Reassessment of the Microbial Role in Mn-Fe Nodule Genesis in Andean Paleosols

W. C. MAHANEY, D. H. KRINSLEY, C. C. R. ALLEN, J. DITTO, K. LANGWORTHY, A. D. BATCHELOR, M. LECOMPTE, M. W. MILNER, K. HART, S.S. O'Reilly, B. P. KELLEHER, and R. G. V. HANCOCK

QUERY SHEET

This page lists questions we have about your paper. The numbers displayed at left can be found in the text of the paper for reference. In addition, please review your paper as a whole for correctness.

Q1. Au: Please confirm all authors and affiliations appear correctly.
Q2. Au: Please confirm correspondence address appears correctly.
Q3. Au: Is short title Ok?
Q4. Au: Please confirm acknowledgments and funding information appear correctly.
Q5. Au: In the Canelon 1976 reference, please provide city for Michigan Technological University.
Q6. Au: For the Giegengack 1984 reference, please provide the publisher location.
Q7. Au: For the Hem 1989 reference, please provide the publisher location.
Q8. Au: For the Lugo 1994 reference, please provide publisher and publisher's location.
Q9. Au: Is there a page range for the Malagon 1982 reference citation?
Q10. Au: For the Mason 2008 reference, please provide location of conference.
Q11. Au: Please provide the publisher location for Oyama and Takehara 1970.

TABLE OF CONTENTS LISTING

The table of contents for the journal will list your paper exactly as it appears below:

Geomicrobiology Journal (2014) **0**, 1–15
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-0451 print / 1521-0529 online
DOI: 10.1080/01490451.2014.920939

Reassessment of the Microbial Role in Mn-Fe Nodule Genesis in Andean Paleosols

W. C. MAHANEY[1]*, D. H. KRINSLEY[2], C. C. R. ALLEN[3], J. DITTO[4], K. LANGWORTHY[4], A. D. BATCHELOR[5], M. LECOMPTE[6], M. W. MILNER[7], K. HART[8,9], B. P. KELLEHER[9], and R. G. V. HANCOCK[10]

[1]*Quaternary Surveys, Thornhill, Ontario, Canada*
[2]*Department of Geological Sciences, University of Oregon, Eugene, Oregon, USA*
[3]*School of Biological Sciences, Queen's University Belfast, Belfast, Northern Ireland*
[4]*CAMCOR, University of Oregon, Eugene, Oregon, USA*
[5]*Analytical Instrumentation Facility; North Carolina State University, North Carolina, USA*
[6]*Center of Excellence in Remote Sensing Education and Research; Elizabeth City State University, Elizabeth, North Carolina, USA*
[7]*MWM Consulting, Toronto, Ontario, Canada*
[8]*School of Biological and Chemical Sciences, Queen Mary's University of London, Mile End, London, United Kingdom*
[9]*School of Chemical Sciences, Dublin City University, Dublin, Ireland*
Q1 [10]*Medical Physics and Applied Radiation Sciences, McMaster University, Hamilton, Ontario, Canada*

Received November 2013, Accepted April 2013

The presence of Mn-Fe nodules in the epipedons (surface horizons) of paleosols of presumed Upper Neogene age in the northwestern Venezuelan Andes have been interpreted as products of inorganic oxidation and reduction processes operating over the full range of glacial and interglacial cycles that affected paleosol morphogenesis. New microscopic/chemical data from combined SEM-EDS-FIB analyses of representative Mn-Fe nodules indicate microbes play an important role in Mn/Fe precipitation leading to their genesis in alpine Mollisols (Argiustolls). Although the prevailing new data is based mainly on fossil forms of filamentous bacteria and fungi and other biogenic pseudomorphs that may represent the former resident bacteria, the presence of extant microbes must await field experiments/collection, followed by a molecular microbiology approach to determine the biological drivers of metal precipitation. As in other terrestrial niche environments, microbes are seen here to play a role, perhaps a key one, in the morphogenesis of paleosols of importance in upper Neogene paleoenvironmental reconstruction.

Keywords: andean paleosols, microbial assisted soil nodule growth, Mn nodules, redox role in nodule genesis reassessed

Introduction

Relict paleosols in the northwestern Venezuelan Andes, formed in a metaargillite residual regolith, are home to Mn-Fe nodules in their surface epipedons (Mahaney et al. 2002). Although relatively dry now, the paleosols are considered to have been wetter in the past with soil moisture capable of translocating appreciable amounts of clay to form argillic horizons and with fluctuating redox conditions conducive to the genesis of the nodules. The paleosols are similar to Placosols (Tilsley 1977) of the Canadian taxonomy (Canada Soil Survey Committee, 1977) which form in the cool moist climates, especially wetlands of the Pacific and North Atlantic Provinces of Canada. In the U.S. taxonomy these profiles classify as Typic or Aridic Argiustolls and some are known to contain Mn-Fe nodules (Soil Survey Staff 1999). In some localities similar nodular forms are referred to as concretions (Alhonen et al. 1975; Arshad and St. Arnaud 1980; Childs 1975; Orel'skaya 1974) or accretionary growth structures (Baker 1962). Because such forms in soils and paleosols are called nodules, we retain the usage of the USDA taxonomy (Soil Survey Staff 1999).

Because the nodules contain an "onion skin" spherical internal morphology, contain inordinately high concentrations of Mn and Fe, and are associated with well-formed Bt horizons, their antiquity is considered to date at least to the earliest stages of Pleistocene glaciation and possibly earlier to the Middle Neogene (~10–12 Ma). Previously, the red profiles with which the nodules are associated were thought to have formed at low elevation prior to recent uplift and fault displacement of the surface (Vivas 1974), and these were later termed paleo-Oxisols by Giegengack (1984). This classification and link to recent tectonic uplift was disputed by Ochoa and Malagon (1981), Malagon (1982) and Bezada and Schubert (1987) and Mahaney et al. (2002). The final argument

---

Q2 *Address correspondence to W. C. Mahaney, Quaternary Surveys, 26 Thornhill Ave., Thornhill, Ontario L4J1J4, Canada; Email: arkose41@gmail.com

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/ugmb.

against a paleo-Oxisol history of these profiles rests on the presence of the nodules since such are unknown or very rare in tropical lowland pedons (Soil Survey Staff 1999).

At least four hypotheses can be invoked to explain the nodules and the paleosols in which they reside. Pre-Pleistocene tropical soils might have been developed in low elevation tropical forests and later elevated into the cool alpine environment, but then rapid development of the nodules would have had to occur within <100 kyr. Second, Mn-Fe solutions may have been hydromorphically delivered from fractures in the Boconó Fault to drain across an erosion surface in the Boconó Trench with alternating wet and dry climates, and hence, fluctuating redox potential, all dating from the Pliocene or possibly Early to Middle Pleistocene which is in accord with the expected genesis time for the nodules. Third, *in situ* development of alpine soils, later converted to paleosols with alternating ice age climates, formed in accordant upland levels in a paludic environment from Mn-Fe rich argillaceous metasediments, culminating in a red paleosol with nodules forming from wet-dry cycles. A fourth hypothesis invokes combined hydrogeochemical and microbial interactions leading to Mn-Fe nodule genesis.

Although hydrogeochemical processes are completely compatible with known climatic perturbations over the Plio-Pleistocene-Holocene time frame, previous work (Mahaney et al. 2002) was unable to confirm the presence of microbes to comply with microbial models (Bougerd and De Vrind 1987; Ghiorse 1980, 1984; Robbins et al. 1992). Recent investigations of selected nodules using SEM-EDS-FIB instrumentation yielded new data corroborating with the presence of internal prokaryotic and fungal components that support a microbial influence mediating nodule genesis (Golden et al. 1992). A significant recent study has shown, for the first time, that there are unique microbial communities that are associated with Mn-Fe nodules that differ from the surrounding environment (He et al. 2008; Tully and Heidlberg 2013). Here we establish new evidence supporting a microbial role in Mn nodule genesis in ancient paleosols, fine-tuned to Andean tectonics and multiple glaciations, that is based on the use of Mn and Fe possibly being reduced by anaerobic bacteria through respiration.

The field site is located in a prominent flat interfluve south of the Rio Chama at 2200 m above sea level (Figure 1). Although relatively dry now (MAP = 750 mm), these sites

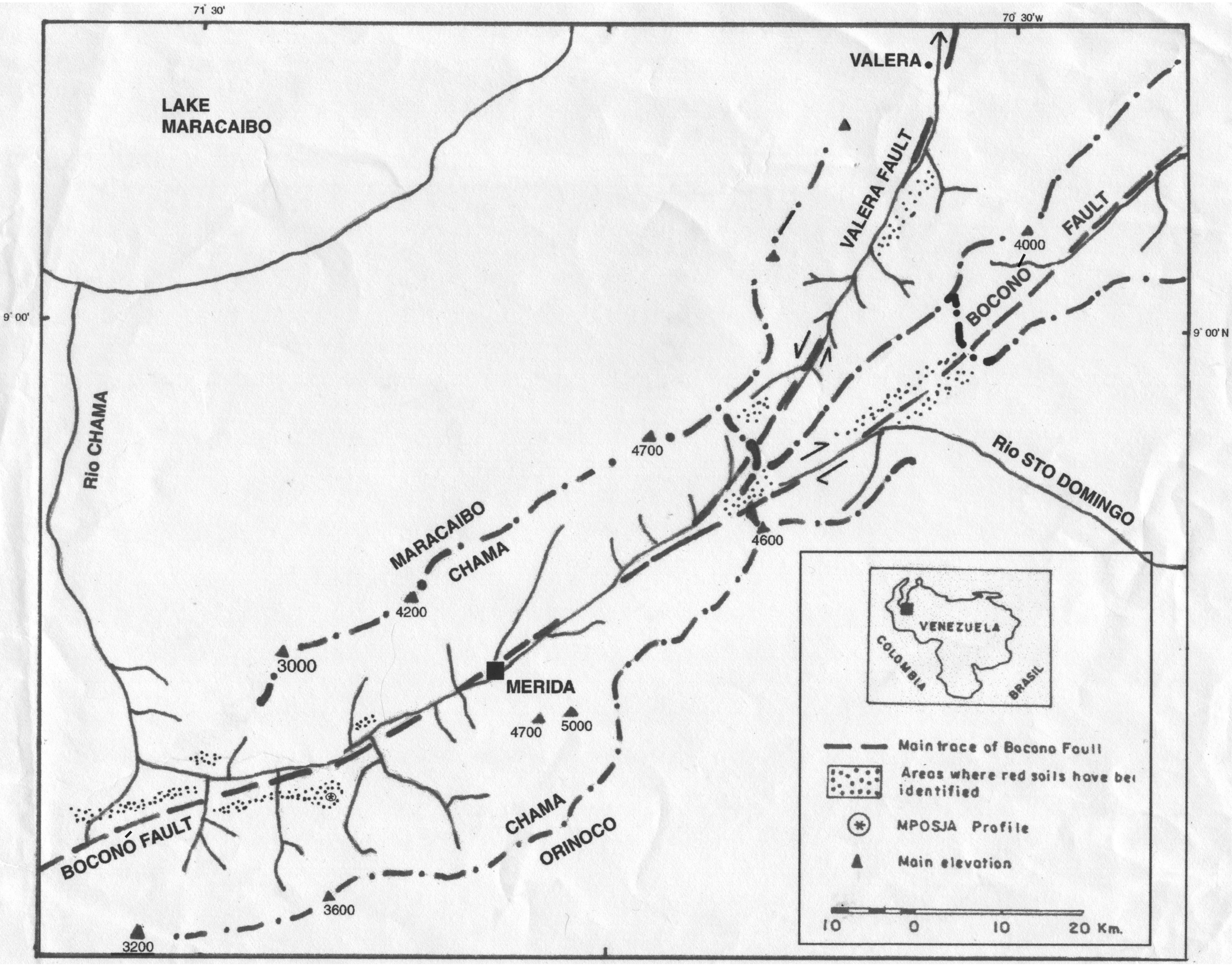


Fig. 1. Location of the MPOSJA Profile southwest of Mérida, Venezuela near the Boconó Fault and red paleosols. Catchment boundaries for the Rio Chama, Lake Maracaibo, and Rio Orinoco are indicated.

during wetter climates supported a dry woodland. Bedrock in the field area belongs to the Tostosa Formation of Late Paleozoic age, described by Canelon (1976) and Canelon and Garcia (1977), which comprises slate, phyllite, schist, gneiss and amphibolite. The bedrock at the field site is phyllite, overlain with locally derived regolith (2Cox horizons) and aeolian (Ah, Bt horizon complex)-influxed silt. The original lithic sediment is argillite with minor arenite that includes both *in situ* chemical and detrital facies, as implied by metamorphic minerals rich in elements inherited from sediment that contain anomalous Mn, Fe, S, C, P, and Ti.

Regional Background

As part of a Precambrian to Paleozoic metamorphic complex cut by igneous rocks of Permian age, the basement comprises the Mérida Arch, active beneath Cretaceous and Paleogene basin sediments dating from 150 to 100 Ma and again from 56 to 50 Ma (Cordani et al. 2000; Lugo 1994; Pindell et al. 1998).

The geologic history and sedimentation accompanying the uplift here allow for the preservation of paleosols. It also places constraints on the time component in the development and preservation of lowland tropical soils. The Mérida Arch basement complex emerged as the southern and central Mérida Andes in very late Oligocene time (~25 Ma) (Higgs 1993), accompanied by deposition of conglomerates in adjacent sedimentary basins. Much of the Mesozoic cover and Paleogene alluvial apron sediment was eroded as the Andes continued to rise through the Upper Neogene.

The regional paleodrainage pattern southwest of the Mérida Andes (Hoorn et al. 1995) highlighted a paleo-Orinoco River draining through much of Colombia and Venezuela. Uplift of the eastern Cordillera in Middle Miocene time restricted northward drainage by allowing eastward capture by the neo-Orinoco River drainage basin. Initially this drainage was north of the present Orinoco, close to the proto-Mérida Andes, later shifting southward (Pindell et al. 1998). Concomitant with this pattern of evolution, a high gradient proto-Rio Chama extended headward into the rising Mérida Andes and eastward along the Boconó Fault zone (Figure 1).

Materials and Methods

The profile (Figure 2A) was described using standard nomenclature and terminology (Birkeland 1999; Mahaney 1990; Soil Survey Staff, 1999); and Canada Soil Survey Committee (1977). Soil colors are from Oyama and Takehara (1970). Organic carbon was determined following methods established by Walkley (1935).

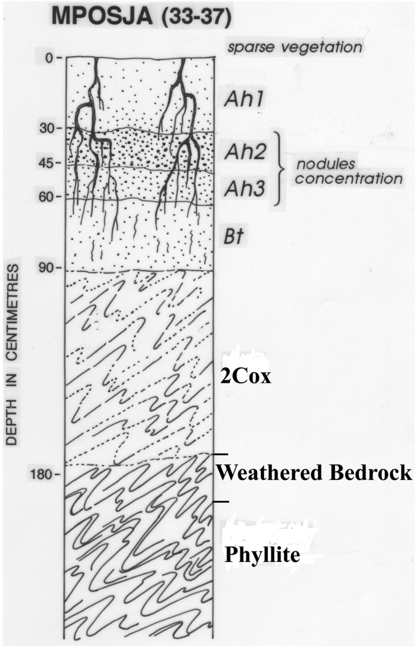
Samples from each horizon were air dried in the laboratory and later sieved to separate coarse material (>2 mm) from sand, silt and clay. The silt/sand boundary of 63 μm (see Folk 1968) follows the Wentworth scale and the silt/clay boundary of 2 μm conforms to the Soil Survey Staff (1999). The <2 mm fraction was subsampled for moisture content and the air-dried equivalent of 50 g oven-dried soil was analyzed for particle size. The coarse fraction (2 mm–63 μm) was fractionated by wet sieving and oven-drying the sands; the fine fraction (<63 μm) was analyzed by hydrometer (Day 1965).

The Mn-Fe nodules were pulverized in a mortar and centrifuged onto ceramic tiles. The clay fraction, also centrifuged onto ceramic tiles, was analyzed on a Philips X-ray diffractometer following procedures established by Whittig (1965). A portion of the Ah2, Ah3 and 2Cox horizons were examined for heavy minerals and general mineralogy, the results of which are fully documented by Mahaney et al. (2002) and follow from the lithology mentioned above. Some nodule chemical content may derive from solutes in ground water or organo-metallic compounds in plant porphyrins. Iron and Al extractions follow methods outlined by Coffin (1963) and Mahaney et al. (1999) with leach concentrations analyzed by atomic absorption spectrophotometry (AAS) using a Perkin Elmer 373 instrument. The Fe/Al extracts analyzed include Na-pyrophosphate (Al_p), acid ammonium oxalate (Fe_o) and Na-dithionite (Fe_d) following methods fully outlined by Mahaney et al. (2013).

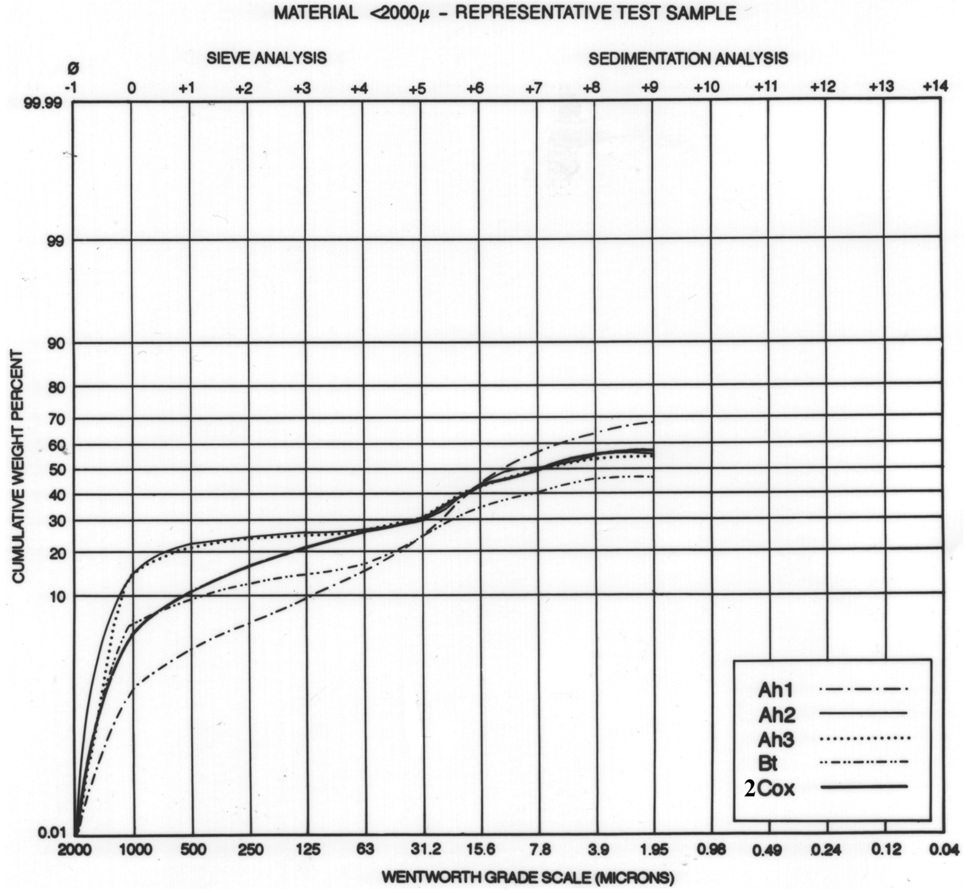
Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS), following procedures established by Vortisch et al. (1987) and Mahaney (1990, 2002) was used to study the nodules. Samples were analyzed in SE mode at 15 keV unless otherwise noted. All samples were carbon coated unless otherwise noted and excited at 15 keV. Several hundred individual nodules were selected for study from the surface horizons of the profile. A portion of these nodules were cross-sectioned but not polished to reveal internal structure and compositional variations, and others were ground for mineral and chemical analyses. In order to determine elemental compositional differences between fossilized microbial remains and the nodule, the SEM was operated in static probe mode.

That is the electron beam was placed on the feature to be analyzed and held there while characteristic X-rays were collected and analyzed by the EDS system. For this part of the SEM/EDS analysis the sample was not carbon coated or sputter coated with a conductive metal. The SEM was operated in variable pressure mode at an analysis chamber pressure of 30 Pa to help dissipate surface charge on the area of interest under the electron beam. The sample was imaged with a scanned electron beam at an accelerating voltage of 20 kV utilizing an annular scintillater Robinson backscattered electron detector. A light element SiLi drift X-ray detector with an ultra thin window was used to collect and analyze the characteristic X-rays emitted from the region of interest underneath the static 20 kV electron probe.

Total Fe was determined by instrumental neutron activation analysis (INAA) at the SLOWPOKE Nuclear Reactor at the University of Toronto. Calibration was achieved using suitable standards following methods established by Hancock (1984).



(A)



(B)

Fig. 2. (A) MPOSJA paleosol in the northern Venezuelan Andes; B, Grain size curves for the horizons in the MPOSJA profile. Sand is read directly from the curves, all horizons contain <30%; silt is read at the ~2.0 μm line less the sand quantity; and clay is read at the 2.0 μm line less 100%. With the exception of the Ah1 horizon, all samples are >40% clay content. The Bt horizon contains 10% more clay than horizons above and below and all samples classify as clay and silty clay loam in the USDA texture classification.

Results

Paleosol

The paleosol containing the Mn nodules is in residual regolith derived from phyllite and fluvial and wind-blown sediment. With a total depth of 180 cm, the epipedon of Ah and Bt horizons comprises a thickness of 90 cm. The underlying 2Cox horizon, formed entirely in residual and transported regolith shows little variation in mineralogy/chemistry throughout, and consists of rounded sands of presumed fluvial origin. Colors in the epipedon all fall within the 5YR hue, ranging from 1.1/1 in the Ah1 horizon, becoming lighter with depth to 5YR 4/6 in the Bt horizon (Oyama and Takehara 1970). Horizon boundaries are sharp and distinct. Details of the lithology of the coarse fractions are in Mahaney et al. (2002).

The Mn/Fe nodules, although most abundant in the middle of the epipedon in the Ah2 and Ah3 horizons, are also found to a lesser extent in the Bt horizon and all have diameters between 1 and 3 mm, occasionally larger. Spheroidal to ellipsoidal forms dominate, a minor percentage with elongate structure, sometimes with a drip edge, suggestive of previous leaching. All the nodules have both whole grain and asymmetric shell structures, the latter showing an 'onion skin' morphology of overlapping layers. Shells contain variable Si-rich zones and detrital quartz (10–100 μm) appears embedded within the shell structures in variable quantities. XRD analysis of one ~2.5 mm nodule showed prominent quartz with trace concentrations of glauconite (Mahaney et al. 2002), the latter, possibly from nearby marine rocks in Colombia, a likely source for Fe in the nodules.

Because the profile contains a thick Ah horizon complex over a thoroughly leached Bt horizon, which in turn overlies impermeable bedrock, all without any previous evidence of a microbial influence, the presence of the Mn/Fe-rich nodules was interpreted (Mahaney et al. 2002) to relate to a unique geohydrological regime requiring variable redox fluctuations over a long time period, perhaps dating from the Middle Neogene. A perched water table subject to considerable fluctuation was invoked, based on spikes of ferrihydrite (Fe_o), to explain the origin of the nodules.

As a member of the Mollisol soil order, the suspected antiquity warrants classification as a paleo-Mollic paleosol. In the U.S. soil taxonomy these paleosols classify as Typic or Aridic Argiustolls and many are known to contain Mn nodules. The Mollisol assignment is based upon color darker than 10YR 3/1 when moist and higher organic carbon in the Ah compared with the C horizons, fine granular structures in the epipedon and thickness of the argillic horizon. Soil texture shows an upward fining sequence typical of Mollisols (Figure 2B), with elevated silt in the Ah1 horizon.

Particle size distributions throughout the profile (Figure 2B) vary from silty clay loam to clay loam, with silt dominating in the surface epipedon. The upward fining sequence in the profile indicates an aeolian influence (Ah/Bt epipedon) of some magnitude and presumably considerable age as previously outlined by Mahaney et al. (2002). The subsoil 2Cox horizon, comprised of weathered and well-rounded residual material and fluvial sands mostly weathered to clay, presents a lithologic discontinuity in contrast to the aeolian origin of the paleosol epipedon.

The profile is moderately acidic (Table 1A) with pH uniformly close to ~6.0. Conductivity is bimodal, somewhat higher in the surface epipedon, decreasing in the Bt horizon and rising again in the 2Cox horizon. Organic carbon, while not high throughout, decreases from ~2.0% in the Ah1 horizon to a negligible 0.04% in the 2Cox horizon. Nitrogen follows suit with depth but increases markedly in the Ah2 and Bt horizons which may signal fluctuations in the microbial population where nodules are present. The cation exchange capacity (CEC) remains low in the Ah group of horizons, increasing somewhat with depth probably correlated to slight increases in clay content. Matching the percentage carbon against clay content indicates most of the CEC results from the <2 μm fraction.

Mn/Fe minerals in the nodules have a source presumably from the soil mineral composition itemized previously above and in Mahaney et al. (2002). Given the flat topography and impermeable substrate with no upslope moisture source, fluctuating water in the soil system is considered to be climate generated altering the redox potential either physically or biologically. The nodules presumably formed from a combination of oxidation/reduction events, caused by fluctuation of soil water modulated by capillary losses up profile in accordance with annual fluctuations in precipitation/evapotranspiration and further mediated by microbial influences.

Iron and Al extract data in Table 1B is of special interest regarding the age and microbial mediation of Mn-Fe nodule genesis. As originally discussed by Mahaney et al. (2002), the importance of Fe_o (acid ammonium oxalate extract) relative to microbial processes was overlooked, despite the ability of bacteria such as *Leptothrix* spp., or *Geobacter metallireducens* (Nealson and Saffarini 1994) to precipitate ferrihydrite, which is elevated in the Ah2 horizon (Table 1B). Additional weathering indices of Fe and Al, as shown in Table 1B, are based on raw data in Mahaney et al. (2002, Table 2). The

Table 1A. Chemical data for the MPOSJA profile, northwestern Venezuelan Andes

Horizon	Depth (cm)	pH (1:5)	Cond ($\mu S/cm^{-1}$)	Organic Carbon(%)	N (%)	C.E.C. (cmol/kg)
Ah1	0–30	6.2	39.4	2.19	0.210	18.0
Ah2	30–45	6.2	20.5	0.88	0.840	11.6
Ah3	45–60	6.0	23.6	0.44	0.560	18.1
Bt	60–90	6.0	26.8	0.18	0.800	25.5
2Cox	90–180	5.9	31.3	0.04	0.050	30.7

Table 1B. Extractable Fe and Al weathering indices

Horizon (material)	Alp/Alt	$Fe_o \times 1.7$	Fe_d/Fe_t	Fe_d-Fe_o	Fe_o/Fe_d
Ah1	0.02	0.7	0.65	1.68	0.20
Ah2	0.01	3.4	0.86	2.39	0.46
Ah3	0.01	1.4	0.83	3.05	0.21
Bt	0.01	0.6	0.71	2.71	0.11
2Cox	0.01	0.4	0.70	3.33	0.07
Wx (Cr)	0.01	0.3	—	—	—

Al_p/Al_t distributions, which act as proxies for organic carbon translocations (Parfitt and Childs, 1988), show almost no movement, values representing the low organic carbon reported in Table 1A. The Fe_o raw data in Mahaney et al. (2002), adjusted to represent an approximation of ferrihydrite (Parfitt and Childs 1988), show a near-fourfold increase in the Ah2 horizon, which likely indicates the activity of Mn-oxidizing bacteria, possibly *Leptothrix* (Chapnick et al. 1982; Nealson 1983). At the very least the high ferrihydrite (Feo) zone in the profile indicates a high soil water line and high reduction state.

The high ratios of Fe_d/Fe_t reported here equate to the near total consumption of Fe_t, which argues for considerable weathering time, quite possibly stretching into Pre-Pleistocene time. The function Fe_d-Fe_o reveals the approximate concentration of hematite plus goethite produced, less the amount of ferrihydrite. Taking the actual amounts as percentages, suggest that the lower 2Cox horizon is older than the aeolian-modified upper epipedon horizon complex. The Fe_o/Fe_d ratio, formerly the activity ratio of Dormaar and Lutwick (1983) and used to measure podzolization (Daly 1982), is now taken to be a measure of the slow conversion of Fe_o to Fe_d, which is substantiated by the raw data reported by Mahaney et al. (2002), and which shows a uniformly high concentration of total secondary Fe in the Ah3 and lower horizons.

Table 2. Chemistry of EDS spectra in Figs. 6B—10B

Sample	Element	WT %	Atomic %	Compound %	Formula
6B	Al K	4.32	5.04	8.15	Al_2O_3
	Si K	6.37	7.14	13.62	SiO_2
	K K	0.19	0.15	0.23	K_2O
	Mn K	36.11	20.72	46.63	MnO
	Fe K	19.01	10.73	24.46	FeO
	Ba L	6.19	1.42	6.91	BaO
	O	27.81	54.79	—	—
7B	C K	5.91	12.56	21.66	CO_2
	Al K	2.70	2.55	5.10	Al_2O_3
	Si K	4.89	3.99	9.39	SiO_2
	Mn K	24.61	11.43	31.78	MnO
	Fe K	21.55	9.84	27.72	FeO
	Ba L	3.89	0.72	4.35	BaO
	O	36.95	58.91	—	—
8B	C K	6.94	10.92	25.45	CO_2
	F K	1.00	0.99	0.00	
	Al K	0.67	0.47	1.27	Al_2O_3
	Si K	30.51	20.51	65.27	SiO_2
	Mn K	3.54	1.22	4.57	MnO
	Fe K	1.43	0.48	1.84	FeO
	Ba L	0.54	0.07	0.60	BaO
	O	55.36	—	—	—
9B	C K	16.06	23.68	58.86	CO_2
	F K	0.63	0.59	0.00	
	Al K	1.16	0.76	2.18	Al_2O_3
	Si K	9.48	5.98	20.28	SiO_2
	Mn K	9.63	3.10	12.43	MnO
	Fe K	3.07	0.97	3.95	FeO
	Ba L	1.49	0.19	1.66	BaO
	O	58.48	64.73		
10B	C K	6.17	9.78	22.62	CO_2
	Al K	1.93	1.36	3.65	Al_2O_3
	Si K	31.36	21.24	67.08	SiO_2
	Mn K	2.97	1.03	3.83	MnO
	Fe K	2.19	0.75	2.82	FeO
	O	55.38			

Microbial Data

Onion skin layers of the nodules are shown in Figure 3 and in the split nodule shown in Figure 4A show the "onion skin" layers as pointed out with arrows on the image. The porosity is also shown which argues against using $^{18}O/^{16}O$ to recover data on precipitation that might equate to paleoclimatic variations between glacials and interglacials. Within the inner core of the nodule a large rod-shaped microbe (Figures 4B, 4C), protrudes out of the mineral matrix. This may be a mineral sheath with bacterial cells encased within.

The chemistry determined by EDS indicates a composition of Fe $>$ Mn, Si, Al and minor Ti and K. It is possible the fossil contains orthoclase which is infrequently found in the mineral matrix. The Ti is probably from anatase which may have weathered from rutile, which is also infrequently encountered

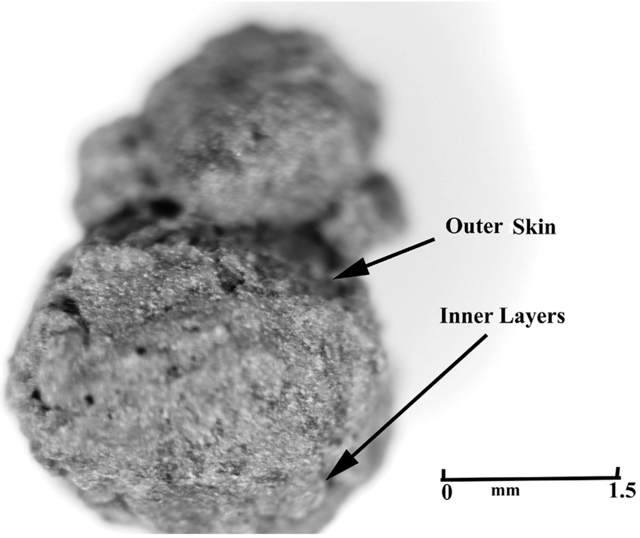
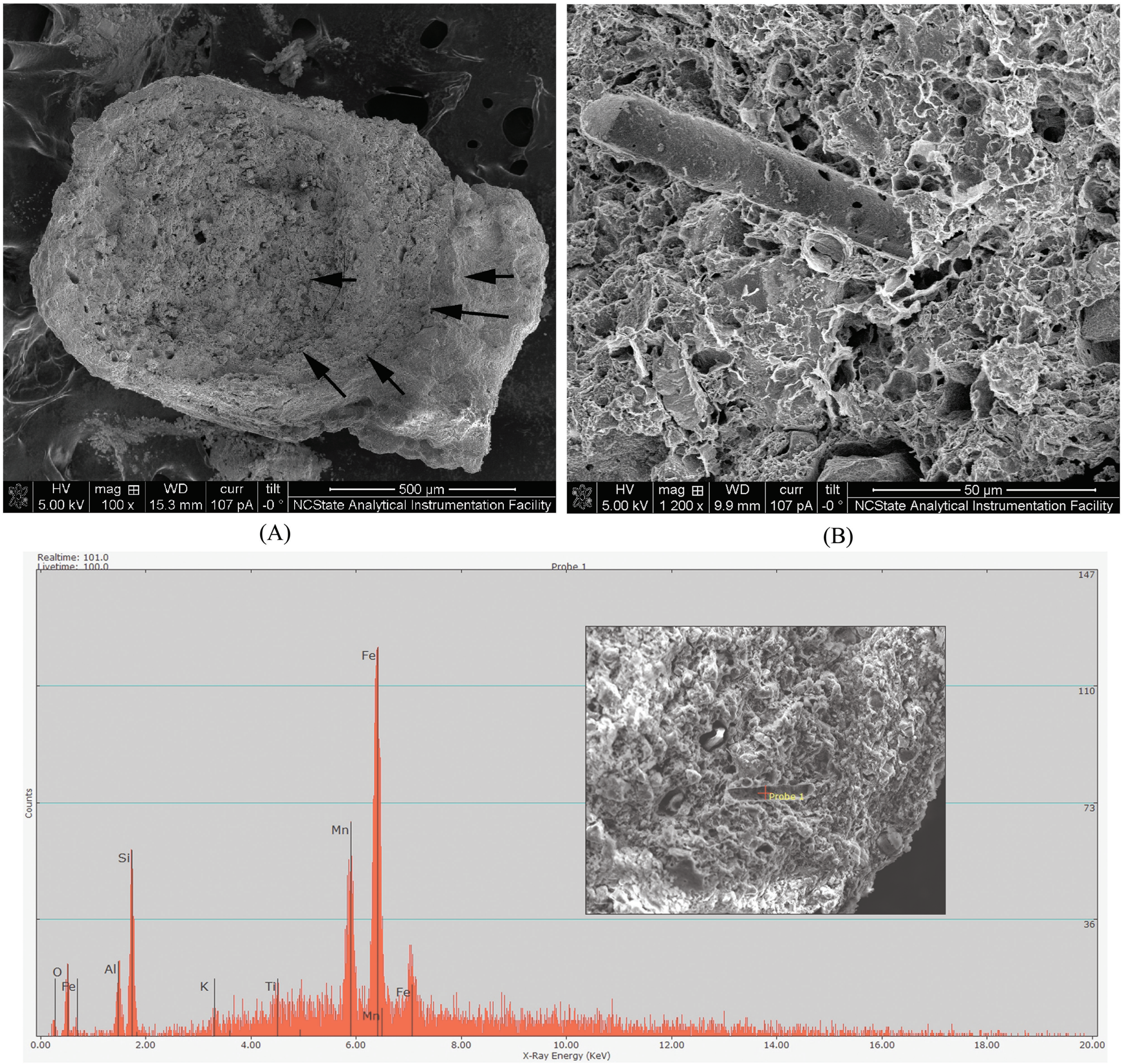


Fig. 3. Macrophotograph of representative nodules cemented together. "Onion skin" wrapping is identified (arrows) from the outer layer into the nodule.



(A)

(B)

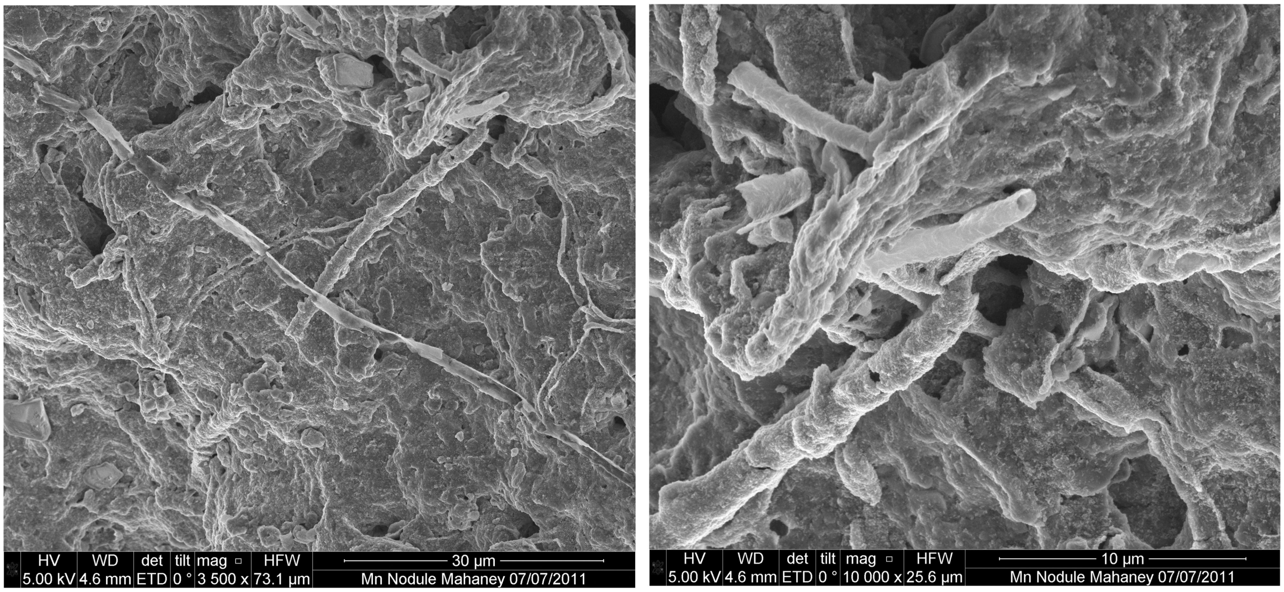
(C)

Fig. 4. (A) Cross-sectioned nodule (unpolished) showing concentric spherical layer; (B) Large fossilized bacteria rod (arrow; possibly *Leptothrix* spp.) (50–80 microns) protruding through a matrix of dehydrated cuspate clays and angular silt grains (parallel replicate of cross-section A); (C) Chemistry of the fossil bacteria pictured in Figure 4B. The relative abundance of Mn/Fe and absence of carbon in the static probe analysis shown in the inset in comparison to nearby points in the bulk. The spectrum shows oxy-hydroxide of Fe-Mn-Ti.

in the nodule matrix material. It should be noted that the rod-shaped feature was clearly richer in Mn and Fe by relative spectral comparison with the EDS data collected in static probe mode from locally probed background areas in the nodule. The presence of well-formed rods indicative of some bacteria (Emerson and Ghiorse 1993; Hashimoto et al. 2007) is strong evidence that microbes may play a significant role in nodule genesis in these Andean paleosols.

The presence of microbial filaments of 2–7 μm diameter (Figures 5A, 5B) argue for additional specimens of rod-shaped or filamentous bacteria similar in morphology to the specimen apparent in Figure 4B. Although this specimen may be of a fungal origin, it lacks the typical hyphae morphology common with soil fungi. The absence of hyphae is unsurprising due to the delicate structure of the fungal components, especially over geological time periods (Pirozynski 1976), and the loose nature of the surrounding mineral substrate.

Even if diagenesis resulted in slow degeneration of the hyphae, minor movement of sediment *in situ* or during sample retrieval processing, may have resulted in breakages and subsequent dispersion of the material. These filaments appear



(A) (B)

Fig. 5. (A) SEM image of nodule interior showing filaments of bacteria and fungi overgrowing silt sized detrital grains and dehydrated clay minerals. The delicate filaments preserved with the nodule suggest they grew *in situ* and that the nodule was a niche environment for these microbes if not caused by them. A biogeochemical origin is suggested by preservation of this delicate tissue and clay mineral coatings suggest the bacteria are not modern. (B) SEM enlargement of the upper right corner of Figure 5A. Individual filaments are up to 1 μm in diameter and greater than 10 μm long.

to be in different stages of diagenesis, some with nearly robust forms, others having lost considerable mass but all encrusted to varying degrees with mineralized coatings of Si and Fe oxides. These were, however, fully permineralized as none register relatively discernable carbon content with the EDS.

The filament shown in Figure 6A, with EDS spectrum in Figure 6B, reveals a specimen with minor carbon, which could indicate the organism is still extant and contributing Mn to the nodule matrix or is a contaminant. It may also indicate the presence of siderite, a Fe-carbonate, which has been linked to soil bacteria (Mason 2008). A more highly degraded filament is marked with an arrow in Figure 6A. Both specimens are within the range of normal bacteria dimensions (≥ 2 to ≤ 5 μm dia.). A similar situation is shown in Figures 7A and 7B (chemistry in Table 2). A slight adjustment of the chemistry in Figure 7B highlights the variable presence of residual carbon in Figure 7A.

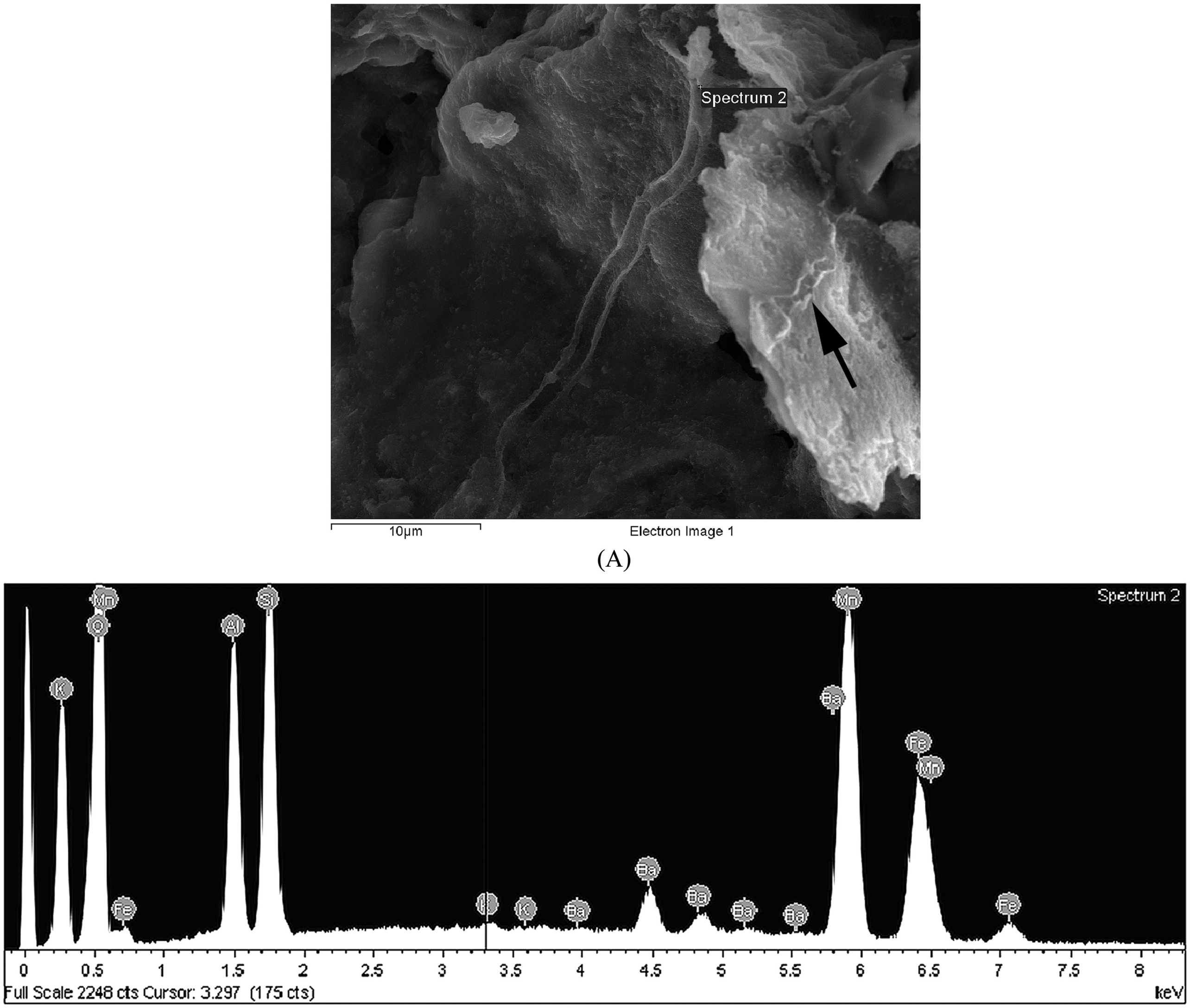
A ring structure microbe shown in Figure 8A contains rod and coccoid shapes detected on quartz near the outer nodule periphery. Elevated C in the structure suggests the candidate microbes may be recent and thus still active, although the imagery indicates minor encrustation. The carbon concentration is about 150% that of the coated mat, which is the carbon surface upon which the sample is fixed.

Encrusted and somewhat distorted filaments with what appear to be possible rod-shaped bacteria are shown at higher magnification (Figure 9A). The chemical composition in Table 2, with high carbon and low Si/Al, suggests the material is largely encrusted organics, the size further suggesting the forms are microbiological. Somewhat similar rod-shaped entities shown in Figure 10A register with less carbon, suggesting a quartz mineral dominated fabric (see Table 2 for chemistry).

Discussion

Existing bacteria, if extant, may well benefit from the presence of glauconite (Fe-rich analogue of illite), previously determined by XRD (Mahaney et al. 2002) and presumably of importance in microbe respiration. Because glauconite is a common Fe-silicate, known to form and degrade diagenetically (Ireland et al. 2006), it presumably may play a major role in microbe mediated nodule genesis over exceedingly long periods of time. Also, the presence of high concentrations of cerium (monazite-indicating chemical element) indicates appreciable phosphorus in a subsample of 15 nodules pulverized and analyzed by INAA (Mahaney et al. 2002). It should be remembered that inorganic phosphate may also have a microbial origin (Kulakova et al. 2011); however, INAA does not measure total P. Taken together, the documented presence of appreciable Fe determined by extract AAS measurements and XRD, together with the presence of P derived from monazite determined by INAA, previously considered by Mahaney et al. (2002) to postulate a microbe influence in nodule genesis, are now considered important evidence supporting the biologic proof presented herein.

Previously, Mahaney et al. (2002) tested three hypotheses to explain the origin of the Mn-Fe nodules in Andean paleosols. A tropical soil model with considerable longevity in the tropical lowlands, followed by recent uplift providing a chilled period during the last glaciation [originally proposed



(A)

(B)

Fig. 6. (A) Bacterial filaments in various stages of diagenesis—flattened (right), robust (left), the latter without a C signature; The spectrum (2) is derived from a spot analysis-upper left of the word spectrum. The robust form may have been fully permineralized whereas the flattened filament (arrow) was either still 'live' until it was desiccated and presumably coated; (B) EDS spectrum of the spot analysis (spectrum 2) indicated in Figure 6A; See chemistry in Table 2.

by Vivas (1974) and further supported by Weingarten 1977], was considered to produce a reddish tropical soil. Such a proposition requires the paleosol to classify as an Oxisol (Soil Survey Staff 1999), which is clearly not in agreement with the profile morphology. The tectonic/climatic interpretation of lowland weathering followed by recent uplift is not compatible with the frequent presence of garnets in the paleosol, minerals that are unlikely to survive tropical lowland weathering.

Manganese-Fe nodules are known to form in areas of cool, humid climate with seasonal rain (*see* Birkeland 1999). Waterlogged soils build up dense layers of decayed vegetation and organic matter which creates high water tables and reducing conditions. In the opposite mode of low water tables, B horizons become leached and oxidized. With an impermeable bedrock layer at <2 m depth, and any residual soil organics or water soluble organics, water saturation tends to promote anaerobic, reducing conditions, with reduction of Fe^{3+} to Fe^{2+} (Garrels and Christ 1965). As illustrated by Mahaney et al. (2002), these are the tenets of the geo-biochemical hypothesis, which make it a likely, but not the only, explanation of Mn-Fe nodule genesis in Andean paleosols. Allied with this model the aperiodic forced ejection of fluids from the Boconó Fault near the MPOSJA site locality may have produced a similar effect to climatic perturbations which created the hydrogeochemical fluctuating redox potential.

In the aforementioned conceptual model, by whichever source of fluids, the entire soil profile becomes saturated and slowly dries out from the top down. As this occurs organic matter is lost through oxidation, which most likely accompanies a transition from peaty surface horizons under wet conditions to A or Ah horizons in dry

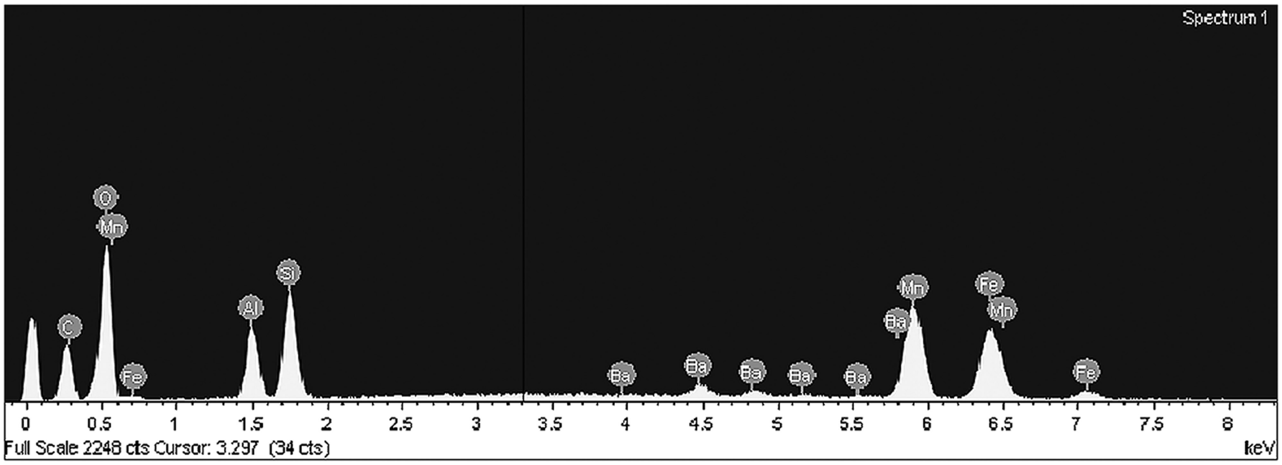
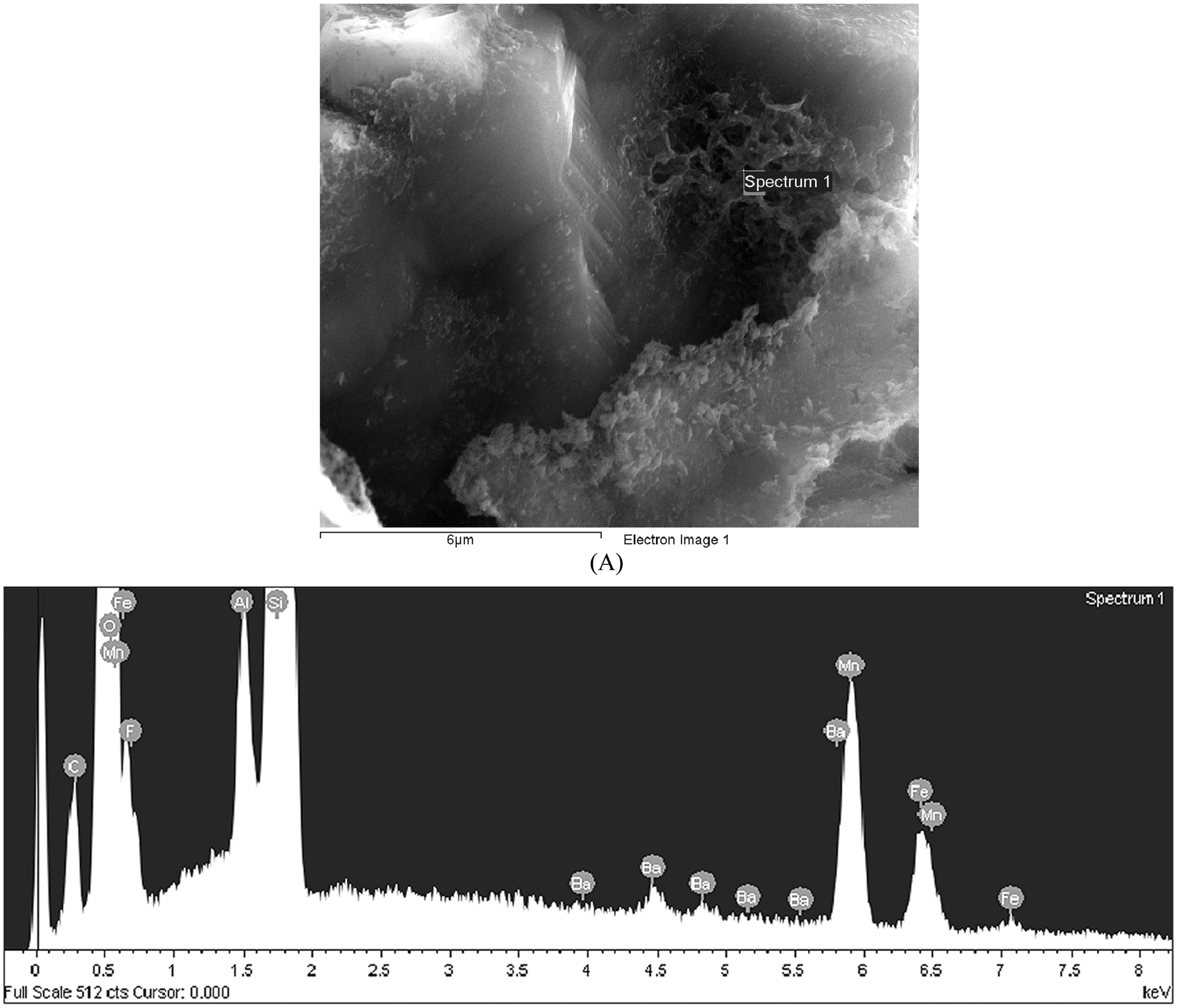


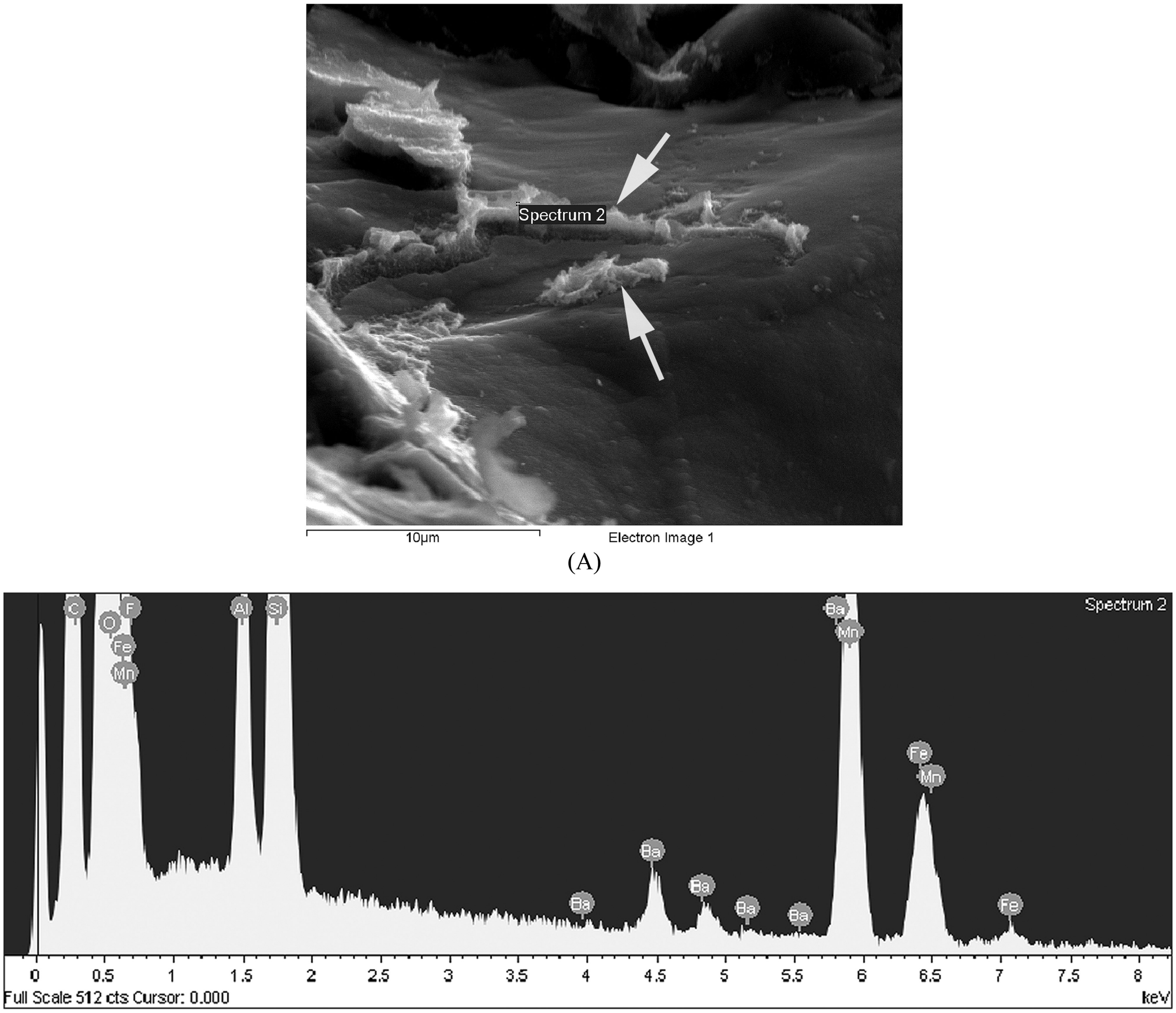
Fig. 7. Bacterial filaments in Figure 6A (Spectrum 1) showing carbon signature EDS. See Table 2 for chemistry.



(A)

(B)

Fig. 8. (A) Bacterial precipitates with a lacy overgrowth on detrital quartz in the nodule interior; (B) EDS spectrum taken from a spot analysis as shown on image in A. See chemistry in Table 2.



(A)

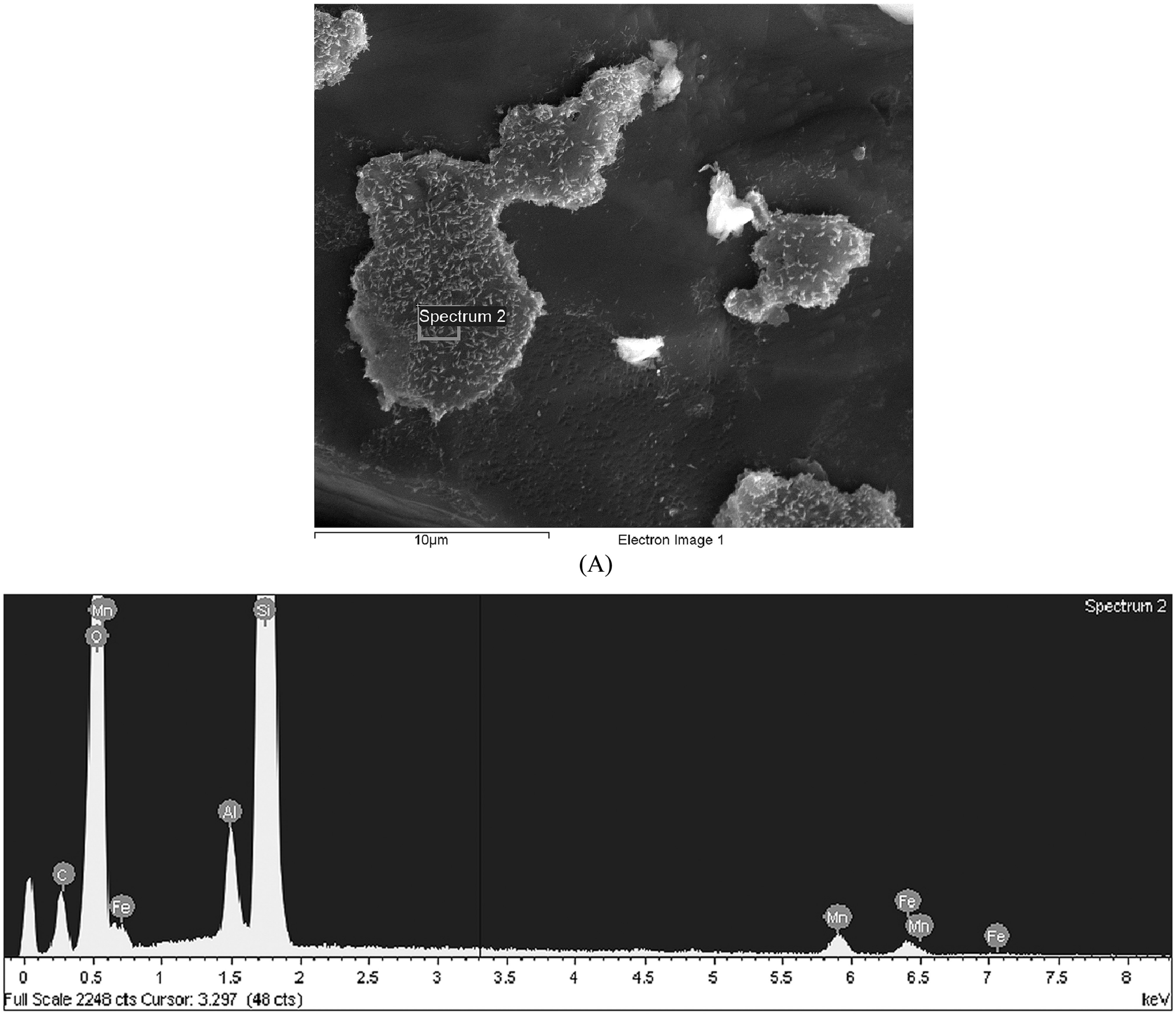
(B)

Fig. 9. (A) Encrusted microbial filaments (arrows) narrowly within the size range of bacteria and fungi. The microbial specimens are within the nodule surface. The coated surface carries a carbon coat wt.% of ~4%; (B) EDS showing considerable carbon retained by the microbes. See chemistry in Table 2.

times. It would be difficult to drain these soils laterally because the land surface is nearly flat. The Mn-Fe nodules, formed during wet periods (either during seasonal changes, long climatic cycles or fault zone emissions), which produced anaerobic conditions; they remained behind as relict features, modified in a freely dried-out Mollisol. The nodule diameters may be related to the length of time and/or number of times anoxic-reducing conditions occurred in the past. Certainly the observations support several oxidizing-reducing episodes.

Along with nodule growth and high concentrations of Mn, the accumulation of secondary Fe argues for an advanced age, possibly older than the Pliocene which supports previous tectonic interpretations of a Neogene age for the Andes (Erikson et al. 2012). Moreover, Fe extracts, principally Fe_d/Fe_t, have been used elsewhere to support weathering/age pedon interpretations of paleosols from young Holocene age (Mahaney et al. 2010; Mahaney and Kalm 2013) pedons to advanced but variable Neogene ages (Birkeland 1999; Birkeland et al. 1989; Mahaney et al. 2009, 2013) in pole to equator localities. The Fe extract data reported by Mahaney et al. (2002), and reinterpreted here, are fully in accordance with an advanced age for the Mn nodules. Given the concentric "onion skin" structure of the nodules, it is likely extractable Fe growth underwent punctuated development, stronger during wetter/warmer periods with a higher oxidation potential, and weaker during dry/colder times.

Concomitantly, increased moisture, coupled with higher temperatures and increased Fe release, produced robust microbial activity, and hence, Mn production. It is these cyclic events that have led to the concentric nodule



(A)

(B)

Fig. 10. (A) Rod-shaped bacteria colony distributed across or internal layer within an Mn-Fe nodule with considerable carbon compared with the surrounding carbon coated surface; (B) EDS showing considerable Si indicating the substrate is likely quartz. Chemistry in Table 2.

morphology making it likely Mn production is both a product of microbial reduction with saturation, and oxidation above. Attempts to elicit an ^{18}O archived record have been frustrated by nodule porosity and lack of an accessible or 'sealed-in' stable isotope record. A nanoscale probing of the internal structure of the nodules may well reveal ^{13}C fluctuations of changing vegetative biome cycles coupled to Plio/Pleistocene climatic oscillations.

This second hypothesis postulates the Mn-Fe nodules may have formed from Mn-Fe bearing argillaceous sediment maturing within a reddish paleosol with *in situ* growth of concentric "onion skinned" Mn-Fe nodules, with growth modulated by fluctuating redox conditions during Pleistocene glacial/interglacial cycles. Without microbial input the supply of Mn is essential to this model, the source limited to the presence of Mn garnets (spessartine) which are present throughout the 2Cox horizon of the profile. Alternatively, highly reactive clay minerals may provide an additional and more likely source of Fe/Mn.

Similar situations are known in slate belts of the subhumid temperate climatic belt, where Mn-Fe-Si nodules have been observed (Beals 1966; Schiller and Taylor 1965), a process that includes some bacterial amelioration (Chapnick et al. 1982; Ghiorse 1980, 1984; Ghiorse and Hirsch 1982). As enticing as this hypothesis is, the actual metal involved is not achievable in the parent material and the flat, nearly level bedrock at the site does not allow for the input of additional Fe and Mn from higher slopes (Mahaney et al. 2002). As an open system the site has been affected by climatic/biotic shifts, some of appreciably high magnitude which has modulated chemical weathering of the parent substrate and aeolian influxed sediment. Porphyrin disintegration from chlorophylls provide a wide metal spectrum but while the organic geochemistry of each horizon is unknown, abundant organics in the surface horizons may act as a filter to trap fines, i.e., clay and fine silt.

Given the previous absence of proof of microbial content, extant or fossil in these nodules, the data available up to 2002 supported a hydrogeochemical model rooted in inorganic oxidation/reduction processes similar to that discussed by Alhonen et al. (1975) and Milner et al. (1996). Because Mn and Fe are insoluble within similar pH and Eh ranges (Childs, 1973; Hem, 1989), dissolution and precipitation of Mn by microbes as opposed to inorganic redox fluctuations was considered likely (Burdige and Kepkay 1983; Ghiorse 1980, 1984; Ghiorse and Hirsch 1982; Robbins et al. 1992 and others), even if previously unsubstantiated (Mahaney et al. 2002). Although Chukrov et al. (1973) found that Mn oxidation is facilitated by Fe-oxidizing bacteria, Fredrickson and Gorby (1996) and Robbins et al. (1992) discovered the most common bacteria reducing Mn is *Leptothrix discophora*.

Interestingly, Chapnick et al. (1982) and Nealson (1983) showed the main Fe-hydroxide precipitated by *Leptothrix* is ferrihydrite, which was previously shown (Mahaney et al. 2002) to be most abundant in the Ah2 horizon of the MPOSJA paleosol where most Mn-Fe nodules reside. While we do not have microbial population sequencing data (e.g., bacterial 16S rRNA metagenome analysis) for the MPOSJA paleosol—and with the available data reported here, it is impossible to confirm changes in solubility of Mn^{2+} to less soluble Mn^{3+} and Mn^{4+} (all presumably microbially generated) (Tebo et al. 2005)—it is possible to confirm that microbes are present in the early stage of nodule genesis and extant forms existing are also observed in the outer nodule shell.

The presence of Ba (Table 2) in nearly all horizons, despite its low concentration, indicates that it may play a role in nodule genesis (ATSDR 2007). Barium is one of the most biologically inert elements – although it may have a role in some organisms that is largely unexplored (Wackett et al. 2004). Although Ba is considered much less effective as a substitute for Ca^{2+} or Mg^{2+} in microbial physiology, Ba sulfate does play a role in mechanoreceptor organelles found in members of the protozoa (genus Loxodes) *(Hubert et al. 1975)*.

While Mahaney et al. (2002) preferred an inorganic oxidation-reduction process similar to that described by Alhonen et al. (1975), it is shown here that microbial processes play an important role in the genesis of some nodules despite previous studies that indicate the apparent absence of bacteria in the Andean soil nodules (Milner et al. 1996). If we accept the concept of a microbial role in Fe/Mn nodule morphogenesis, it is then possible to propose that under anaerobic conditions bacteria may utilize available electron acceptors such as Mn/Fe oxides to facilitate energy metabolism, subsequently producing highly redox-sensitive Mn^{2+} and Fe^{2+} in reduced forms. These may then be reprecipitated as solid Fe and Mn minerals under oxic conditions by, perhaps, other bacteria (e.g., *Leptothrix spp*.). Essentially this is the same process as proposed by Mahaney et al. (2002) but with different bacteria enzymatically accelerating the process in various niches within the nodule.

Assuming prolonged anaerobic conditions occur during interglacial times, anaerobic biomineralization of organic matter would produce considerable quantities of soluble Mn^{+2} and Fe^{+2} for later precipitation. Such a cycle presumes the presence of both oxidizing and reducing bacteria (He et al. 2008) – facultative anaerobes would even perform both functions. The presence of both obligately aerobic and obligately anaerobic bacteria growing in a specific microenvironment is unlikely, but facultative anaerobes may play a role in complex biological processes taking place at aerobic/anaerobic boundary layers. Also, many aerobes and facultative anaerobes can survive in a dormant state under anaerobic conditions (perhaps as endospores) until the right metabolic conditions arise for further proliferation.

Conclusions

Mn/Fe nodules in Andean paleosols, formerly considered to be relict features formed during wet intervals when fluctuating redox conditions led to the growth of coarse sand to granule size layered elliptical spheres, are now known to have an origin partly mediated by microbes. The paleosol in which the nodules reside is now dry and part of a sparse vegetation complex of grassland with sparse trees. The working hypothesis that the nodules formed in water-saturated soils during wet paleoclimatic intervals without microbial input was based upon a lack of microbiological evidence. Recent evidence reported here shows that microbial forms, both fossil and possibly extant, exist within selected nodules, with the fossil specimens more deeply buried in nodule interiors.

Therefore, this new evidence indicates that while nodule genesis is assisted by redox fluctuations, microbial processes are likely responsible for Mn buildup. Further work incorporating metagenomic/molecular biology approaches may be required to determine the microbial diversity within these microsites to further expand upon the outlined hypothesis. Iron, especially Fe^{3+} as indicated by the Fe_d/Fe_t ratio, not only indicates advanced age and long-lived diagenesis, it also suggests Fe is an important requirement in microbial respiration in this particular ecosystem.

Acknowledgments

We wish to thank CAMCOR at the University of Oregon for the use of their facilities.

Funding

This research was funded by Quaternary Surveys, Toronto. Q4

References

Alhonen P, Koljonen T, Lahermo P, Uusinoka R. 1975. Ferruginous concretions around root channels in clay and fine sand deposits. Geol Soc Finl Bull 47:175–181.

Arshad MA, St. Arnaud RJ. 1980. Occurrence and characteristics of ferromanganiferous concretions in some Saskatchewan soils. Can J Soil Sci 60:685–695.

ATSDR (Agency for Toxic Substances and Disease Registry). 2007. Toxicological Profile for Barium and Barium Compounds. U.S. Department of Health and Human Services. Available at http://www.atsdr.cdc.gov/toxprofiles/tp24.html.

Baker G. 1962. Accretionary growth structures, southwest Victorian coast. Australia National. Museum, Victoria, Memoir no. 25, 17–46.

Beals HL. 1966. Manganese-iron concretions in Nova Scotia lakes. Marit Sedim 2(2):70–72.

Bezada M, Schubert C. 1987. Cronología cuaternaria en Venezuela. Algunos problemas metodológicos y pedológicos. Acta Cientifica Venezolana 38:1–12.

Birkeland PW. 1999. Soils and Geomorphology, 3rd edition. New York: Oxford University Press.

Birkeland PW, Burke RM, Benedict JB. 1989. Pedogenic gradients for iron and aluminum accumulation and phosphorous depletion in arctic and alpine soils as a function of time and climate. Quatern Res 32:193–204.

Bougerd FC, De Vrind JMP. 1987. Manganese oxidation by *Leptothrix discophora*. J Bacteriol 169:489–494.

Burdige DJ, Kepkay PE. 1983. Determination of bacterial manganese oxidation rates in sediments using an in situ dialysis technique I. laboratory studies. Geochim Cosmochim Acta 47:1907–1916.

Canada Soil Survey Committee. 1977. Soils of Canada, vol. 1. Ottawa: Supply and Services Canada.

Canelon G. 1976. Geology of the area of Mesa Bolivar-La Grita, States of Mérida and Tachira, Venezuelan Andes, M.Sc. Thesis, Michigan Technological University. Q5

Canelon G, Garcia R. 1977. Consideraciones sobre rocas del Paleozoico Inferior, Formacion Tostosa, en el flanco Norte de la Cordillera de los Andes, Memorias V Congresso Geologico Venezolano, Tomo I, Caracas, Venezuela, p227–252.

Chapnick SD, Moore WS, Nealson KH. 1982. Microbial mediated manganese oxidation in a freshwater lake. Limnol Oceanogr 27:1004–1014.

Childs CW. 1973. Relative mobility of iron and manganese in sedimentary processes. Nature Physical Science (London) 241(110):119.

Childs CW. 1975. Composition of some iron-manganese concretions from some New Zealand soils. Geoderma 13:141–152.

Chukrov FV, Zvyagin BB, Gorshkov A, Yermilova LP, Balachova VV. 1973. Ferrihydrite. Inter Geol Rev 16:1131–1143.

Coffin DE. 1963. A method for the determination of free iron in soils and clays. Can J Soil Sci 43:7–17.

Cordani UG, Milani J, Thomaz Filho A, Campos DA. (Editors) 2000. Tectonic Evolution of South America, 31st International Geological Congress.

Daly BK. 1982. Identification of podzols and podzolised soils in New Zealand by relative absorbance of oxalate extracts to A and B horizons. Geoderma 28:29–38.

Day P. 1965. Particle fractionation and particle size analysis. In: Black CA, (editor), Methods of Soil Analysis, Madison, Wisconsin, American Society of Agronomists, pp. 545–567.

Dormaar JF, Lutwick LE. 1983. Extractable Fe and Al as an indicator for buried soil horizons. Catena 10:167–173.

Emerson D, Ghiorse WC. 1993. Ultrastructure and chemical composition of the sheath of *Leptothrix discophora* SP-6. J Bacteriol 175:7808–7818.

Erikson JP, Kelley SA, Osmolovsky, P., Verosub, K.L. 2012. Linked basin sedimentation and orogenic uplift: the Neogene Barinas basin sediments derived from the Venezuelan Andes. J South Amer Earth Sci 39:138–156.

Folk RL. 1968. Petrology of Sedimentary Rocks. Austin, TX: Hemphill Press.

Fredrickson JK, Gorby YA. 1996. Environmental processes mediated by iron-reducing bacteria. Curr Opin Biotechnol 7(3):287–294.

Garrels RM, Christ CL. 1965. Soils, Minerals and Equilibria. San Francisco, CA: Freeman, Cooper and Company.

Ghiorse WC. 1980. Electron microscopic analysis of metal-depositing microorganisms in surface layers of Baltic Sea ferromanganese concretions. In: Trudinger AR, Walter MR, editors. Biogeochemistry of Ancient and Modern Environments. New York: Springer-Verlag. p345–354.

Ghiorse WC. 1984. Bacterial transformations of manganese in wetland environments. In: Klug MJ, Reddy CA, editors. Current Perspectives in Microbial Ecology. Washington, DC: American Society of Microbiologists. p615–622.

Ghiorse WC, Hirsch P. 1982. Isolation and properties of ferro-manganese-depositing budding bacteria from Baltic Sea ferromanganese concretions. Appl Environ Microbiol 43:1464–1472.

Giegengack R. 1984. Late Cenozoic tectonic environments of the Central Venezuelan Andes. In: Bonini WE, Hargraves RB, Shagam R, editors. The Caribbean-South American Plate Boundary and Regional Tectonics, Geological Society of America, Memoir 162:343–364. Q6

Golden DC, Zuberer DA, Dixon JB. 1992. Manganese oxides produced by fungal oxidation of manganese from siderite and rhodochrosite. Catena Supplement 21:161–168.

Hancock RGV. 1984. On the source of clay used for Cologne Roman Pottery. Archaeometry 26: 210–217.

Hashimoto H, Yokoyama S, Asaoka H, Kusano Y, Ikeda Y, Seno M, Takada J, Fujii T, Nakanishi, M, Murakami R. 2007. Characteristics of hollow microtubes consisting of amorphous iron oxide nanoparticles produced by iron oxidizing bacteria, *Leptothrix ochracea*. J Magnet Magnet Mater 310:2405–2407.

He J, Zhang L, Jin S, Zhu Y, Liu F. 2008. Bacterial communities inside and surrounding soil iron-manganese nodules. Geomicrobiology 25:14–24.

Hem JD. 1989. Study and interpretation of the chemical characteristics of natural water. 3rd edition. U.S. Geological Survey Water-Supply Paper 2254. Q7

Higgs R. 1993, Sedimentological evidence for early uplift (Oligocene)of the Venezuelan Andes (abs), American Association of Petroleum Geologists Bulletin 77:325.

Hoorn C, Guerrero J, Sarmiento GA, Lorente MA. 1995. Andean tectonics as a cause for changing drainage patterns in Miocene northern South America. Geology 23:237–240.

Hubert G, Reider N, Schmitt G, Send W. 1975. Accumulation of barium in Mueller's bodies of the Loxodidae (Ciliata, Holotricha). Z Naturforsch Sect C Biosci`18;30:422–423.

Ireland BJ, Curtis CD, Whiteman JA. 2006. Compositional variation within some glauconites and illites and implications for their stability and origins. Sedimentology 30(6):769–786.

Kulakova AN, Hobbs D, Smithen M, Pavlov E, Gilbert JA, Quinn J.P., McGrath, J.W., 2011. Quantification of inorganic polyphosphate in microbial cells using 4 ‘-6-diamidino-2-phenylindole (DAPI). Environ Sci Technol 45(18):7799–7803.

Lugo J. 1994, The Merida Arch: tectonic control on deposition from Late Mesozoic to Early Cenozoic in western Venezuela: Puertola Cruz, V Simposio Bolivano de la Exploracion Petrolera en las Cuencas Subandean, p291–310. Q8

Mahaney WC. 1990. Ice on the Equator, Ellison Bay, WI: Wm. Caxton Ltd.

Mahaney WC. 2002. Atlas of Sand Grain Surface Textures and Applications. Oxford, UK: Oxford University Press.

Mahaney WC, Barendregt RW, Hamilton TS, Hancock RGV, Costa, P. J.M. 2013. Soil mineralogy and chemistry of late Pliocene-early Pleistocene paleosols on Mount Kenya: Age and Paleoclimate reconstruction. Geomorphology 204:217–228.

Mahaney WC, Dohm JM, Kapran B, Hancock RGV, Milner MW. 2009. Secondary Fe and Al in Antarctic paleosols: correlation to Mars with prospect for the presence of life. Icarus 203:320–330.

Mahaney WC, Kalm V. 2013. Late Holocene Paleoclimate and weathering history in the Norra Storfjället Mountains, Sweden: solifluction and ^{14}C dated pedostratigraphy. Geomorphology 173–174:43–51.

Mahaney WC, Kalm V, Hancock RGV, Michel F, Kapran B. 2010. Geochemistry and extractable Fe and Al in cold temperature soils of northwestern Siberia. J Quatern Sci 25(2):178–189.

Mahaney WC, Milner MW, Bezada M, Hancock RGV. 2002. Paleosols and Andean uplift in Venezuela: Assessing competing hypotheses of relict tropical soils versus paleohydrogeochemical variations. J South Amer Earth Sci 15(5):525–542.

Mahaney WC, Sanmugadas K, Hancock RGV. 1999. Extractable Fe and Al soils in the middle Teton chronosequence, Western Wyoming, U.S.A. Zeitschrift für Geomorphologie 43(3): 393–407.

Malagón, D. 1982. Evolucion de suelos en el páramo andino (NE del Estado Mérida Venezuela), CIDIAT Serviso Suelo y Clima, Mérida (56), 222p. Q9

Mason GM. 2008. Eocene age fossilized filamentous bacteria: new evidence suggesting a bacterial genesis of siderite in the Green River formation, Wyoming. 28th Oil Shale Symposium, Colorado School of Mines, 13–15 October, p1–7. Q10

Milner MW, Mahaney WC, Beveridge TJ, Bezada M. 1996. Concretionary manganese-iron-silica pedoliths in Andean paleosols. In Abstracts for the International Conference on Quaternary Glaciation and Paleoclimate in the Andes Mountains, UPEL, Mérida, Venezuela.

Nealson KH. 1983. The microbial manganese cycle. In: Krumbein WE, editor. Microbial Geochemistr*y*. London: Blackwell. p191–221.

Nealson KH, Saffarini D. 1994. Iron and manganese in anaerobic respiration: environmental significance, physiology, and regulation. Ann Rev Microbiol 48:311–343.

Ochoa G, Malagón D. 1981. Mineralogia de algunos suelos desarrollados sobre diferentes tipos de materiales en la Cuenca Alta y Media del Rio Motetan, Estados Mérida y Trujillo, Venezuela. Agrochimica 25(5–6):427–436.

Orel'skaya IG. 1974. Manganese-iron concretions in Sod-Podzolic Gley soils. Soviet Soil Sci 6:26–32.

Oyama M, Takehara H. 1970. Standard Soil Color Charts. Japan Research Council for Agriculture. Q11

Parfitt RL, Childs CW. 1988. Estimation of forms of Fe and Al: A review and analysis of contrasting soils by dissolution and Moessbauer methods. Austral J Soil Res 26:121–144.

Pindell JL, Higgs R, Dewey JF. 1998. Cenozoic palinspastic reconstruction, paleogeographic evolution and hydrocarbon setting of the northern margin of South America, in Geographic Evolution and non-glacial Eustasy, Northern South America. SEPM Special Publication No. 58:45–85.

Pirozynski, K A. 1976. Fossil fungi. Ann Rev Phytopathol 14:237–246.

Robbins EI, D'Agostino JP, Ostwaid J, Fanning DS, Carter V, Van Hoven RL. 1992. Manganese nodules and microbial oxidation of manganese in the Huntley Meadow, Virginia, U.S.A. Catena Supplement 21:179–202.

Schiller EA, Taylor FC. 1965, Spessartite-quartz rocks (coticules) from Nova Scotia. Amer Mineral 50(9):1477–1481.

Soil Survey Staff. 1999. Soil Taxonomy, Agriculture Handbook 436, 2nd Edition, Washington, DC: USDA.

Tebo, B M, Johnson, J A, McCarthy, J K, Templeton, A S. 2005. Geomicrobiology of manganese II oxidation. Trends Microbiol 13:421–428.

Tilsley JE. 1977. Placosols: Another problem in exploration geochemistry. J Geochem Explor 7: 21–30.

Tully BJ, Heidlberg JF. 2013. Microbial communities associated with ferromanganese nodules and surrounding sediments. Front Microbiol 4(161): 1–10.

Vivas L. 1974. Estudio geomorfológico de la cuenca superior de la quebrada Tuñame. Revista Geografica (Universidad de los Andes) 11:69–112.

Vortisch WB, Mahaney WC, Fecher K. 1987. Lithology and relative weathering in a paleosol sequence on Mount Kenya, East Africa. Geol Paleontol 21:245–255.

Wackett LP, Dodge AG, Ellis LBM. 2004. Microbial genomics and the periodic table. Appl Environ Microbiol 70:647–655.

Walkley A. 1935. An examination of methods for determining organic carbon and nitrogen in soils. J Agri Sci 25:598–609.

Weingarten B. 1977. Tectonic and paleoclimatic significance of a late-Cenozoic paleosol from the Central Andes, Venezuela, M.Sc. Thesis, University of Pennsylvania, Philadelphia, PA.

Whittig LD. 1965. X-ray diffraction techniques for mineral identification and mineralogical composition, in Black, C.A., (editor), Methods of Soil Analysis, Madison, Wisconsin: American Society of Agronomy, p671–696.