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Neodymium and strontium isotopic constraints on soil sources in Barbados, West Indies

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Abstract—Neodymium and strontium isotopic compositions and Sm/Nd ratios are used to constrain the sources of silicate-rich soils developed on uplifted Pleistocene coral-reef limestones on Barbados, West Indies. The geographic and geologic setting of Barbados facilitates the application of these tracers to the evaluation of the following soil sources: (1) Pleistocene reef limestone regolith, (2) Tertiary carbonate rocks, sandstones, and mudstones that are exposed in northeastern Barbados, (3) volcanic ash erupted from the Lesser Antilles arc, (4) Saharan dust transported by trade winds, and (5) fertilizer. The soils have ϵ_{Nd} values that range from −6.6 to −1.9, $^{87}Sr/^{86}Sr$ values of 0.70890 to 0.71067, and Sm/Nd ratios of 0.223–0.260. The Pleistocene limestone component is the most significant source of Sr in the soils and a negligible source of Nd. Comparison of Sm and Nd concentrations and neodymium isotopic compositions of soil samples that are weathered to varying extents indicates that Sm and Nd are relatively unfractionated and retained in the soils during weathering. ϵ_{Nd} and Sm/Nd variations in the soils, therefore, primarily reflect the compositions and proportions of the silicate sources. Mass balance calculations based on Sm-Nd systematics require that the silicate soil components contain between 30–85% volcanic ash, with the remaining silicate fraction comprised of old, continentally-derived sediment. In contrast to Sm and Nd, Sr is mobilized and removed from the soils during weathering. Strontium from volcanic and carbonate sources is preferentially removed relative to continental silicate sources. The strontium isotopic compositions of the soils, therefore, reflect the combined effects of the degree of weathering and the compositions and proportions of the soil sources. Mass balance calculations indicate that at least 35–60% of the initial Sr in the soils has been removed by weathering. These results illustrate (1) the utility of radiogenic isotopes in identifying and quantifying soil sources and weathering processes, (2) the compositional influence of numerous sources on soils, even those developed in a relatively isolated area such as Barbados, and (3) the domination of Barbados soil Sm-Nd systematics by nonregolith eolian components.

1. INTRODUCTION

Quantification of soil sources provides fundamental information for studies of weathering rates, groundwater geochemistry, and cation/nutrient cycling in ecosystems (e.g., Miller et al., 1993). The variable solubility and mobility of cations in the soil environment, however, has made constraining the components from which soils and paleosols are derived problematic. Many geochemical studies of soils have focused on the effects that weathering has on the concentrations of elements derived presumably from a single igneous or metamorphic regolith source (e.g., Nesbitt, 1979; Middelburg et al., 1988; Marsh, 1991). In most geologic settings, however, there are numerous potential sources that contribute to soils via fluvial and eolian transport mechanisms (e.g., Brimhall et al., 1988). Unfortunately, the geochemical compositions of these sources is often poorly constrained making their contribution to soil chemistry difficult to ascertain. In this study we use radiogenic isotopes to identify and quantify nonregolith soil components from Barbados, West Indies.

Barbados is an excellent locality to evaluate the contribution of wind transported soil components, such as atmospheric dust and volcanic ash, because of its geographic isolation from many

continental sources and the lack of fluvial systems in the island's Pleistocene section. In addition, the development of soils on relatively pure limestone regolith (Fig. 1) facilitates the identification of nonregolith eolian components. Previous workers have identified potential endmember soil sources using petrography and trace-element geochemistry. These studies suggest that the soils are mixtures of atmospheric components dominated by Saharan dust with smaller amounts of Lesser Antilles volcanic ash, and underlying Pleistocene limestone and Tertiary siliciclastic components (Muhs et al., 1987, 1990). We use neodymium and strontium isotopic compositions and Sm-Nd concentrations of soils and potential soil sources, along with mass balance modeling, to quantify both weathering processes and soil sources. The results demonstrate the numerous components (i.e., regolith, three local eolian, and two far-traveled atmospheric sources) that can contribute to soils in even a relatively isolated area such as Barbados. The results also underscore the potential for neodymium and strontium isotopes to constrain the origin of soils and paleosols, and therefore the sources and cycling of elements in ecosystems and groundwaters from more complex continental settings.

2. GEOLOGIC SETTING

The island of Barbados is built upon a portion of the uplifted Lesser Antilles accretionary prism (Fig. 1; Speed and Larue, 1982; Torrini et al., 1985). Barbados is composed of a lower section of

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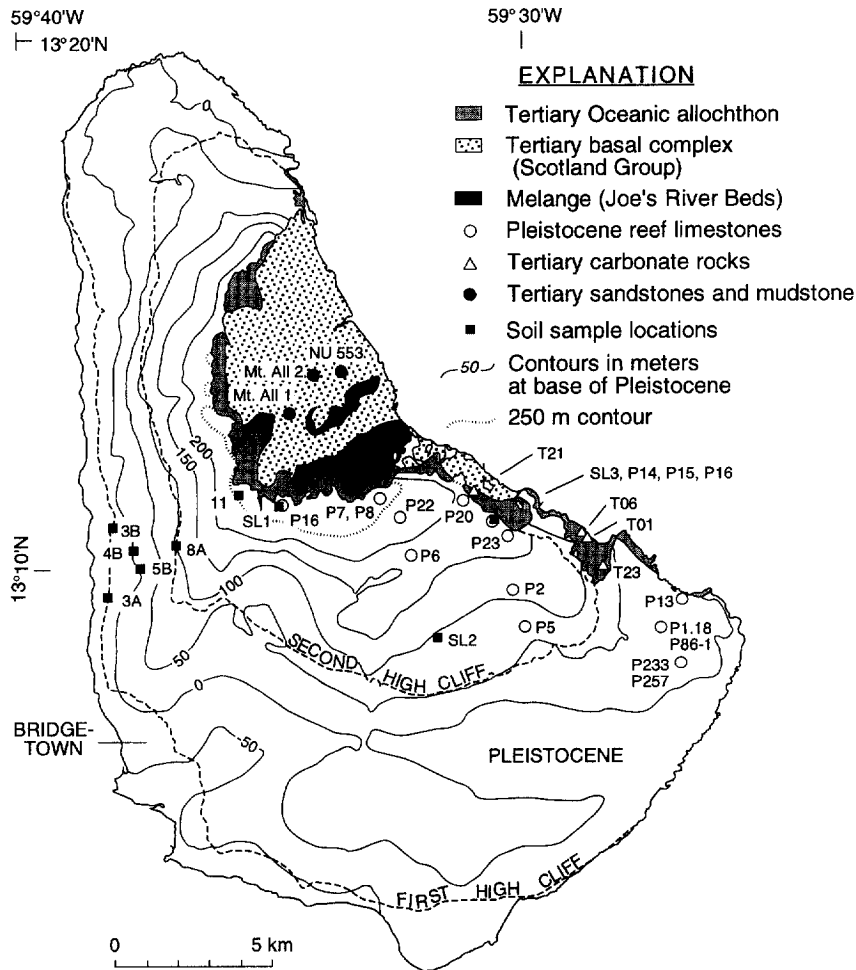
Fig. 1. Simplified geologic map of Barbados illustrating distribution of Pleistocene reef limestones, Oceanic allochthon, Tertiary basal complex, and melange (after Poole and Barker, 1983). Locations of soil samples, Pleistocene reef carbonates, Tertiary carbonate rocks, and siliciclastic rocks from Muhs et al. (1987; soils 3A through 11) and Banner et al. (1994; soils SL1 through SL3). Coral reef terraces between coast and First High Cliff range in age from 0–105 ka; terraces between First and Second High Cliff range from 117–490 ka; terraces above Second High Cliff and 150 m contour (~200 m elevation at top of Coral Cap) range from 440–640 ka (Mesolella et al., 1969; Bender et al., 1979; Banner et al., 1991; Gallup et al., 1994). Near-pervasive alteration of marine aragonite and high-Mg calcite has precluded radiometric age determinations for terraces older than 640 ka. Strontium isotope values for these undated terraces indicate that they are <2 Ma old (Banner et al., 1994).

Tertiary pelagic and hemipelagic rocks that are capped by Pleistocene reef limestones (Fig. 1). The Tertiary rocks are quartzose turbidites interpreted to be derived from South America (Senn, 1940; Speed, 1981), Eocene to Miocene biogenic calcareous pelagic marlstones and chalks, and volcanogenic rocks (Larue and Speed, 1984; Torrini et al., 1985). Coral reefs growing on the Tertiary rocks are uplifted as the island is raised, forming a series of terraces. Coral mineral compositions grade from predominantly aragonite in topographically low coastal areas to low-Mg calcite in higher central regions of the island (Matthews, 1968). Uranium-series dating of the Pleistocene limestones demonstrates that the coral-reef terraces become progressively older toward the central, elevated part of the island (Fig. 1). Ages of coral-reef terraces place maximum age estimates on overlying soils (Muhs et al., 1987, 1990).

3. ANALYTICAL METHODS

Major and trace element analyses of soils and some soil sources were determined by XRF and are presented in Muhs et al. (1987, 1990, and unpubl. data). Large and variable loss on ignition (LOI) of major-

element XRF analyses required compositions be normalized to 100% for comparison. Major and trace element analyses of Tertiary soil sources were determined by ICP-AES at the University of Texas.

The Sm and Nd concentrations and strontium and neodymium isotopic compositions of soils and soil sources were determined using a multi-collector Finnigan MAT 261 mass spectrometer at the University of Texas. Samples were completely digested in a combination of HNO_3, HCl, and HF, and Sr, Sm, and Nd were separated using cation exchange columns. Unless otherwise indicated, all soil analyses reported and discussed in this paper refer to this complete digestion procedure. Strontium and neodymium isotopic ratios were corrected for mass fractionation using $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$, respectively, and an exponential law. $\epsilon_{Nd}(0) = (^{143}Nd/^{144}Nd_{measured}/^{143}Nd/^{144}Nd_{CHUR}-1)*10000$, where $^{143}Nd/^{144}Nd_{CHUR} = 0.512638$. Sixteen measurements of NBS-987 Sr standard (±2 sigma) completed during the investigation averaged 0.710247 ± 20. Fourteen measurements of Caltech nNd Beta standard averaged $\epsilon_{Nd} = -14.45 ± 0.24$. The uncertainties of $^{87}Sr/^{86}Sr$ and ϵ_{Nd} based on replicate soil and standard analyses is estimated to be ±0.00002 and ±0.3, respectively. Strontium and

neodymium blanks range from 28–55 and 20–30 pg, respectively. Neodymium and samarium concentrations were determined by isotope dilution with a reproducibility of ±1%.

4. RESULTS

The geographic isolation of Barbados limits the potential sources that contribute to the soils. We have examined the mineralogical and chemical compositions of soils and potential soil sources in order to constrain the role of these sources in soil genesis. These results are presented below.

4.1. Mineralogic and Chemical Composition of Soils

The soil samples analyzed in this study were collected and analyzed for mineral composition and major and trace elements by Muhs et al. (1987, 1990). Sampling was confined to topographically high reef crests that appear not to have been cultivated (Muhs et al., 1987). The soils are composed of carbonate and silicate minerals (kaolinite-smectite clays, quartz, plagioclase, and pyroxene sand and

silt), oxides, organic matter, sea spray salts, and possibly fertilizer (Harris, 1971; James, 1972; Muhs et al., 1987, 1990). The abundance of calcium carbonate is highly variable, making up between 0.4 and 64 wt% of the soils studied (Table 1). Carbonate components of the soils are typically recrystallized (James, 1972). In contrast, the amount of organic matter is approximately constant, comprising 1–5% of the soils studied by Muhs et al. (1987). Detailed studies of two Barbados soil profiles (3A and 4B), show that the soils are composed primarily of clay (40–94%), sand (4–60%), and silt-sized particles (0.4–14%; Muhs et al., 1987).

The soils have highly variable major and trace-element compositions (Muhs et al., 1987, 1990). Major element contents of the soils range from 21–76 wt% SiO_2, 4–38 wt% Al_2O_3, and 0.1–1.6 wt% TiO_2. Trace-element concentrations are equally variable with Y ranging from 2–173 ppm, Nd from 5.7–82 ppm, and Sm from 1.3–18 ppm. The total concentration ranges for Al_2O_3, TiO_2, rare earth elements (REE), and Y (if the two lowest analyses are excluded) are

Table 1. Major and trace element and isotopic data for Barbados soils and soil sources.

Sample			Terrace age (ka)	Si/Al	CaCO₃ wt.%	Sr ppm	Nd ppm	Sm ppm	Sm/Nd	$^{87}Sr/^{86}Sr$	ε_{Nd}
Soils											
Profile	**Depth (cm)**	**Horizon**									
3A	0-6	A1	117	2.77	5.79	220	16.9	4.10	0.243	0.709143	-1.9
3B	24-66	Bt1	117	5.29	46.1	---	16.8	3.85	0.229	0.709161	-5.1
5B	0-21a	A	220	2.71	0.83	---	35.3	8.48	0.241	0.708909	-2.5
5B	0-21b						35.1	8.44	0.241	0.708898	
5B	0-21c									0.708914	
5B	21-29	BA	220	2.33	1.26	---	47.8	11.7	0.244	0.709098	-2.4
8A	0-13	A	460	1.34	0.39	---	42.5	9.87	0.232	0.709067	-3.5
8A	39-52	Bt		1.20	2.62	---	19.1	4.97	0.260	0.709775	-5.6
11	23-32	Bt2	~700	1.05	1.26	---	81.9	18.3	0.223	0.709814	-5.5
4B	0-8	A	190	4.66	5.21	137	14.0	3.34	0.239	0.709336	-4.5
4B	8-17	A		5.09	5.53	144				0.709256	-4.3
4B	17-26	A		5.34	6.26	141	40.7	9.70	0.238	0.709400	-4.7
4B	26-35a	A		5.27	3.70	110	13.9	3.27	0.236	0.709581	-4.9
4B	26-35b									0.709567	
4B	35-41a	Bw1		4.43	1.70	64	13.4	3.22	0.240	0.710672	-5.4
4B	35-41b						13.6	3.28	0.240	0.710497	
4B	41-48a	Bw1		4.63	11.9	143	43.3	10.0	0.232	0.709771	-5.2
4B	41-48b									0.709769	
4B	48-54a	Bw2		4.64	53.6	729	9.51	2.18	0.229	0.709222	-6.1
4B	48-54b									0.709261	
4B	54-60	Bw2		5.04	63.5	886	5.73	1.32	0.231	0.709171	-6.6
Soil Sources											
Pleistocene reef limestone (P2)						2100	0.054	0.011	0.210	0.709136	
Pleistocene reef limestone (P16)						301				0.709114	
Tertiary carbonate rock (T06a)							14.9	2.98	0.200	0.708219	-8.5
Tertiary carbonate rock (T06b)										0.708214	-8.5
Tertiary carbonate rock (T06-HCl)						1420				0.707767	
Tertiary sandstone (Mt. All 1)				40.9		17	6.50	1.20	0.185	0.731110	-15.5
Tertiary sandstone (Mt. All 2)				10.9		61					
Tertiary mudstone (NU 553)				2.89		131	42.7	8.18	0.192	0.717882	-10.6
Average Saharan dust				3.26		286	42.6	8.3	0.195	0.715742	-12.7
St. Vincent ignimbrite (471-2)				2.61		185	7.60	2.61	0.343	0.704092	6.3
St. Vincent ignimbrite (471-114)				2.56		214	11.0	3.22	0.292	0.704378	5.5
Phosphate fertilizer						520	36.8	7.85	0.213	0.708894	-7.5
Potassium fertilizer						18	0.19	0.035	0.184	0.740236	
Nitrogen fertilizer						0.11	0.0017	0.0004	0.210	0.709461	
Modern seawater						8				0.709174	

a, b, and c denote replicate analyses on sample powders. Composition of Saharan dust is average of values in Biscaye et al. (1974), Muhs et al. (1987), and Grousset et al. (1988, 1992). Si/Al values for St. Vincent ignimbrites from Muhs et al. (1987). Sr concentrations of P2, P16, T06-HCl (a 2.5N HCl leachate), and fertilizers, and $^{87}Sr/^{86}Sr$ of P2, P16, and T06-HCl from Banner et al. (1994). Sr isotopic data from Banner et al. (1994) adjusted to our measured value of NBS-987 Sr standard. Terrace ages from references in Fig. 1.

all between a factor of 10 and 16, suggesting that these elements behave similarly in the soil environment on Barbados. Note that REE (and Y) abundances in some soils are more than double the values observed in typical continental shales (e.g., Nd = 33 ppm, Sm = 5.7, and Y = 27 in North American shale composite; Gromet et al., 1984), suggesting that the REE are concentrated within the soils. The strontium isotopic compositions of the soils (0.70891–0.71059) are similar to or slightly more radiogenic than those of Pleistocene limestones on Barbados (Table 1). The ϵ_{Nd} values (−6.6 to −1.9) and Sm/Nd ratios (0.223–0.260) of the soils are intermediate between (1) old continental siliciclastics observed on the island and in Saharan dust, and (2) volcanic ash from the Lesser Antilles arc (Fig. 2a, b; Table 1). Abundances of rare earth elements in many of the soils, however, are higher than binary mixtures of old continental and young volcanic sources (Fig. 2b), again suggesting the REE are concentrated in the soils.

4.2. Potential Soil Sources

Potential sources of the soils' components include: Pleistocene reef limestones, sea spray salts, Tertiary pelagic carbonate rocks, continentally-derived Tertiary siliciclastics from the basal complex, volcanic ash from the Lesser Antilles arc, dust transported from the Sahara desert by trade winds, and fertilizers. We use major and trace-element concentrations and strontium and neodymium isotopic compositions to evaluate the contribution of these sources to the soils.

4.2.1. Reef limestones

Pleistocene reef limestones are relatively pure carbonate rocks composed of aragonite, calcite, and dolomite. The limestones have high Sr and very low REE concentrations, and $^{87}Sr/^{86}Sr$ and Sm/Nd ratios that are similar to modern Atlantic seawater (Fig. 2a, b; Table 1). Schmedeman (1948, 1950), Ahmad and Jones (1969a,b), and Scholten and Andriesse (1986) among others have proposed that the siliciclastic component in the soils is derived from accumulation of insoluble residue during chemical weathering of reef limestones. Muhs et al. (1987), however, argue that generation of the soils by carbonate dissolution is not possible given the relatively pure nature of the limestones and the preservation of original reef morphology in marine terraces on the island. This conclusion is supported by very high REE concentrations in the soils (e.g., 6–82 ppm Nd) relative to Pleistocene reef limestones from Barbados (54 ppb Nd, Table 1) and modern corals (2–5 ppb; Sholkovitz and Shen, 1995). In order to produce the Nd concentrations observed in the soils through dissolution of reef limestones with 54 ppb Nd, dissolution of approximately 1 kilogram of limestone for every gram of soil is required. This mechanism for soil development is clearly not feasible, because observed soil thicknesses of up to 1 m would require unreasonably large amounts of limestone dissolution. High $CaCO_3$ contents in a few of the soils, however, is indicative of a relatively large contribution of carbonate. High Sr and low REE concentrations in the reef limestones (Table 1; Banner et al., 1994),
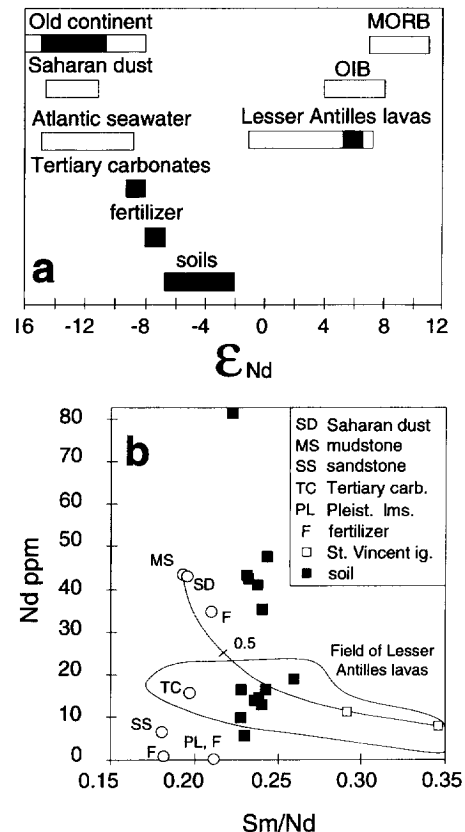

FIG. 2. (a and b) REE systematics of Barbados soils and potential soil components. Note that Barbados soils have ϵ_{Nd} and Sm/Nd that are intermediate between old continental sources with low ϵ_{Nd} and Sm/Nd and young mantle-like sources with high ϵ_{Nd} and Sm/Nd. Volcanic rocks from the Lesser Antilles are the only proposed silicate source with radiogenic ϵ_{Nd} and high Sm/Nd, and must, therefore, be a significant component in the soils. (a) ϵ_{Nd} values of Barbados soils and potential soil sources. Open bars represent ranges taken from the literature, and solid bars are ranges measured in this study. Data for MORB from White et al. (1987) and Hegner and Tatsumoto (1987); Hawaiian OIB from Tatsumoto et al. (1987), Lesser Antilles arc lavas (open) from White and Dupre (1986) and Davidson (1986) and this study (solid), Atlantic seawater values summarized by Shaw and Wasserburg (1985), and Saharan dust from Groussett et al. (1988, 1992). Old continent range (open) from Faure (1986) and from Tertiary sandstone and mudstone (solid, this study). (b) Sm/Nd vs. Nd concentrations of Barbados soils and potential soil sources. SD symbol denotes average Saharan dust value from Groussett et al. (1988, 1992), MS is mudstone from Tertiary basal complex NU 553, SS is sandstone from Tertiary basal complex Mt. All 1, TC is Tertiary carbonate rock from Oceanic allochthon T06, PL is Pleistocene reef limestone P2, F is K- and P-based fertilizers, and St. Vincent ignimbrites are samples 472-2 and 472-114 (see Table 1 and Fig. 1). Note the wide range of Nd concentrations and narrow, intermediate Sm/Nd ratios of the soils. Curve represents binary mixture between volcanic ash and Tertiary mudstones. A 50:50 mixture of mudstone and volcanic ash (St. Vincent ignimbrite) marked by 0.5 on mixing line. Most soils fall above the mixing line indicating that REE are concentrated in the soils relative to their sources. Soils that fall below the mixing line can be accounted for by the addition of one of the low REE sources shown (e.g., SS, PL, TC, F).

indicate that the presence of this component in the soils will potentially dominate the soils' $^{87}Sr/^{86}Sr$ values, but have little effect on their ϵ_{Nd} values. This is evidenced by the high

correlation between the abundances of $CaCO_3$ and Sr in the soils ($r = 0.87$).

4.2.2. Sea spray salts

The cycling of sea spray salts through the soils may contribute REE and Sr. Given the extremely low concentration of REE in seawater (Piepgras and Wasserburg, 1980), the effects of this cycling on soil ϵ_{Nd} values and Sm/Nd ratios is probably small. The high solubility of sea spray salts and the mobility of Sr in soil water will likely result in minimal incorporation of Sr into the soils. Any Sr incorporated from sea spray will have modern to Pleistocene marine $^{87}Sr/^{86}Sr$ values and, therefore, have the same signatures as Sr contributed by the limestone regolith.

4.2.3. Tertiary carbonate rocks and underlying Tertiary sandstones and mudstones

Zans (1959) and Chubb (1963) have proposed that the soils are derived from the Tertiary basal complex exposed in the northeastern part of the island (Fig. 1). The basal complex is composed of quartz turbidites and mudstones inferred to be derived from the South American craton (Senn, 1940; Verbel, 1980; Speed, 1981; Pudsey and Reading, 1982; Torrini et al., 1985). This unit is overlain by pelagic beds of the Oceanic allochthon that were deposited in the Lesser Antilles forearc. These beds are dominated by calcareous, siliceous, and volcaniclastic components, and are an additional potential source of the soils. Transport of both silicate and carbonate components to the soils likely occurs by eolian rather than fluvial processes because (1) the Tertiary basal complex and Oceanic allochthon are exposed in an erosional window that lies below the oldest Pleistocene coral-reef terraces and (2) the Pleistocene section is extensively karstified.

Similar to the Pleistocene reef limestones, high Sr concentrations in Tertiary carbonate rocks of the Oceanic allochthon result in potential domination of the strontium isotopic signature of the soils by this component. The Tertiary carbonate rocks have strontium isotopic compositions that are similar to Eocene to Miocene seawater (Banner et al., 1994) and will, therefore, manifest their presence in the soils by lowering $^{87}Sr/^{86}Sr$ towards values of 0.7078–0.7082 (Table 1). Unlike the reef limestones, however, these rocks also have moderate Nd concentrations and unradiogenic neodymium isotopic values ($\sim$15 ppm, $\epsilon_{Nd} = -8.5$) and may, therefore, add a significant amount of Nd with an old continental isotopic signature to the soils.

The abundance of medium to fine quartz sand in the soils indicates that a large portion of the siliciclastic fraction of some of the soils is derived from erosion of Tertiary sandstone turbidites of the basal complex (Muhs et al., 1987). The basal complex is the only likely source of quartz sand because other potential sources are too fine grained. The turbidites are quartz- and feldspar-rich sandstones and shales, with accessory minerals that include ilmenite, zircon, garnet, epidote, zoisite-clinozoisite, hypersthene, and augite (Senn, 1940). This mineralogy is very similar to that observed in (1) Quaternary turbidites in the South Barbados

accretionary prism and (2) sediment supplied to the prism from the Orinoco and Amazon rivers (Faugeres et al., 1991). We analyzed a medium-grained sandstone and a mudstone from the exposed Tertiary basal complex to bracket potential endmember sources. The mudstone has a moderate Sr and a high Nd concentration, and Sm/Nd ratio and strontium and neodymium isotopic compositions that are similar to old continental material (Fig. 2a). The sandstone has significantly lower concentrations of Sr and Nd but more radiogenic Sr and less radiogenic Nd than the mudstone (Fig. 2a, Table 1). The addition of a quartz component (derived from the basal Tertiary sandstones) to the soils will not effect bulk soil trace element or isotopic ratios, given the low trace element abundances in quartz (Muhs et al., 1987). Based on our analyses of the Tertiary sandstones, other mineralogical components of the sandstones can, however, contribute significant amounts of Sr and Nd to the soils (Table 1; Fig. 2b). Eolian transport of both sandstone and mudstone components may, therefore, have a marked influence on the neodymium and strontium isotopic compositions of the soils.

4.2.4. Saharan dust

Many authors have discussed the generation of Barbados soils through eolian deposition of Saharan dust (e.g., Syers at al., 1969; Prospero et al., 1981; Foos, 1987; Muhs et al., 1987, 1990). Dust transported in trade winds from the Saharan desert has been observed in traps stationed on Barbados and throughout in the western Atlantic region (Prospero and Carlson, 1972; Prospero and Nees, 1986). Saharan dust particles are on average <10 μm in diameter and are composed of about 77% clay, 14% quartz, 4% plagioclase, 4% calcite, and 1% mica (Glaccum and Prospero, 1980). Saharan dust has a Sm/Nd ratio and strontium and neodymium isotopic signature that are similar to those of the siliciclastics of the basal complex and reflect derivation from old continental material (Fig. 2a, b, Table 1). The dust has a moderate concentration of Sr but a high concentration of REE. Thus, both the mudstone component of the Tertiary basal complex and Saharan dust may strongly influence the ϵ_{Nd} of the soils as a result of high REE contents. Contributions of the mudstones and the Saharan dust to the soils cannot be distinguished, however, because both have similar mineral compositions, REE concentrations, and isotopic compositions.

4.2.5. Volcanic ash

Historical volcanic eruptions in the Lesser Antilles have deposited ash throughout the Caribbean (e.g., Diller and Steiger, 1902; Flett, 1902; Harrison et al., 1980). Although the mineralogical and chemical composition of the ash is expected to vary, the 1902 and 1979 eruptions of La Soufriere on St. Vincent, both of which deposited ash on Barbados, are probably typical of the ash component in the soils. These ashes contain 40–60% glass, 20–40% plagioclase, 5–20% hypersthene, less than 5% clinopyroxene and magnetite, and less than 0.5% zircon and apatite (Harrison et al., 1980). We analyzed two ignimbrites from St. Vincent to constrain the composition of the volcanic ash component in the soils (Table 1). The ignimbrites have low REE concen-

trations and neodymium and strontium isotopic compositions that are close to typical mantle values (Fig. 2a). Although some lavas erupted from other volcanoes in the Lesser Antilles have more continental isotopic signatures, most values are similar to those for St. Vincent (White and Dupre, 1986; Davidson, 1986). It is important to note that the volcanic component is the only potential source in the region with higher ϵ_{Nd} and Sm/Nd than the soils.

4.2.6. Fertilizers

Although the soils were sampled to avoid cultivated areas (Muhs et al., 1987), the redistribution and accumulation of fertilizer in the soils potentially contributes to their isotopic signatures. Three types of fertilizer are used on Barbados: N-based, K-based, and P-based. Relatively low concentrations of Sr and REE in the first two fertilizers (Table 1) indicate that their contribution to the isotopic composition of the soils is likely to be minimal. Despite the fact that the P-based fertilizer has significantly higher Sr and REE concentrations than the other fertilizers, it is unlikely to be a significant component in the soils analyzed for this study because it represents only about 10% of the fertilizer used on Barbados (Banner et al., 1994).

5. DISCUSSION

Compositional and isotopic parameters must be demonstrated to be independent of weathering prior to their application as indices of soil source in quantitative mixing models. The quantification of soil sources in turn allows the effects of weathering on the geochemical and isotopic composition of multicomponent soils to be evaluated. In this section we discuss the relative mobility of Sm, Nd, and Sr during weathering, the relationships exhibited between mineralogy and chemistry in a single soil profile, the roles of the various soil sources in soil genesis, and the effects of weathering on the isotopic compositions of the soils.

5.1. Effects of Weathering on Nd and Sr

Geochemical quantification of weathering processes is difficult because the amount of an element removed from a particular soil during weathering is a function of several factors, including (1) the concentration of the element in the minerals and components (such as volcanic glass or limestone) that comprise the soil, (2) the proportions of minerals and components in the soil, (3) the stability of these minerals and components, (4) the solubility of the element in soil waters, and (5) the compatibility of the element in secondary mineral phases that form during weathering (Nesbitt, 1979; Humphris, 1984). Elemental concentrations and isotopic ratios of soils comprised of numerous components may, therefore, be altered as a result of weathering processes. In order to assess this potential alteration, an index of weathering that is applicable to all of the soils, regardless of source, is required.

As a result of the many processes that govern element behavior during weathering, the relative mobility of elements in soils is usually determined by comparing their abundance in the soil to their abundance in the soil protolith (e.g.,

Brimhall and Dietrich, 1987) or empirically estimated by comparing their concentrations to elements that are thought to be immobile. Since the Barbados soils are mixtures of numerous potential sources, the composition of the soil protolith cannot be used to evaluate the geochemical effects of weathering. We are, therefore, required to estimate the extent of weathering from the geochemistry of the soils themselves.

Analysis of weathering processes in a range of soil environments indicates that Ca, Na, K, Mg, and Si are highly soluble in soil waters and are preferentially removed from soil profiles, whereas Al, Fe, and Ti are conserved in the soils because they are significantly less mobile and tend to be concentrated in typical weathering products like clays and oxides (e.g., Chesworth et al., 1981; Middelburg et al., 1988). We, therefore, use the Si/Al ratio as an index of weathering (e.g., Birkeland, 1984; Muhs et al., 1987, 1990). The large carbonate content of the soils and potential influx of sea spray prohibit the use of ratios of Ca, Mg, Na, and K to Al as monitors of soil weathering. Because Si is more mobile than Al, highly weathered soils are characterized by low Si/Al, whereas less weathered soils have high Si/Al.

The Si/Al ratios of the soils are only slightly affected by variable proportions of volcanic ash, Tertiary mudstone, and Saharan dust that comprise the soils, because these potential components have similar Si/Al ratios (Table 1). Addition of quartz-rich Tertiary sandstone will raise the Si/Al of the soils, however, because this component has Si/Al ratios that are higher than the soils or other soil components (Table 1). The use of the Si/Al ratio as a weathering index is supported by the observations that (1) the soils developed on younger terraces have higher Si/Al than the soils developed on older terraces, indicating that the Si/Al weathering index is age dependent, as expected (Muhs et al., 1990), (2) in profiles where modal mineralogy is known there is little correlation between the abundance of sand and the Si/Al ratio (Muhs et al., 1987), and (3) there are good inverse correlations of Si/Al ratio with typically conservative (immobile) elements such as Ti and Fe ($r = 0.87-0.96$). The Si/Al ratio is also independent of the carbonate content of the soils and is, therefore, an appropriate monitor for weathering in both carbonate-rich and carbonate-poor soils, as long as the soils contain at least some silicate components. It must be emphasized that although Si/Al is probably the best geochemical index of weathering for the heterogeneous soils of Barbados, it is only a qualitative estimate because of the effect that the addition of quartz-rich sands can have on soil Si/Al ratios.

The Si/Al ratios of the soils range from 1.05–5.34 (Muhs et al., 1987, 1990). Covariations of Y, Nd, Sr, and isotopic ratios with Si/Al demonstrate their variable behavior during weathering (Fig. 3). The similar geochemical behavior of Y and REE in most geologic systems accounts for the correlation between Nd and Y in the soils ($r = 0.88$). For the purpose of this analysis we use Y as a proxy for REE because of the three times larger sample population for Y analyses. The concentration of Y generally increases with increased weathering (lower Si/Al) as well as with increased age (Muhs et al., 1987, 1990, unpubl. data). The increased concentration of Y (and apparently REE) in the soils with increased weathering is, therefore, consistent with studies that
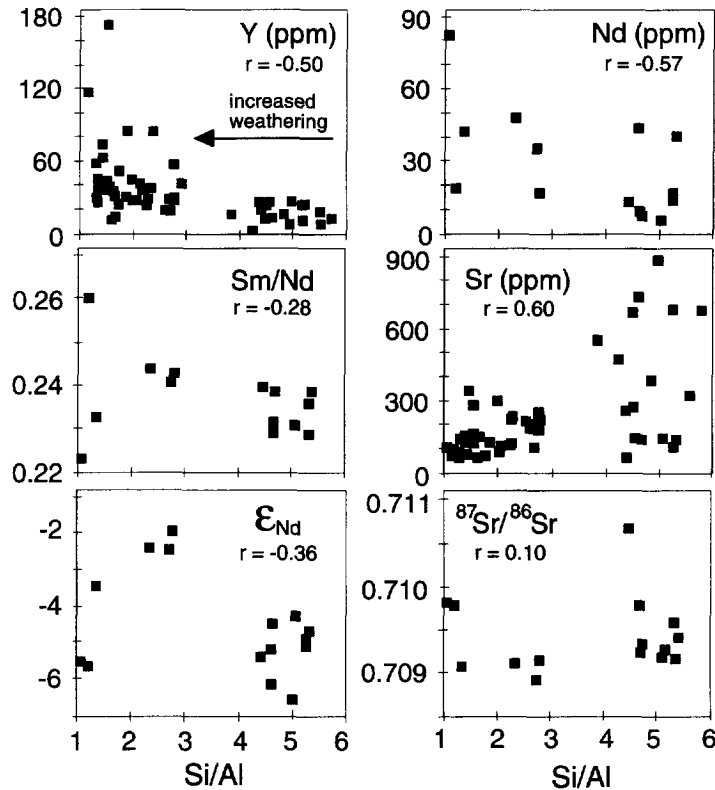
Fig. 3. Covariation of Si/Al with Y, Nd, Sr, Sm/Nd, ϵ_{Nd}, and $^{87}Sr/^{86}Sr$ for Barbados soils. Si/Al, Y, and Sr from Muhs et al. (1987, 1990) and (Muhs, pers. commun.). Si/Al is abscissa in each plot. Si/Al is a geochemical weathering index that decreases as Si is removed and Al is concentrated in soils (clays and oxides) during weathering. Correlation coefficients (r) are calculated for linear regressions through the data. The increase of Y and Nd with increased weathering indicates that REE are concentrated in the soils by weathering, whereas the decrease of Sr with Si/Al indicates that Sr is removed from the soils by weathering processes. The poor of correlations of $^{87}Sr/^{86}Sr$, Sm/Nd, and ϵ_{Nd} with Si/Al require that these ratios are not controlled by silicate weathering processes alone.

have documented the relative immobility of REE in the soil environment resulting in the concentration of these elements during weathering (Middelburg et al., 1988; Braun et al., 1990; Marsh, 1991). The concentration of REE by weathering is likely to explain why the REE and Y abundances in the soils are up to double typical values for other clay-rich rocks such as shales (Gromet et al., 1984). In addition, Nd contents in some soils are significantly higher than any mixture of potential Barbados soil sources (Fig. 2b; and discussed later). Only moderate correlations of Si/Al with REE and Y abundances ($r = -0.57$ to -0.50) suggest, however, that the abundances of Y and REE are probably also dependent to some degree on soil sources. The presence of low REE carbonate or sandstone components in the soils, for example, effectively dilutes the REE abundances. In summary, Y and REE concentrations in the soils reflect (1) their conservative behavior during weathering and (2) the multiple sources that comprise the soils.

The relative immobility of REE is a likely result of the low solubility of REE in soil waters and the probable incorporation of REE in secondary mineral phases such as interstratified kaolinite-smectite clays that are observed in the soils (Muhs et al., 1987). In order to alter the neodymium isotopic composition of the soils by weathering, Nd from

various soil sources must be preferentially removed. Although the soil components are weathered at different rates, Nd is concentrated in the soils. The apparent immobility of REE in the soils implies that their neodymium isotopic composition is not strongly effected by weathering, and accounts for the poor correlation between ϵ_{Nd} and Si/Al (Fig. 3; $r = -0.36$). The weak correlation between Si/Al and ϵ_{Nd} values are likely to result from the variable addition of high Si/Al, low ϵ_{Nd}, sandstone component to the soils. Very poor correlation of ϵ_{Nd} with conservative elements such as Al ($r = -0.06$) and Fe ($r = 0.03$) suggests that the neodymium isotopic compositions of the soils are not significantly effected by weathering processes. The ϵ_{Nd} values of the soils are, therefore, one of the best geochemical indices of the proportions and compositions of sources that comprise the soils.

Many authors have discussed the fractionation of REE in relatively low temperature diagenetic, metamorphic, and soil environments (e.g., Banner et al., 1988; McLennan, 1989; Banfield and Eggleton, 1989; McDaniel et al., 1994; Ohr et al., 1994). The limited mobility and consequent concentration of REE in the soils by weathering processes does not preclude the potential for fractionation of Sm from Nd by weathering. In fact, weathering of typical soil profiles in a

range of geologic settings is characterized by enrichment of light-REE/heavy-REE (LREE/HREE) in the residual products, as a result of the greater solubility of HREE compared to LREE (Nesbitt, 1979; Duddy, 1980; Topp et al., 1984; Braun et al., 1990). Thus, fractionation of REE through the transference of REE from detrital to authigenic phases in the soils is possible. The Barbados soils, however, demonstrate no clear correlation of Sm/Nd with either Si/Al (Fig. 3; $r = -0.28$) or age (Table 1). As in the case with ϵ_{Nd}, the weak correlation between Sm/Nd and Si/Al is a likely result of the variable addition of high Si/Al, low Sm/Nd, sandstone component to the soils. Sm/Nd ratios do not vary with increased abundances of conservative elements such as Al, Fe, Ti, Th, or Nd of the soils (Fig. 2b; $r = 0.10-0.28$), indicating that as these elements are concentrated in the soils by weathering, Sm and Nd are not significantly fractionated. It is, therefore, concluded that Sm/Nd of the soils primarily reflects the proportions and Sm/Nd of sources that comprise the soils. This is supported by analyses of soil leachates that demonstrate that although REE are redistributed into various mineralogic sites within the soils during weathering, the Sm/Nd and ϵ_{Nd} values of the soils do not change (Borg and Banner, 1996; and unpubl. data).

The concentration of Sr decreases with increased weathering (lower Si/Al) and is consistent with the conclusion of Middelburg et al. (1988) that Sr is not retained in soils (Fig. 3). The correlation between Si/Al and Sr is only moderate ($r = 0.60$), however, because of the control that small amounts of the carbonate soil component can have on Sr abundances of the soils. The mobility of Sr in the soil environment implies that weathering may affect the strontium isotopic composition of the soils through preferential dissolution or recrystallization of a soil component. The rapid weathering of the volcanic ash component relative to old continental clay-rich components, for example, will drive the $^{87}Sr/^{86}Sr$ of the soils to more radiogenic values. Despite the lack of correlation between $^{87}Sr/^{86}Sr$ and Si/Al, which suggests that the strontium isotopic composition of the soils is not strongly controlled by weathering processes (Fig. 3), quantitative mixing models detailed in a later section require the removal of unradiogenic Sr derived from volcanic ash and/or Tertiary carbonates from the soils. The lack of correlation between Si/Al and $^{87}Sr/^{86}Sr$ is attributed to (1) dominance of the $^{87}Sr/^{86}Sr$ in the soils by the carbonate component and (2) variable $^{87}Sr/^{86}Sr$ ratios of the noncarbonate soil component. The latter hypothesis is supported by the negative correlation between $^{87}Sr/^{86}Sr$ and ϵ_{Nd} of the low CaCO$_3$ soils (Table 1) that suggests that both strontium and neodymium isotopic compositions of the soils reflect mixing between volcanic ash and other silicate sources to some degree. Thus, the strontium isotopic composition of the soils is likely to be affected by both varying proportions of soil sources and weathering processes.

5.2. Soil Profiles

A detailed analysis of a single soil profile illustrates the relationships between mineralogy, major element and trace element concentrations, and isotopic composition. Although there are several geochemical trends observed in the profiles

that correlate with mineralogy of the soils, it is important to note that neither the modal mineralogy nor the geochemistry of the soils correlates well with the Si/Al weathering index (Fig. 4). There is a direct correlation between CaCO$_3$ and Sr contents of the soils, as well as between 1/Sr and $^{87}Sr/^{86}Sr$ throughout the profile. The $^{87}Sr/^{86}Sr$ values of the samples from the upper part of the A horizon and the lower Bw2 horizon are similar to values for Pleistocene reef limestones, but are much higher in the middle of the profile, where there are low abundances of CaCO$_3$ and Sr.

Petrographic examination of the carbonate soil components led Muhs et al. (1987) to the conclusion that the CaCO$_3$ concentration of the soils reflects the amount of limestone regolith that is present, rather than the amount of secondary CaCO$_3$ that has precipitated from soil waters. This suggests that the correlations between CaCO$_3$, Sr, and $^{87}Sr/^{86}Sr$ observed in the 4B profile are produced by the variable contribution of Pleistocene limestones and/or Tertiary carbonate rocks to the soils. The involvement of Pleistocene limestones, as opposed to Tertiary carbonate rocks, is supported by (1) the fact that carbonate-rich soils at the base of the profile have $^{87}Sr/^{86}Sr$ values that are within the range of Pleistocene reef limestones (Fig. 4), and (2) HCl leachates of eleven soils with >3 wt% CaCO$_3$ have Pleistocene marine $^{87}Sr/^{86}Sr$ values (Borg and Banner, 1996).

Horizons with low CaCO$_3$ and Sr have $^{87}Sr/^{86}Sr$ that is more radiogenic than the reef limestones, indicating involvement of old continental components. The silt- and clay-rich fractions may affect the strontium isotopic composition of low CaCO$_3$ soils because of the moderately high Sr content of the silt and clay (e.g., Mt. All 2, NU 553, and Saharan Dust; Table 1). Some carbonate-poor soils (5B 0-21 and 8A 0-13) have $^{87}Sr/^{86}Sr$ values that are lower than those of the Pleistocene reef limestones, indicating that the strontium isotopic composition of these soils reflects the involvement of a low $^{87}Sr/^{86}Sr$ component, such as volcanic ash or Tertiary carbonate rocks (Table 1). The presence of Tertiary carbonate rocks are unlikely to produce the low $^{87}Sr/^{86}Sr$ values observed in soils 5B 0-21 and 8A 0-13, however, because unlike the Tertiary carbonate rocks these soils have (1) low CaCO$_3$ contents and (2) high ϵ_{Nd}. Thus, the strontium isotopic composition of the soils are primarily mixtures of Pleistocene reef limestone, old continental siliciclastic, and volcanic ash components. It must be noted, however, that the most weathered horizon (i.e., lowest Si/Al) has the most radiogenic Sr (Fig. 4), suggesting that there is some alteration of strontium isotopes by weathering processes, as discussed in more detail in a later section.

The relatively immobile nature of the REE during weathering implies that the ϵ_{Nd} variations in the 4B profile primarily reflect variations in the proportions of silicate sources (reef-limestones have very low Nd and, therefore, have negligible effects on ϵ_{Nd} values of the soils). Preferential weathering and loss of specific soil components, such as volcanic ash, is not consistent with both the high concentration of Nd and high ϵ_{Nd} values in the top of the profile. Instead, high ϵ_{Nd} values in the upper horizons of the 4B profile are indicative of relatively large amounts of the volcanic component, whereas lower ϵ_{Nd} at the base of the profile indicates a greater proportion of old continental material. The neodymium iso-
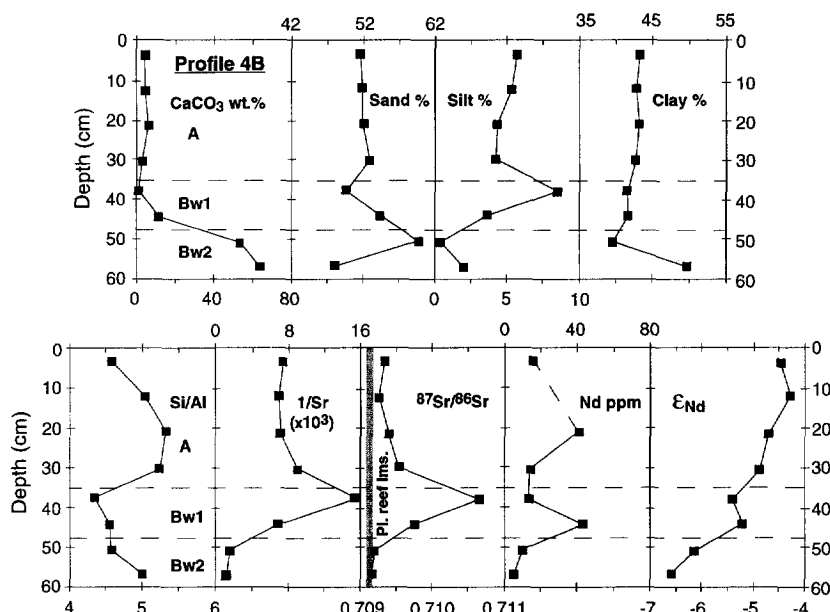
FIG. 4. Depth profiles of percent $CaCO_3$, sand, silt, and clay (normalized to 100%), Si/Al, 1/Sr, Nd, $^{87}Sr/^{86}Sr$, and ϵ_{Nd} for the Barbados 4B soil locality (data from Muhs 1987, 1990, and this study). Increase of $CaCO_3$ and Sr with depth results from increased incorporation of limestone regolith into the soils. Note that the horizon with low $CaCO_3$ (at 38 cm. depth) has a high $^{87}Sr/^{86}Sr$ value, suggesting that potential soil components, such as siliciclastics from the Basal complex or Saharan dust, dominate the noncarbonate Sr fraction in this profile. ϵ_{Nd} decreases with depth, indicating that there is a greater proportion of the volcanic component in the upper part of the profile. This may result from a progressive increase of the volcanic ash component to the soils (see text).

topic variation with depth, therefore, likely reflects temporal changes in the fluxes of volcanic vs. continental atmospheric sources to the soils.

5.3. Quantification of Soil Sources by Mixing Models

Mixing models based on measured ϵ_{Nd} and Sm/Nd of soils and potential sources are constructed to quantify the roles of the sources in the genesis of Barbados soils. These calculations are based upon the neodymium isotopic composition and Sm/Nd ratios measured for the soils because neither ϵ_{Nd} nor Sm/Nd appear to be significantly fractionated by weathering processes (as discussed earlier), and, therefore, may be a good geochemical representation of soil sources. It is emphasized that the removal of REE from the soils by weathering will not change the results of the mixing models as long as neither ϵ_{Nd} nor Sm/Nd of the soils are significantly fractionated by this process. Small degrees of fractionation of ϵ_{Nd} and Sm/Nd will not affect the results of the mixing models because of the large compositional differences between potential endmembers.

One end of the mixing array is defined by volcanic ash, which is the only potential component in the soils with high ϵ_{Nd} and Sm/Nd values (Fig. 2a, b). Compositional and isotopic similarities between the potential soil sources that define the other end of the mixing array preclude a unique solution to the mixing models. The mixing models are, therefore, used to constrain the contribution of the volcanic ash source to the soils assuming binary mixing between the St. Vincent ignimbrites and each of the three endmembers: sandstone, mudstone, and Saharan dust.

The results of selected binary mixing models are presented in Fig. 5. The modeling demonstrates that 30–85% of the REE in the soils are derived from volcanic ash, depending which soil source is assumed to define the other end of the mixing array. The soils contain 30–55% volcanic ash if they are composed of volcanic ash and sandstone alone, 60–80% volcanic ash if they are composed of volcanic ash and mudstone alone, and 70–85% volcanic ash if they are composed of volcanic ash and Saharan dust alone. The overall contribution of volcanic ash in the soils will be lower than 30–85% because of the contribution of non-REE bearing components, such as Pleistocene limestone, that essentially dilute the other components. Nevertheless, most of the soils analyzed in this study have low $CaCO_3$, indicating that the amount of volcanic ash calculated from REE-based mixing models closely represents the amount of ash component presently in the soils.

The variable Sm and Nd concentrations in potential siliciclastic soil components result in two endmember mixing scenarios that bracket the proportions of volcanic ash in the soils. Low Sm and Nd concentrations in the Tertiary sandstone require relatively small amounts of volcanic ash to generate the Sm/Nd and ϵ_{Nd} variations observed in the soils. On the other hand, relatively high Sm and Nd concentrations in the clay-rich soil components require larger amounts of volcanic ash to generate the REE systematics of the soils in the mixing models. Potential clay-rich soil components include (1) Tertiary mudstones, (2) Saharan dust, and (3) the clay-rich component in the Tertiary carbonate rocks. Although most soils have low $CaCO_3$ contents, dissolution of the Tertiary carbonate rocks during weathering of the soils
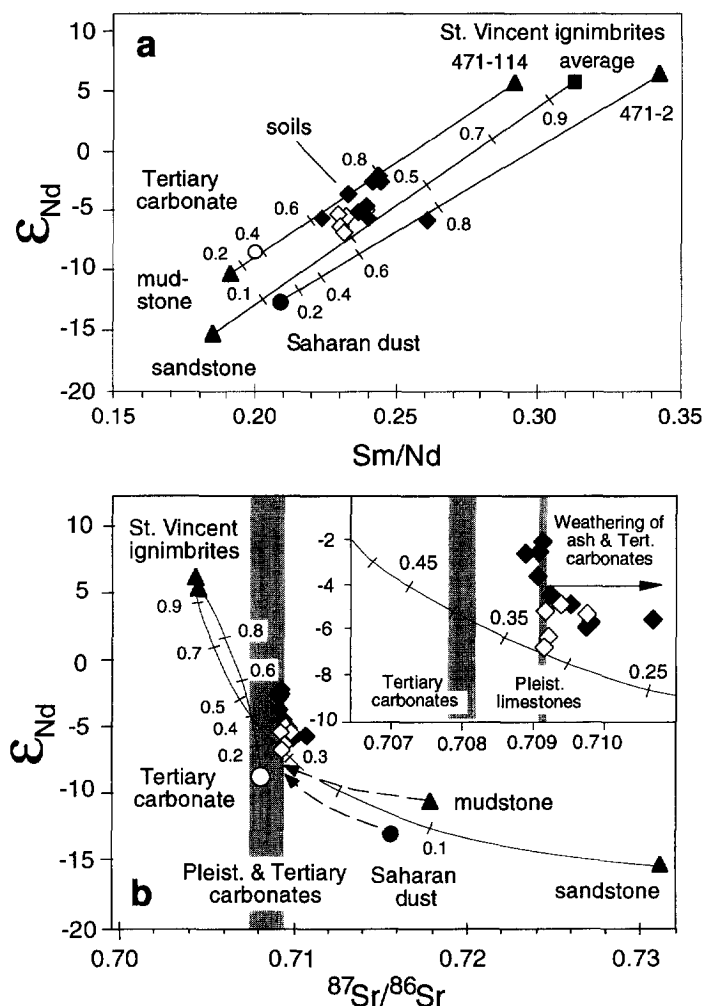
FIG. 5. (a and b) Selected binary mixing curves demonstrating compositions generated by various mixtures of soil sources. Open diamonds are high carbonate soils (>6 wt% $CaCO_3$) and solid diamonds are low carbonate soils (<6 wt% $CaCO_3$). Numbers on curves represent fraction of volcanic ash component in modeled mixtures. Volcanic ash compositions shown are for St. Vincent ignimbrites 471-2 and 471-114, and the average of these two samples (Table 1). (a) REE-based binary mixing models of St. Vincent ignimbrites and Tertiary mudstone NU 553, Tertiary sandstone Mt. All 1, and average Saharan dust (Table 1). Models demonstrate that the Sm/Nd and neodymium isotopic ratios of the soils are reproduced by a 60:40 to 80:20 mixture of volcanic ash:mudstone, or by a 30:70 to 55:45 mixture of volcanic ash:sandstone, or by a 70:30 to 85:15 mixture of volcanic ash:Saharan dust. (b) Sr-Nd isotope-based binary mixing models of average St. Vincent ignimbrites with sandstone (Tertiary sandstone sample Mt. All 1) and Tertiary carbonate rock (sample T06). Shaded area is $^{87}Sr/^{86}Sr$ field of Pleistocene reef limestones and Tertiary carbonate rocks. Curved-dashed arrows represent mixing paths for average St. Vincent volcanic ignimbrites and mudstone and average St. Vincent volcanic ignimbrites and Saharan dust. Modeling demonstrates that the soils have $^{87}Sr/^{86}Sr$ that is more radiogenic than theoretical mixing curves. Addition of Pleistocene limestones to the mixtures shown can account for the range of Sr-Nd isotopic compositions of some of the soil samples, i.e., samples lying on or to the left of the Pleistocene limestone composition ($^{87}Sr/^{86}Sr$ field of Pleistocene reef limestones = 0.70911–0.70919; see inset). Soil samples lying to the right of the Pleistocene limestone field cannot be accounted for by any mixing models involving the soil sources considered. The inability of the mixing models to reproduce the soil data is interpreted to be the result of alteration of strontium isotopes values by weathering processes in the soils. Inset is detail of ϵ_{Nd} and $^{87}Sr/^{86}Sr$ of soils showing the effect that the removal of volcanic ash or Tertiary carbonate Sr has on isotopic composition of the soils. Curved line in inset is the mixing curve for average St. Vincent ignimbrites and sandstone Mt. All 1.

will likely result in the removal of the high-Sr carbonate component and retention of the high-REE clay-rich component. Similar Sm and Nd concentrations and neodymium isotopic compositions in all of the clay-rich soil components will result in relatively small differences in the proportions of volcanic ash and clay-rich siliciclastic components deter-

mined by the different mixing models that involve clay-rich components (Fig. 5a).

The compositional and isotopic similarities between sandstone, mudstone, and Saharan dust (Fig. 5a, b) do not allow tight constraints to be placed on the amount of volcanic ash in the soils using geochemistry alone. The presence of up

to 60% sand- and silt-sized grains in some of the soils, combined with the predominance of quartz in these soil fractions (Muhs et al., 1987), indicates that the sandstone source is the dominant nonvolcanic siliciclastic component in these soils. The fact that the mixing models require between 45–70% sandstone (Fig. 5a) is consistent with the modal mineralogy of these soils. Some soils, however, have only about 5% sand-sized grains. If the contribution of the sandstone is assumed to be represented by the modal mineralogy of the soils then ternary mixing models can be constructed to constrain the amount of clay-rich components required to produce the REE composition and neodymium isotopic signature of the soils. If the soils are assumed to have only 5% sandstone component, then the amount of volcanic component ranges from 70–80% and the amount of mudstone and/or Saharan dust ranges from 15–25%. It is, therefore, concluded that the low $CaCO_3$ soils are primarily mixtures of 5–55% sandstone and 30–80% volcanic ash, with 0–25% clay-rich mudstone, Saharan dust, and/or clays from the Tertiary carbonate component, whereas the high $CaCO_3$ soils have an additional Pleistocene limestone and/or Tertiary carbonate component.

5.4. Alteration of Strontium Isotopes during Weathering

Mixing models based on $^{87}Sr/^{86}Sr$ and ϵ_{Nd} values of soils and potential sources are constructed to assess the behavior of $^{87}Sr/^{86}Sr$ during weathering (Fig. 5b). Note that binary mixing lines between any combination of volcanic ash with sandstone, mudstone, Saharan dust, or Tertiary carbonate rocks (Fig. 5b) do not intersect the soil data. Given our previous conclusion that ϵ_{Nd} values of soils primarily represent the original mixture of different silicate soil sources, the departure of soil compositions in $^{87}Sr/^{86}Sr$-ϵ_{Nd} space requires that the strontium isotopic composition of the soils has been altered. The fact that the soil compositions lie to the right of the mixing lines in Fig. 5 indicates that the strontium isotopic composition of the soils has been raised. The soil data may be shifted to the right of the mixing curve through (1) the addition of a high Sr/Nd component, such as Pleistocene limestone or (2) preferential weathering and removal of unradiogenic Sr initially derived from volcanic ash or Tertiary carbonate soil components. Simple addition of Pleistocene limestone, however, cannot account for all of the differences between observed $^{87}Sr/^{86}Sr$ of the soils and the $^{87}Sr/^{86}Sr$ predicted by the mixing models because some of the soils have $^{87}Sr/^{86}Sr$ that is more radiogenic than Pleistocene limestone. Instead, the heterogeneous nature of the soils combined with the mobility of Sr during weathering suggests that strontium isotopes are likely to be altered by weathering processes.

Preferential removal of unradiogenic Sr from the soils is supported by the observation that the strontium isotopic composition of vadose groundwaters collected from caves, which have only interacted with soils and Pleistocene limestones on Barbados, have strontium isotopic compositions that are less radiogenic (0.70903–0.70910) than Pleistocene limestones (0.70911–0.70919) observed on the island (Banner et al., 1994, 1996). The strontium isotopic composition

of speleothems precipitated from similar vadose groundwaters between 0 and 5500 years ago records $^{87}Sr/^{86}Sr$ values (0.70903–0.70915) that range lower than Pleistocene limestone values as well (Banner et al., 1996). It is, therefore, concluded that the shift in strontium isotopic compositions towards more radiogenic values is a result of the preferential breakdown and removal of unradiogenic Sr within the soils that is derived from either volcanic ash or Tertiary carbonate rock components.

The amount of Sr that has been removed from the soils by weathering can be approximated using the mass balance relationship:

$$[Sr]^{soil} = [Sr]^{sil} + [Sr]^{carb} - [Sr]^w,$$

where $[Sr]^{soil}$ is the measured concentration of Sr in the soil, $[Sr]^{sil}$ is the amount of Sr derived from silicate soil sources, $[Sr]^{carb}$ is the amount of Sr derived from carbonate sources, and $[Sr]^w$ is the amount of Sr removed from the soils by weathering, assuming that (1) the $[Sr]^{sil}$ reflects the proportions of volcanic ash and Tertiary sandstones, mudstones, or Saharan dust as determined by REE-based binary mixing models, and (2) the amount of Sr contributed to the soils by carbonates is quantified by the measured weight fraction of $CaCO_3$ in the soils and the highest Sr content (2600 ppm) of a suite of recrystallized Pleistocene limestones (Banner et al., 1994). Thus, the calculations are maximum estimates of Sr removal.

The amount of Sr removed from the soils by weathering varies depending on the sources assumed to comprise the soils. Two calculations that are based on the best estimates of the proportions of sources from the mixing models are presented. In the first case, the soils are assumed to contain no clay-rich components (i.e., mudstones or Saharan dust) and have volcanic ash, Tertiary sandstones, and Pleistocene reef limestones in the proportions determined by the methods outlined above. In this case, the average amount of Sr removed from the soils (i.e., $[Sr]^w$) is about 35% of the initial Sr present prior to weathering (i.e., preweathering Sr concentration). In the second case, the soils are assumed to contain the maximum amount of clay-rich components (25%) allowed by the REE-based mixing models. In this case, about 60% of the initial Sr has been removed from the soils. The difference between the two calculations stems from the much greater concentration of Sr in the clay-rich mudstone (131 ppm) or Saharan dust (286 ppm) compared to the Tertiary sandstones (17 ppm), resulting in higher values of $[Sr]^{sil}$. Thus, the minimum amount of Sr removed from the soils is about 35%, whereas the maximum is near 60% of the initial Sr present before weathering.

The removal of Sr from the soils is accomplished through the dissolution of Sr originally in unweathered mineral components (i.e., glass, silicates, carbonates, and oxides). During weathering, the silicate soil fraction is typically broken down to form clays and oxides (e.g., Middelburg et al., 1988). The breakdown of at least one silicate soil component is confirmed by the retention of volcanic ϵ_{Nd} and Sm/Nd signatures by the Barbados soils despite the relative paucity of original glass and minerals derived from the volcanic ash. The removal of Sr from the carbonate soil fraction occurs via dissolution and/or recrystallization of the carbonates.

Petrographic evidence for a range of carbonate dissolution and recrystallization processes are found in Barbados soils (James, 1972). A decrease in Sr/Ca with increased age observed in the high $CaCO_3$ soils (D. R. Muhs, unpubl. data) corresponds to similar trends in the underlying reef limestones (Banner et al., 1994), suggesting that recrystallization results in the loss of Sr from the carbonate soil fraction. Thus, the breakdown of volcanic ash and dissolution and recrystallization of carbonates removes relatively unradiogenic Sr from the soils raising their $^{87}Sr/^{86}Sr$ values. Preferential removal of unradiogenic Sr is supported by the fact that the strontium isotopic composition of the most radiogenic soils can be reproduced from typical preweathering soil compositions by subtracting approximately 65% of their initial Sr with a volcanic strontium isotopic signature. This result is in agreement with the mass balance calculations discussed in the previous paragraph that indicate that the average soils have had 35–60% of their original Sr removed by weathering.

6. IMPLICATIONS

The contribution of dissolved constituents to groundwaters from soils is a function of (1) the composition and proportions of components that comprise the soils, (2) the stability of each component during weathering, and (3) the solubility of a particular constituent in soil water. In the case of Barbados, soluble elements such as Sr are concentrated in relatively unstable components such as carbonates and volcanic ash and will be incorporated into groundwaters relatively rapidly. Low $^{87}Sr/^{86}Sr$ of Barbados groundwaters, relative to the Pleistocene limestones (Banner et al., 1994), reflects the presence of volcanic ash and/or Tertiary carbonate-derived soil components. Thus, radiogenic Sr tends to be concentrated in the soils as unradiogenic Sr is removed by groundwaters.

The effects of weathering on Nd systematics in the soil-groundwater system are less pronounced as a result of the stability of primary and secondary REE-enriched minerals (probably clays and oxides) in the soils and low solubility of REE in soil waters. The large amount of relatively unstable volcanic ash incorporated into the soils during the Pleistocene may result in some preferential mobility of volcanic REE during weathering. Relatively high ϵ_{Nd} and Sm/Nd of the soils compared to potential old continental soil sources, however, suggests that the loss of volcanic REE to groundwaters is small and, therefore, unlikely to significantly effect the soil compositions. Instead, the relative immobility of REE during weathering suggests that Sm/Nd isotope systematics may provide a tracer that is relatively unaffected by weathering, as well as being diagnostic of potential sources. The Sm/Nd ratios and ϵ_{Nd} values of soils may, therefore, be used in conjunction with geographic, petrographic, and geochemical data to help constrain the sources of multicomponent soils. Reconstructing temporal changes in the relative proportions of components of atmospheric deposition to soils is likely to provide new constraints for the study of paleoclimate (e.g., Muhs et al., 1990). In ancient geologic settings where soil sources are poorly constrained, Sm/Nd and ϵ_{Nd} values of soils may provide the clearest insights into the general geochemical affinities of the sources.

7. CONCLUSIONS

The geographic isolation of Barbados from continental soil sources and the lack of fluvial systems in the island's Pleistocene section allow multiple eolian soil components to be identified and evaluated. Potential sources of soils developed on Pleistocene reef terraces include: (1) Pleistocene reef limestones, (2) Tertiary carbonate rocks, sandstones, and mudstones that are exposed in northeastern Barbados, (3) volcanic ash erupted from the Lesser Antilles arc, (4) Saharan dust transported by trade winds, and (5) fertilizer. The neodymium isotopic signature of the soils is dominated by their silicate component and the strontium isotopic signature is dominated by their carbonate component. Comparison of soil samples that have been weathered to varying degrees indicates that their Sm/Nd ratios and neodymium isotopic compositions are not significantly altered by weathering. In contrast, unradiogenic Sr derived from volcanic ash and/or Tertiary carbonate components is removed from the soils as a result of relatively rapid weathering of these components and high solubility of Sr in soil waters. This is reflected by the shift in the strontium isotopic compositions of the most weathered soils to more radiogenic values. Relatively radiogenic neodymium isotopic compositions and high Sm/Nd ratios of the soils indicate that the silicate fraction of the soils primarily reflects contributions from the volcanic ash component. Consideration of the isotopic variability in the other soil components and soil mineral compositions indicates that the silicate fraction is composed of between 30–85% volcanic ash, with the remainder composed of old terrigenous sediment. Sr-Nd isotope studies of modern and ancient soils can provide information on both weathering processes and soil sources.

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