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## The influence of soil age and regional climate on clay mineralogy and cation exchange capacity of moist tropical soils: A case study from Late Quaternary chronosequences in Costa Rica



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#### ABSTRACT

Tropical soils exhibit large differences across landscapes in many attributes, notably clay mineralogy (2:1 vs. 1:1 clays), bulk geochemistry (Ca, Al), pH, cation exchange capacity (CEC), organic matter and soil texture. In order to examine the factors controlling these variables, a series of three chronosequences ( $\leq$  120 ka) of tropical soils on uplifted terraces along the Pacific coast of Costa Rica were studied. The three study locations differ mainly as a function of soil moisture and leaching, with conditions ranging from 2700 mm/yr mean annual precipitation (MAP) on the southern Nicoya Peninsula (4-month dry season), to 3200 mm/yr in the Esterillos region (3-month dry season), and 4250 mm/yr on the Osa Peninsula (no dry season). Analytical methods include X-ray diffraction (XRD), transmission-analytical electron microscopy (TEM-AEM), inductively coupled plasma optical emission and mass spectrometry (ICP-OES, ICP-MS), ammonium acetate extraction (1 M NH<sub>4</sub>OAc, pH = 7, for CEC) and C:N analysis.

Soil weathering reactions and related decrease in CEC occur three-to-four times faster in a sequence of Inceptisol-to-Oxisol soils in the wettest climate (Osa) compared to the less-moist Esterillos area; in the even drier monsoon climate soils (Nicoya), this evolved, low-CEC (  $< 10 \text{ cmol}_c/\text{kg}$ ) state does not occur, even after 120 ka of soil formation, and rate of compositional alteration is approximately five to ten times slower than at Osa. The dominant exchangeable cation at all sites is Ca. Interlayer K and Al increase relative to Ca over time, resulting in interstratified K-S with smectite layers that become progressively more vermiculite-like and illite-like.

The age-related evolution of tropical soils appears to be a predictable sequence in lowland tropical landscapes where periodic tectonism, erosion or volcanism produces unweathered parent material at the land surface. Empirical data from this project enables the extrapolation of simple equations applicable to tropical volcanic arc landscapes where presence of uplifted marine terrace soils facilitates determination of soil age. The two variables controlling soil composition can be combined into an effective age (age<sub>eff</sub>) that takes into account soil age and weathering intensity (factoring in MAP and wet-dry months from climate data), and equations are of the form, e.g. ECEC =  $-18.1 * \ln(age_{eff}) + 77$ , with R<sup>2</sup> values of 0.75 to 0.87. Greatest scatter occurs in the youngest soils. Given the apparent prevalence of this sequence and the systematic nature of its reaction progression, these results could be useful for modeling tropical soils.

#### 1. Introduction

Chemical weathering in the humid tropics depletes soils of soluble components, notably mineral-derived plant nutrients (e.g. Ca, K, Mg), which over time results in nutrient-poor conditions with low cation exchange capacity (CEC) and enrichment of plant-toxic Al in the soil solution (Birkeland, 1999; Ryan and Huertas, 2009). This evolved state is particularly true of Oxisols, the paradigmatic tropical lateritic soil characterized by abundant kaolinite, low cation exchange capacity (< 10 cmol<sub>c</sub>/kg), low amounts of available base cations, high amounts of exchangeable Al, and low pH (e.g. < 5) (Birkeland, 1999; Mizota et al., 1988; Nieuwenhuyse et al., 2000; Shoji et al., 1982). However, it is important to recognize that approximately 60% of soils in moist-to-humid tropical environments do not fit this description (Porder et al.,

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2005; Szott et al., 1991); for example, in tectonically and volcanically active tropical environments where unweathered parent material is periodically exposed at the land surface (e.g. by uplift, erosion or deposition), the newly-forming soils on these geologically-young surfaces (e.g. Holocene age) typically have high CEC (e.g. > 40 cmol<sub>c</sub>/kg; Delvaux et al., 1990; Kantor and Schwertmann, 1974; Messmer et al., 2014). These soils are often rich in smectite or interstratified kaolinite-smectite (K-S), possess high concentrations of base cations and low amounts of exchangeable Al, and are less acidic than older (e.g. Pleistocene) Oxisols or Ultisols (Alvarado et al., 2014; Erswaran and De Coninck, 1971; Ojanuga, 1990; Ryan and Huertas, 2009; Thanachit et al., 2006).

Previous studies of tropical lateritic soils indicate that CEC varies widely and is controlled by soil age, mineralogy and grain size. Ludwig et al. (2001) and Soares et al. (2005) documented very low CEC in Amazonian Ultisols ( $< 3 \text{ cmol}_c/\text{kg}$  exchangeable base cations), where base cation depletion and Al toxicity are characteristic of these highly-weathered, kaolinitic soils; in the Congo, Mareschal et al. (2011) documented Oxisols with CEC  $< 0.5 \text{ cmol}_c/\text{kg}$ . Lima et al. (2002) studied two end-members of humid tropical soils in Western Amazonia: floodplain Entisols (young) and upland Oxisols (old). CEC of the Entisols ranges from 17–23 cmol<sub>c</sub>/kg, 67–87% of exchange sites are occupied by Ca and Mg, and the soil contains expandable 2:1 minerals; by comparison, CEC of nearby Oxisols is 4-9 cmol<sub>c</sub>/ kg, > 98% of exchange sites are occupied by Al or H, and soil mineralogy is dominated by kaolinite, gibbsite and hematite, with no expandable clay. Aprile and Lorandi (2012) similarly documented CEC of 3 to 6 cmol<sub>c</sub>/kg in lateritic soils from Brazil. Examples of relatively high CEC in humid tropical soils were documented in lateritic soils in the Caribbean plain of Costa Rica (Nieuwenhuyse et al., 2000) and piedmonts of Panama (Messmer et al., 2014) and Venezuela (Daugherty and Arnold, 1982), areas where CEC ranges from 5 to 93 cmol<sub>c</sub>/kg. Thus, CEC in humid tropical soils appears to decrease with increasing soil age, yet the literature contains few studies that systematically examine the role of soil age on CEC. He et al. (2008) and Jiang et al. (2011) observed that CEC decreases from  $\sim 20 \text{ cmol}_{c}/$ kg to  $\sim 7 \text{ cmol}_c/\text{kg}$  with increasing soil age in chronosequences. However, these studies were both performed on Hainan Island, China, a subtropical location that is cooler (23-24 °C) and drier (1400 to 1800 mm/yr mean annual precipitation [MAP]) than much of the humid tropics (typically 25-27 °C and 2000-4000 mm/yr MAP). Improved understanding of the role of time and soil evolution on CEC should enable improved modeling of soil characteristics. Chronosequences of soils developed on marine terraces along the Pacific coast of Costa Rica (e.g. Gardner et al., 1992; Marshall and Anderson, 1995; Sak et al., 2004a; Fisher and Ryan, 2006; Ryan et al., 2016) provide an opportunity to gain a deeper understanding of this critical soil property along both temporal and climatic gradients.

Context on temporally-driven changes in tropical soil is provided by geochemical and mineralogical analysis of the transition from Entisols and Inceptisols to Oxisols in the humid tropics. This transition occurs over a ~30 ka to 120 ka time span (Ryan and Huertas, 2009; Ryan et al., 2016). Decrease in base cations occurs simultaneously with the transformation from early-stage pedogenic smectite (< 8 ka) to intermediate-stage interstratified K-S and eventually late-stage halloysite and kaolinite ( $\geq$  40 ka) (Ryan and Huertas, 2009; Ryan et al., 2016); however, no study is known of that systematically investigates the rate at which CEC of humid tropical soils decreases with time, so the purposes of this study are as follows: (1) to determine CEC of the clay fraction of three soil chronosequences formed on marine terraces along the Costa Rica Pacific coast; and (2) to understand factors that control the CEC of tropical soil clays, particularly crystallochemistry, soil age, kinetic and thermodynamic considerations, and climate (mean annual rainfall). This study aims to test the hypothesis that CEC of moist tropical soil decreases with soil age and does so at rates that are greatest in soils exposed to the rainiest climate.

#### 2. Study area

The landscape of the Pacific and Caribbean coasts of Costa Rica contains uplifted marine and fluvial terraces ranging in age from 1 ka to  $\geq$  120 ka (Alvarado, 1990; Gardner et al., 1992; Marshall and Anderson, 1995; Sak et al., 2004a). On the Pacific coast of the isthmus, Holocene terraces are dominated by smectite and primary minerals (e.g. plagioclase, clinopyroxene, quartz, magnetite, and sometimes heulandite, biotite calcite); over time, leaching of base cations and Si results in a Pleistocene soil mineralogy that in nearly all cases is lacking in primary minerals — other than quartz — and has experienced the transformation of early-stage smectite to later-stage K-S, halloysite and kaolinite (Fisher and Rvan, 2006; Rvan and Huertas, 2009). These changes have been documented over a geographic span of 2° of latitude and a range in MAP of 2700 to 4250 mm/yr MAP (Pincus, 2014; Ryan and Huertas, 2009; Ryan et al., 2016); other than difference in climate, though, soil-forming factors are similar (Ryan et al., 2016); e.g., parent material is dominantly basaltic-andesitic sediment, topography is horizontal or shallowly-dipping (terrace surfaces, sometimes dissected), and the landscape is dominated by forest and pasture. Mean annual temperature (MAT) at all three sites is 26–27 °C, so the main difference in climate of the three sub-regions is MAP and dry season, from  $2700 \pm 300 \text{ mm/year}$  on the southern Nicoya Peninsula (4-month dry season) to 3200 ± 200 mm/year in the Esterillos region (3-month dry season) and 4250  $\pm$  250 mm/year at sites sampled on the Osa Peninsula (no dry season, all months receive > 100 mm of rainfall). Evapotranspiration on the southern Nicoya Peninsula and Esterillos Region is  $1350 \pm 50 \text{ mm/yr}$  and on the Osa Peninsula is  $1250 \pm 50 \text{ mm/yr}$  (IMN).

Terrace ages represent emergence of marine sediments to an elevation  $\geq 2$  m above high tide (Anderson et al., 1999). The absence of sediment reworking allows pedogenic clay to begin to accumulate, and this represents the onset of pedogenesis (Anderson et al., 1999), an age which should be very similar to OSL ages and equal to or younger than radiocarbon ages (Sak et al., 2009). Sources of terrace ages determined by OSL and 14-C are given in Table 1. Ages of terraces without radiometric dates were determined by mineralogical-geochemical correlation or by analysis of uplift rates and sea level change (Ryan et al., 2016; Sak et al., 2004b), and rationale for these ages are also given in Table 1.

#### 3. Materials and methods

#### 3.1. Environmental characteristics and soil conditions

Sixty-one soil samples collected from three regions on the Pacific coast of Costa Rica (Fig. 1) were analyzed: samples sites are on the south end of the Nicoya Peninsula (Ryan et al., 2016), in the Esterillos-Parrita area (Fisher and Ryan, 2006; Ryan and Huertas, 2009), and on the east side of the Osa Peninsula (Falcones, 2014). These sites differ mainly as a function of soil moisture (Section 2). According to the Holdridge classification scheme, Nicoya and Esterillos are moist tropical forest and Osa is wet tropical forest (Holdridge, 1967; Kohlmann et al., 2010). The Köppen system classifies Nicoya as equatorial savanna with dry summer (As), Esterillos as equatorial monsoon (Am) and Osa as equatorial rainforest, fully humid (Af) (Kottek et al., 2006).

The soils examined in this study are developed on uplifted marine terraces that originally consisted of beach sands or gravels. The dominant parent material for the nearshore sediments from which these soils formed is andesitic-basaltic arc rocks as well as basalt, siltstone, and limestone at sites where uplifted ocean floor outcrops. Mineralogically, the sands, gravels, and occasional clay layers that comprise parent material consist of plagioclase, clinopyroxene, and quartz with lesser amounts locally of shell fragments, magnetite, and metamorphic lithic fragments (Fisher, 2004; Fisher and Ryan, 2006; Hobbs, 2012; Lundberg, 1991).

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