MINERALOGICAL CHARACTERIZATION OF THE RÍO NAPO FLOOD-PLAIN AND KNOLL SOILS

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Common Abbreviations (in alphabetical order): Al+H: residual acidity; EDS: energy dispersive X-ray spectrometry; EECA: Estación Experimental Central de Amazonía; FAO: Food and Agricultural Organization; FEG-SEM: field emission gun – scanning electron microscope; INIAP: Instituto Nacional de Investigaciones Agropecuarias; SOTERLAC: Soil and Terrain Database for Latin America and the Caribbean; XRD: X-ray diffraction.

Mineral Names and their unit cell formulas used throughout this article (in alphabetical order, (Sparks, 2003)): albite ($NaAlSi_3O_8$), andesine ($Ca_xNa_{1-x}Al_{1+x}Si_{3-x}O_8$, $0.3 < x < 0.5$), anorthite ($CaAl_2Si_2O_8$), anorthoclase ($Na_{1-x}K_xAlSi_3O_8$, $0.1 < x < 0.35$) , bytownite ($Ca_xNa_{1-x}Al_{1+x}Si_{3-x}O_8$ $0.7 < x < 1.0$), ferrihydrite (Fe5OHO.nH2O, goethite (□-FeOOH), hematite (□-Fe_2O_3), halloysite ($(2H_2O)Al_4Si_4(OH)_{10}O_8$), illite, kaolinite/ dickite ($Al_4Si_4O_{10}(OH)_8$), labradorite ($Ca_xNa_{1-x}Al_{1+x}Si_{3-x}O_8$ $0.5 < x < 0.7$), microcline ($KAlSi_3O_8$), orthoclase ($KAlSi_3O_8$), oligoclase ($Ca_xNa_{1-x}Al_{1+x}Si_{3-x}O_8$ $0.1 < x < 0.3$), quartz (SiO_2), sanidine ($Na_{1-x}K_xAlSi_3O_8$, $0.35 < x < 1.0$), smectite ($((M^+_{0.33}, H_2O)[Si_8][Al_{3.34}(Mg, Fe^{2+})_{0.66}]O_{20}(OH)_4)$), vermiculite ($((M^+_{1.48}, H_2O)[Si_{7.12}Al_{0.88}][Al_{2.8}Mg_{0.6}Fe^{3+}_{0.6}]O_{20}(OH)_4)$).

ABSTRACT

The extent of research conducted in soils, mineralogy and pedogenetic processes in Ecuador is limited despite the country's unique geographic location and properties. The aim of the research is to provide mineralogical and physicochemical characterization of the soils in the northeastern quadrant of the Río Napo floodplains in order to better understand their (trans)formation history and the implications on nutrient dynamics and best agricultural practices to protect the fragile ecosystem. Soils were characterized for texture, pH, percent organic matter and residual acidity in the laboratory. The < 53 µm fraction of the soil was further investigated using powder X-ray diffraction and FEG-SEM analyses. Initial insights from three distinct regions (plinthic niti- and ferralsols; fluvic ali- and acrisols; arenic fluvisols) are reported and discussed. Ali-/acrisols and arenic fluvisols are dominated by primary feldspar minerals and muscovite with secondary mineral formation of kaolinite, illite/smectite and vermiculite. Quartz is not dominant in sandy textured soils. Throughout the landscape plinthic niti- and ferralsols protrude with dominant kaolinite-quartz-amorphous iron oxide mineralogy. These soils are very strongly acidic with significant acidification potential below pH 4, no organic matter and significant hardpan (plinthite) formation. In contrast the ali-/acrisols and fluvisols in the region are moderately acidic with OM accumulations in the A horizon up to seven percent. The substantial differences in mineralogical and physicochemical properties warrant future individual assessments of nutrient dynamics in order to support local farmers in their nutrient management.

KEYWORDS: Pedogenesis, XRD, FEG-SEM-EDS.

INTRODUCTION

The extent of research conducted in soils, mineralogy and pedogenetic processes in Ecuador is limited despite the country's unique geographic location and properties (Figure 1) and concomitant soil forming processes (Buytaert *et al.*, 2006; Buytaert *et al.*, 2007; Buytaert *et al.*, 2005; Quesada *et al.*, 2011; Zehetner and Miller, 2006; Zehetner *et al.*, 2003). Previous research into soil formation has focused primarily on soils in the Cordillera Real and Occidental (Buytaert *et al.*, 2006; Buytaert *et al.*, 2007; Buytaert *et al.*, 2005; Zehetner and Miller, 2006; Zehetner *et al.*, 2003) with few or no published studies from the Amazon or the coastal plains (Dijkshoorn *et al.*, 2005; Quesada *et al.*, 2011; van Engelen and Dijkshoorn, 2013). Soils in Amazonía of Ecuador do not solely consist of red laterites, but instead comprise a broad range of soil types, e.g., acri- and alisols (ultisols, U.S. Soil Taxonomy), cambisols (inceptisols, U.S. Soil Taxonomy), and fluvi- and gleysols (entisols: fluvents and aquents, respectively, U.S. Soil Taxonomy), among others (Quesada *et al.*, 2011). According to the SOTERLAC database of the FAO (Dijkshoorn *et al.*, 2005; Quesada *et al.*, 2011) acri- and cambisols dominate in the Andean foreland of the Ecuadorian Amazon, however, local and regional soil variability suggest that multiple soil taxa coexist on very small/short spatial scales. The history of the landscape formation as summarized by (Hoorn *et al.*, 2010) provides important clues for present day observed variability. Of specific importance to soil and landscape formation in the Andean foreland are the sedimentation events due to the ice melts of the last ice age (Holocence, 0.01 million years ago) and the increased sediment accumulation in the foreland as a function of the Andean orogenesis in general.

The region of study of our work comprises the north-eastern (NE) quadrant of the Rio Napo floodplain near the town of Francisco de Orellana (Orellana, Ecuador). The aim of the research is to provide mineralogical and physicochemical characterization of the soils of this region in order to better understand their (trans)formation history and the implications on nutrient dynamics and best agricultural practices to protect the fragile ecosystem. In this abstract we describe initial insights gained from three distinct sites: *Loma Coloradas* (Parroquia Sacha), the Parroquia San Carlos, and the Parroquia Enokanqui **(Figure 1).**

METHODS AND MATERIALS

Study Site and Sampling Procedure

The study site is located circa 90 Km to the east of the Andean Mountain Range at an average elevation of 260 m.a.s.l **(Figure 1)**. Each location was recorded for its geographic position (longitude, latitude) and elevation (m.a.s.l.) using a GPS (Garmin GPSMAP 62sc; Schaffhausen - Switzerland). Soil samples and profiles were dug with a spade and samples were transferred into clear plastic bags, labeled and stored in the laboratory in a dark, air-conditioned place (~ 25±1ºC) prior to analysis.

Sample Preparation and Laboratory Measurements

All samples were dried under greenhouse conditions for ~ 48-72 h before being disintegrated in a soil mill (Fritsch Soil Mill Pulverisette 8, FRITSCH GmbH, Idar-Oberstein, FRG). The pH (1:2.5 (v/v) in distilled de-ionized water or 1:10 (v/v) 1M KCl), residual acidity (Al+H), soluble Al (in 1 M KCl), and texture were measured in the Laboratory for Soil and Water Anlysis of EECA using standard procedures published elsewhere (Thomas, 1996). A subsample of the whole soil (WS) was size-fractionated using a mechanical sieve (ANALYSETTE 3 PRO, FRITSCH GmbH, Idar-Oberstein, FRG) to obtain a <53 µm fraction for XRD and field emission gun scanning electron microscopy (FEG-SEM) analyses (see subsequent sections).

XRD, FEG-SEM and EDS Analysis

Powder X-ray diffraction (XRD) analyses were conducted at the Centre for Nanoscience and Nanotechnology (CENCINAT) of the Polytechnic School of the Armed Forces (ESPE, Ecuador) using an Empyrean Pananalytical diffractometer in Bragg-Bretano configuration and monochromatic Cu K_a (λ = 1.54056 Å, 45mA, 40 KeV). Eight patterns were measured over a range of 5 to 90º 2 theta (º2θ) at 16 rpm on the <53 µm soil fraction backloaded into a standard Panalytical sample holder. The averaged, co-added patterns were background corrected (HighScorePlus, v. 4.1.0). Diffraction peaks were fitted using Gaussian and Lorentzian functions to obtain a fitted peaklist of 35 to 115 peaks depending on the complexity of the diffraction pattern, and the number and type of phases present. Phase identification was conducted iteratively between the PhaseMatch function of HighScorePlus and manual assignment of the peaks to published peaklists of the suggested phases.

The <53 µm fraction was used for FEG-SEM (TESCAN MIRA 3XM) and energy dispersive X-ray spectrometry analyses (CENCINAT, ESPE - Ecuador). Between 5 and 8 particles were investigated using EDS analysis to determine their composition (F, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd and Pb) in mapping and/or point-acquisition mode.

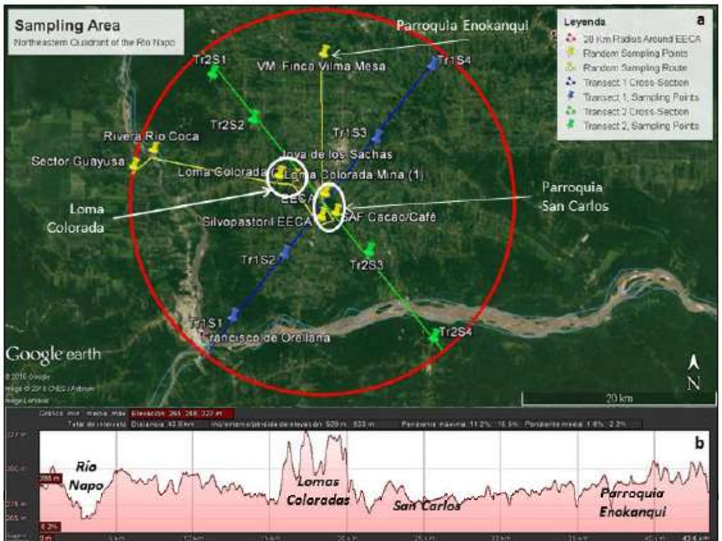

Figure 1. (**a**) Sampling locations of this study in the NE quadrant of the union of the Rios Napo and Coca near the town of Francisco de Orellana (Orellana, Ecudor). The yellow markers were sampled in April 2016, the blue (T1) and green (T2) transects were sampled in July 2016. (**b**) Elevational profile along the yellow sampling route.

RESULTS & DISCUSSION

Plinthic Niti- and Ferralsols, Lomas Coloradas

Laterite-like soils appear in the landscape as isolated knolls named *Lomas Coloradas* by locals and have hill tops starting at ≥ 280 m.a.s.l. with significant inter-knoll undulations whose depressions can lie as low as 230 m.a.s.l. The soils are bright red (5YR 4/4-4/6, **Figure 2**), are very strongly acidic in distilled deionized water (4.80-5.09, ø = 4.85±0.13) and extremely acidic in 1M KCl (3.70-3.79, ø = 3.74±0.03). Their texture is clayey with little or no organic matter. The residual acidity (Al+H) of these soils is significant (ø = 3.90 ±0.54 meq/100 ml soil) of which circa 50% appears to be due to "exchangeable" (in 1M KCl) Al (ø = 1.32 ±0.20 meq/100 ml). The mineralogy of these lateritic soils is dominated by quartz (SiO_2) and 1:1 type clay minerals (halloysite, kaolinite, traces of dickite) with small amounts of goethite present. FEG-SEM micro-graphs **(Figure 2)** show both platy and spherical 1:1 type clay minerals often in close association to each indicating slow transformation of halloysite (spherical particles) to kaolinite (plates, booklets) (Berthonneau *et al.*, 2015) or halloysite to kaolinite (Bobos *et al.*, 2001). Despite the prominence of their 001 reflection, the 1:1 type clay minerals can be considered strongly disordered based on their Hinckley Indices (HI) ranging between 0.24 and 0.57 (Plancon *et al.*, 1988)) Iron appears dominantly as amorphous coatings (ferrihydrite, $Fe_5O_3(OH)_9 \cdot nH_2O$) on all minerals (EDS analysis) consistent with diffraction data. The spheroidal morphology of halloysite is indicative of its rapid precipitation(Berthonneau *et al.*, 2015), likely due to inundation by Al and Si rich pore waters. Such pore waters are known to have descended the Andes as runoff during sedimentation periods during the late Miocene (circa 6.8 million years ago) and during the ice melts of the last ice age (Holocene, 0.01 million years ago) (Hoorn *et al.*, 2010), but may also be the result of in situ dissolution of primary minerals (e.g., feldspars; (Casey *et al.*, 1989)). In addition, hardpans (plinthic layers) may be observed at different depths speaking to periodic subsurface inundation and drying periods. Of all the soils present in this region, the *lomas coloradas* appear to be the most extensively, in situ weathered soils of this region.

Fluvic Ali- and Acrisols, Parroquia San Carlos

Soils in the San Carlos Parroquía occur between 248 and 279 m.a.s.l. Soils sit on planes intersected occasionally by small creeks. Their texture ranges between clayey and sandy clay loams, while the surface horizons tend have more clay than the subsurface horizons, which suggests that the soils formed from alluvial deposits. Texturally these soils are slightly coarser than the soils of the *Lomas Coloradas*, have high moisture content and darker colours (10YR 2/3 – 3/4) without significant redoximorphic features. Soil pH is moderately acidic ranging between 5.5 and 6.2 in distilled deionized water (ø = 5.75±0.25), but becomes very strongly acidic (4.1- 4.7; ø = 4.36±0.24) in 1M KCl. The organic matter content in the surface (A) horizon ranges between 2.6 and 3.0% and declines with depth (1^{st} B horizon: 0.8-1.1 %). The residual acidity in these soils ranges between 0.8 to 1.2 meq/ 100 ml soil (ø = 1.05±0.17), and Al contributes to the residual acidity between 20 and 50% increasing with finer textured soil particles.

The coarser textured particles stem from the presence of quartz and primary feldspar minerals. Feldspars in the surface horizons (oligoclase, albite, anorthite, plagioclase) of these soils are different from those in subsurface horizons (anorthoclase, bytownite, plagioclase). Kaolinite and illite are present in minor concentrations in the sample. Trace to low amounts of Al-goethite, hematite and gibbsite are present.

Arenic Fluvisols, Parroquía Enokanqui

The Parroquía Enokanqui is bound to the south and east by elevations as high as 300 m.a.s.l. to its west, the generally flat terrain (~ 290 m.a.s.l.) is dissected by a water carrying channel suggesting that the some of Parroquía Enokanqui sits on the floodplains of this channel. The soils are sandy over a 60-cm depth without being dominated by quartz but by primary feldspar minerals. The pH of the soils is moderately to slightly acidic (5.6-6-6; ø = 6.20±0.40) in distilled deionized water but becomes very strongly acidic in 1M KCl (4.6-5.3; ø = 5.0±0.30). The organic matter content is variable among A horizons and depends on the land use: 7.2% OM in the A-horizon of a forage field, which decreases to 2.6 and 0.8% OM over a 60-cm depth distance. In a neighboring plot (pasture under partial tree cover), the OM content was 2.6%. The residual acidity did

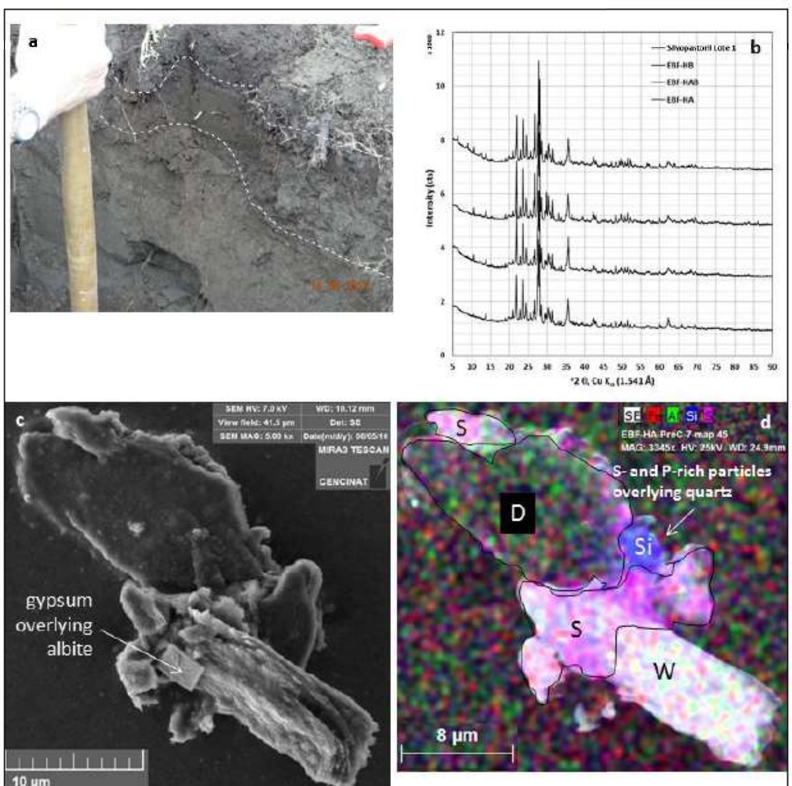

Figure 3. (**a**) Soil profile of a forage bank in the Parroquia Enokanqui. The dashed lines delineate the A, AB and B horizons from each other. All three horizons are dominated by sand sized particles, which according to their diffraction patterns (**b**) are not due to quartz, but feldspars. In addition to feldspar minerals, S- and P-rich minerals can be found according to multi-point EDS analysis. Clearly visible in (**c**) the electron micrograph is a rectangular gypsum ($CaSO_4 \cdot 2H_2O$) particle overlying what is likely albite ($NaAlSi_3O_8$). The Fe-Al-Si-S map (**d**) shows that the macro-agglomerate has distinct zones of different

not vary with depth (0.5-0.8, ø = 0.6±0.10) and was not a function of exchangeable Al, which is consistent with the dominantly feldspar mineralogy and only minor or trace concentrations of quartz, hematite, kaolinite, muscovite, and vermiculite (14- and 17-Å, **Figure 3**). The mineralogy and the lack of a change in texture classes between horizons indicates that the first three horizons in this soil did not weather in situ, but are likely three separate sedimentary layers. This can be in part supported by changes in the feldspar mineral distribution with depth: In the A-horizon, XRD analysis suggests the presence of plagioclase, anorthoclase, oligoclase and sanidinized orthoclase; in the AB horizon, oligoclase, plagioclase and sandinized orthoclase; and finally oligoclase and plagioclase in the B-horizon; i.e., with depth feldspars homogeneity increases. The secondary weathering products are 1:1 type clay minerals and vermiculite. The mineralogy and texture of the soils in the Parroquia Enokanqui strongly suggest that the soils are quite young, recently deposited (Holocene, 0.01 million years ago; (Hoorn *et al.*, 2010)) alluvial deposits and therefore create a substantial contrast to the soils that are present in the *Lomas Coloradas*.

CONCLUSIONS

The soil types and mineralogical properties that can be found in our study area point to distinct soil forming processes which involve alluvial deposition of coarse and fine grained minerals. It is well established that the formation of soils and the extensive channel and river systems in the Andean foreland was significantly affected by mass movement processes with the Andean orogenesis commencing during the late Paleogene period and more recently from ice melts of the last ice age (Holocene, 0.01 million years ago, (Hoorn *et al.*, 2010)). Particularly, these more recent events can well explain the presence of sandy, coarse textured soils in the Parroquia Enokanqui as well as the extensive presence of feldspar minerals in the soils of Parroquia San Carlos. The Lomas Coloradas, which appear as individual, unconnected elements are more problematic to explain, because their actual age and depth remain unclear to us. It is clear from these basic properties that the management of these soils has to take significantly different approaches. Future research in this area therefore needs to focus on establishing these differences based on mineralogical and hydrological properties in order to support local farmers in their fertilizer management.

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