enriched light REE, negative Eu anomalies, and depleted heavy REE, resemble the patterns of both Mississippi River Valley loess and African dust. Nevertheless, complications arise with the presence of negative Ce anomalies in some Barbados soils (soil profiles 5B, 8A and 11) that are not present in either of the eolian parent materials. Within the study region, negative Ce anomalies have been reported in Lesser Antilles island arc rocks [*White and Patchett*, 1984; *White and Dupré*, 1986]. Thus it is possible that the negative Ce anomalies in the older Barbados soils reflect some influence from tephras that have negative Ce anomalies, although none of the tephras analyzed in the present study exhibit this pattern. Alternatively, negative Ce anomalies also have been reported in Atlantic Ocean corals, a reflection of small amounts of REE incorporation from seawater into the

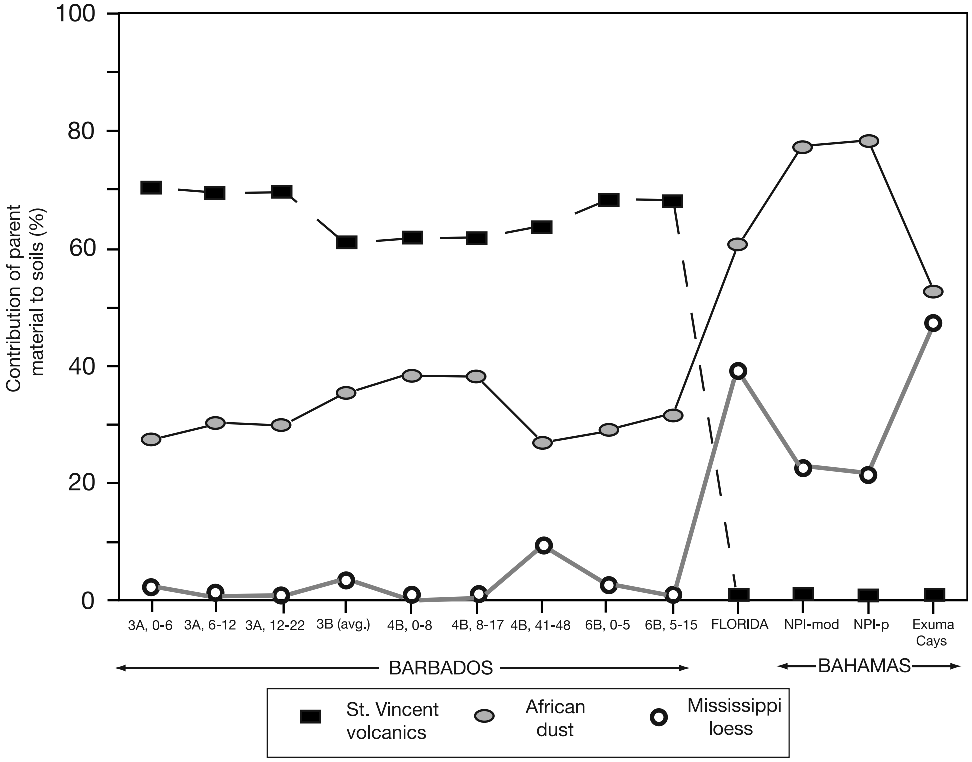


Figure 25. Plot showing the relative contributions of source sediments for soils on the Florida Keys, Bahamas, and Barbados using the MRA geochemical modeling approach. Note that St. Vincent volcanics contribute no significant mass to the soils of the Florida Keys and Bahamas and that tephras from Dominica and St. Lucia make no significant contribution to soils on any island.

aragonite structure [*Sholkovitz and Shen*, 1995]. However, as discussed above, all corals we analyzed show positive Ce anomalies and detrital coral fragments present in the soils would likely show this opposite effect. Furthermore, we found no correlation between negative Ce anomalies in the soils and carbonate content. *Nesbitt and Markovics* [1997] interpreted negative Ce anomalies in a weathering profile developed on granodiorite in Australia to be the result of an intermediate stage of chemical weathering. However, the process by which this takes place on Barbados is not clear and deserves further study.

[57] On the basis of all data, Barbados soils appear to have had a complex history of formation. The bivariate and ternary plots, considered as a whole, suggest that Barbados soils originated from more than one parent material. Barbados soils overlap African dust closely on one plot (Eu/Eu* versus Gd_N/Yb_N) and fall between African dust and St. Vincent volcanics on another plot (Cr-Th-Nd). On still other plots (Eu/Eu* versus La_N/Yb_N, Sc-Th-La, and Sc-Th-Zr), Barbados soils can be interpreted to have been derived either solely from Dominica-St. Lucia tephras *or* from a mix of African dust and St. Vincent tephras. One problem with the interpretation of derivation from Dominica-St. Lucia tephras is that Barbados soils, on the Eu/Eu* versus La_N/Yb_N plot, overlap only a small part of the field defined by Dominica-St. Lucia tephras. If these tephras were the main source of Barbados soils, we would expect to see the extreme variability in Eu/Eu* values characteristic of tephras in that island arc. The interpretation that is consistent with all plots is derivation from a mix of St. Vincent volcanic materials and African dust. In an independent calculation, the MRA geochemical model (integrating all immobile elements) indicates that Barbados soils are derived from a combination of St. Vincent volcanic sources (60–70%), African dust (25–40%), and possibly a minor (<10%) contribution from distal Mississippi valley loess (Figure 25). These results are consistent with the more subjective interpretation of the bivariate and ternary plots and are also consistent with the isotopic data of *Borg and Banner* [1996].

[58] Barbados lies directly along the dominant atmospheric transport trajectories for moderate to large explosive eruptions from Soufrière volcano on St. Vincent, based on historic eruptions in 1902 and 1979 [*Carey and Sigurdsson*, 1978; *Sigurdsson*, 1982]. During much of the Pleistocene, St. Vincent has been quite active volcanically [*Briden et al.*, 1979]. Thus Barbados may have received small but frequent amounts of tephra from St. Vincent over much of the Pleistocene. Because of dispersion by bioturbation, many of these eruptions are unlikely to have formed discrete tephra layers in deep-sea sediments. In contrast, eruptions from the more silicic volcanic centers such as Dominica and St. Lucia are larger and show up as layers in cores (Figure 7), but these eruptions may be far less frequent. Furthermore, Barbados appears to lie at the southern margin of the dispersal plumes from these centers (Figure 6).

7.3. Origin of Soils on the Florida Keys and Bahamas

[59] Soils on the Florida Keys and the Bahamas have enriched light REE, negative Eu anomalies, and depleted

heavy REE. This pattern suggests derivation solely or at least mostly from either or both Mississippi valley loess or African dust. If there was any volcanic influence on these soils, it has been overwhelmed by the inputs of dust. The bivariate plots (Eu/Eu*, La_N/Yb_N, Gd_N/Yb_N) do not indicate any significant volcanic influence and fall mostly within the fields defined by African dust, although the Eu/Eu* versus La_N/Yb_N plot would permit some Mississippi valley loess influence. The Sc-Th-La and Sc-Th-Zr plots also indicate no volcanic influence and would permit an interpretation of either African dust or Mississippi loess (or some mix of the two) as parent materials. The Ta/Th versus Sc/Th plot supports an interpretation of both African dust and Mississippi loess as parent materials for Florida-Bahamas soils. Interestingly, the Cr-Th-Nd plot falls mostly outside of the African dust field and completely outside of all other fields defined by the other possible parent materials. The trend shown by the samples is toward the Cr pole, suggesting the influence of a high-Cr parent material. This trend is unexplained and needs more study.

[60] The MRA geochemical modeling supports an interpretation of Florida-Bahamas soils being derived from a mix of African dust and Mississippi loess. The modeling suggests that soils on the Florida Keys and New Providence Island, Bahamas are derived dominantly (60–80%) from African dust, with some contribution (20–40%) from Mississippi River valley loess. Soils on the Exuma Cays, though farther south, seem to be derived from about equal parts African dust and Mississippi River valley loess. We have no explanation for this unexpected result and suggest that more work on soils of the southern Bahamas is required.

[61] Because the Florida Keys and Bahamas are situated well to the north of the Lesser Antilles island arc, it is not surprising that these carbonate islands record no volcanic influence. The Florida Keys and Bahamas are, however, well within the zone of the easterly trade winds that carry African dust to the region (Figure 1) [*Prospero*, 1999]. Studies at an inland site in Florida show that substantial concentrations of aerosol occur only when African dust is present over the region [*Prospero et al.*, 2001]; other sources, including local soils or sediments, are not significant contributors. A 2-year study of precipitation deposition carried out at nine stations across the length of Florida, from the Florida Keys to the panhandle, shows that by far the greatest deposition of dust occurs during the summer when African dust was present [*Landing et al.*, 1995]. Over a 2-year period, the mean deposition rate of Al was 9.1 $\mu g/cm^2/yr$. On the basis of the average crustal abundance of Al ($\sim$8%), this is equivalent to an overall dust deposition rate of 114 $\mu g/cm^2/yr$. The results of the *Landing et al.* [1995] study are essentially identical to a 1-year study carried out at a coastal site in Miami [*Prospero et al.*, 1987] that yields an Al deposition rate of 10.1 $\mu g/cm^2/yr$ (overall dust deposition rate of 126 $\mu g/cm^2/yr$). Although the age estimates of $\sim$125 ka for the Key Largo Limestone substrate might allow us to calculate a long-term dust deposition rate to compare to the measured modern rates, it would be misleading to do so. As discussed earlier, soils on the Florida Keys are very thin, likely due to erosion by tropical storms and hurricanes for thousands of years. Thus any calculated long-term dust fall rate based on eroded soils is likely to be an underestimate.

8. Summary and Conclusions

[62] Soils on carbonate-rock-dominated islands of the western Atlantic Ocean (Barbados, the Florida Keys, and the Bahamas) are rich in clays. Many of the Quaternary limestones on these islands are of exceptionally high purity and it is unlikely that the soils are derived solely or even mostly from insoluble residues of the local carbonate substrate. Measurement of REE and other trace elements in representative, unrecrystallized corals indicates that these components have very low concentrations. If residual accumulation were the main mode of soil genesis, improbably large amounts of carbonate dissolution would be required to explain the observed soils. Furthermore, geomorphic considerations eliminate other local, noncarbonate bedrock sources, such as Tertiary sedimentary rocks from the Scotland District on Barbados. Thus soils on Quaternary limestones are most likely derived from sources external to the islands, such as tephras from the Lesser Antilles island arc, the fine-grained, distal component of loess from mid-continental North America, or the fine-grained, distal component of dust from Africa.

[63] These three external soil parent materials can be differentiated using REE and other relatively immobile trace elements. Tephras from the Lesser Antilles island arc (St. Vincent, Dominica, and St. Lucia) vary in composition, both in the REE and other immobile trace elements (Sc, Cr, Th, Zr). These observations are consistent with previous studies and indicate that volcanic materials in this island arc system have a wide range of mixed oceanic and continental crustal components. In contrast, African dust and the fine-grained (<20 μm) component of lower Mississippi River Valley loess have a narrow range of compositions, all characterized by enriched light REE, negative Eu anomalies, and depleted heavy REE, a pattern that is typical for loesses found on other continents and upper continental crust in general.

[64] Soils on Barbados have complex REE patterns, depending on age, but all have enriched light REE, negative Eu anomalies and depleted heavy REE. Consideration of the REE plots, bivariate and ternary plots of immobile elements, and geochemical modeling suggests that Barbados soils have developed mostly from volcanic ash from nearby St. Vincent and secondarily, but significantly, from African dust. A possible minor contribution from distal Mississippi valley loess is apparent in the geochemical modeling results.

[65] Soils on the Florida Keys and islands of the Bahamas also have enriched light REE, negative Eu anomalies and depleted heavy REE. Furthermore, these soils have Eu/Eu*, La_N/Yb_N, Gd_N/Yb_N, Sc-Th-La, and Sc-Th-Zr that agree closely with the ranges of African dust and/or Mississippi loess values. Soils on these northerly islands have Ta/Th and Sc/Th that fall between African dust and Mississippi loess. We interpret these data to indicate that neither volcanic ash nor carbonate residue has been an important parent material in the genesis of these soils. Geochemical modeling indicates that soils on the Florida Keys and Bahamas have developed mostly from African dust, but with a significant component of distal Mississippi valley

loess. This interpretation supports the recent modeling results of *Mahowald et al.* [2006], who suggest that the distal component of North American loess may have had long-range transport during the last glacial period, well beyond the continental boundaries. Nevertheless, the modeling results of *Mahowald et al.* [2006] also indicate that during the last glacial period, southern Florida and the Bahamas were situated in a transitional latitudinal zone where they could have received *both* African dust and North American loess.

[66] Our studies indicate that LRT dust from Africa has been a dominant parent material for soils in the Florida Keys and Bahamas and an important source for Barbados soils. We also document here the possibility that distal Mississippi valley loess may have been transported much farther from its source than previously supposed. Furthermore, because of the constraints given by the ages of the underlying reef limestones on Barbados, our results indicate that African dust (and North American loess?) may have been important soil parent materials for much of the past ~700 ka. In light of our current knowledge of present-day African dust transport, it is reasonable to conclude that African dust has a substantial impact on soil formation over a wide latitudinal range in the Caribbean Sea-western Atlantic Ocean region. Many subtropical and tropical soils, which otherwise might lack essential plant nutrients, could be fertilized yearly by inputs of nutrient-rich particles from this distant source. Clay minerals in African dust [*Glaccum and Prospero*, 1980] and distal Mississippi valley loess, with their high cation exchange capacities, increase the nutrient-holding abilities of these soils. We hypothesize that other localities in the region may have been similarly affected. Soils on other Caribbean islands, northern South America [*Swap et al.*, 1992], Central America, Mexico, Bermuda [*Herwitz et al.*, 1996] and perhaps much of the southeastern United States [*Syers et al.*, 1969; *Perry et al.*, 1997] have probably been influenced to some extent by inputs of African dust, and to a lesser extent, by inputs of Mississippi valley loess. Although we cannot say just how widely African dust has influenced soil development across this region, the results presented here suggest that LRT eolian inputs may have greater significance for pedogenesis than previously thought.

[67] **Acknowledgments.** D. Muhs and J. Budahn's work in this study was supported by the Earth Surface Dynamics Program of the U.S. Geological Survey and is a contribution to the "Eolian History of North America" project. J. M. Prospero's and S. Carey's work is supported by the National Science Foundation. We thank Tracy Rowland and Chuck Bush for assistance in the field, Jossh Beann for laboratory work, and the Bellairs Research Station of McGill University for logistical support while conducting field work on Barbados. Our thanks also go to Marith Reheis, Rich Reynolds, Jimin Sun, Suzanne Anderson, and a critical but very helpful anonymous reviewer for very useful reviews on an earlier version of the paper.

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