Geomorphology 116 (2010) 48–57

Contents lists available at ScienceDirect

Geomorphology

journal homepage: www.elsevier.com/locate/geomorph

Evidence from the northwestern Venezuelan Andes for extraterrestrial impact: The black mat enigma

W.C. Mahaney [a,*], V. Kalm [b], D.H. Krinsley [c], P. Tricart [d], S. Schwartz [d], J. Dohm [e,f], K.J. Kim [g], B. Kapran [a], M.W. Milner [a], R. Beukens [h], S. Boccia [i], R.G.V. Hancock [j], K.M. Hart [k], B. Kelleher [k]

[a] Quaternary Surveys, 26 Thornhill Ave., Thornhill, Ontario, Canada L4J 1J4
[b] Institute of Ecology & Earth Sciences, Tartu University, Tartu, EE51014, Estonia
[c] Institute of Geological Sciences, University of Oregon, Eugene, Oregon, 97403-1272, USA
[d] Laboratoire de Geodynamique des Chaînes Alpines, University of Grenoble, Observatoire des Sciences de l'Univers, 38041, Grenoble, France
[e] Department of Hydrology and Water Resources, University of Arizona, Tucson, Az., 85721, USA
[f] The Museum, The University of Tokyo, Tokyo, 113-0033, Japan
[g] Geological Research Division (Prospective Geoscience Research Department), Korea Institute of Geoscience and Mineral Resources (KIGAM), 92 Gwahang-no, Yuseong-gu, Daejeon 305-350, Republic of Korea
[h] IsoTrace Lab, Dept of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7
[i] Department of Materials Science, University of Toronto, Toronto, Ontario, Canada M5S 3E4
[j] Department of Medical Physics and Applied Radiation Sciences and Department of Anthropology, McMaster University, Hamilton, Ontario, Canada L8S 4K1
[k] School of Chemical Sciences, Dublin City University, Ballymun Road, Glasnevin, Dublin 9, Ireland

ARTICLE INFO

Article history:
Received 11 January 2009
Received in revised form 9 October 2009
Accepted 14 October 2009
Available online 24 October 2009

Keywords:
Asteroid impact
Black mat
Younger Dryas
Paleoclimate

ABSTRACT

A carbon-rich black layer encrusted on a sandy pebbly bed of outwash in the northern Venezuelan Andes, previously considered the result of an alpine grass fire, is now recognized as a 'black mat' candidate correlative with Clovis Age sites in North America, falling within the range of 'black mat' dated sites (~12.9 ka cal BP). As such, the bed at site MUM7B, which dates to <11.8 ka ^{14}C years BP (raw dates) and appears to be contemporaneous with the Younger Dryas (YD) cooling event, marks a possibly much more extensive occurrence than previously identified. No fossils (megafauna) or tool assemblages were observed at this newly identified candidate site (3800 a.m.s.l.), as in the case of the North American sites. Here, evidence is presented for an extraterrestrial impact event at ~12.9 ka. The impact-related Andean bed, located ~20 cm above 13.7–13.3 ka cal BP alluvial and glaciolacustrine deposits, falls within the sediment characteristics and age range of 'black mat' dated sites (~12.9 ka cal BP) in North America. Site sediment characteristics include: carbon, glassy spherules, magnetic microspherules, carbon mat 'welded' onto coarse granular material, occasional presence of platinum group metals (Rh and Ru), planar deformation features (pdfs) in fine silt-size fragmental grains of quartz, as well as orthoclase, and monazite (with an abundance of Rare Earth Elements—REEs). If the candidate site is 'black mat', correlative with the 'black mat' sites of North America, such an extensive occurrence may support the hypothesized airburst/impact over the Laurentide Glacier, which led to a reversal of Allerød warming and the onset of YD cooling and readvance of glaciers. While this finding does not confirm such, it merits further investigation, which includes the reconnaissance for additional sites in South America. Furthermore, if confirmed, such an extensive occurrence may corroborate an impact origin.

1. Introduction

The sudden onset of the YD cooling event (~12.9 ka) has been documented by a number of researchers (Birkeland et al., 1989; Reasoner et al., 1994; Hansen, 1995; Osborn et al., 1995; Van der Hammen and Hooghiemstra, 1995; Rodbell and Seltzer, 2000; Mahaney et al., 2007a, 2008). Coinciding with the large-scale Clovis Age extinction in North America, it had far-reaching consequences to the geo-ecological environment of the time. A variety of hypotheses have been put forward to explain this major perturbation in environmental conditions, including an impact event in North America (Firestone et al., 2007a,b; Haynes, 2008). The available data, compiled from sites within the United States and Canada, centers around the presence of a 'black mat' site dating to the YD climatic change, ~13 ka. The grains within this 'black mat' often comprise a thin layer of altered sediment characteristic of extraterrestrial impacts, including but not limited to glassy carbon and/or magnetic spherules, platinum group metals (usually with Ir), pdfs in fine silt, fragmental quartz, orthoclase,

* Corresponding author.
E-mail address: arkose@rogers.com (W.C. Mahaney).

0169-555X/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.geomorph.2009.10.007

and monazite. Although an extraterrestrial origin for the 'black mat' is contentious (Haynes, 2008; Pinter and Ishman, 2008), the site location and evidence described herein (Kennett et al., 2009) point to the existence of additional sites beyond Canada and the United States that may unfold information concerning the development of the 'black mat' and temporally associated megafaunal extinctions approximating ~12.9 ka.

The sheer magnitude of the proposed impact would have caused a continent-wide shock wave, introducing high velocity ejecta material into the atmosphere (Firestone et al., 2007b). A strikingly high percentage of examined sites in N. America (Haynes, 2008) reveal a distinctive 'black mat', lending support to the theory. However, there has not been evidence reported south of the United States. If an impact event, ejecta cycling through the upper layers of the atmosphere would be expected to have dispersed over a wider perimeter than is currently being studied. Such an event recorded in a relatively thin layer would include valuable information regarding the temperature, size, dynamics, and composition of the resulting cloud. In fact, the further unfolding of such possible sites could be key to a more accurate reconstruction of the putative event, which includes the settling patterns of ejecta and location of the impact site.

This analysis aims not to prove the impact hypothesis, but rather to show that the 'black mat' could be more extensive than previously considered and that continued study will better constrain both the YD pattern and the origin of the 'black mat'. The profile in question (MUM7B; see Mahaney et al., 2008, for stratigraphy), located in the northwestern Venezuelan Andes, is found at 3800 a.m.s.l., and dates to within the range of the proposed event. Thin dark spattered coatings of carbon are welded/adhered on sand- and pebble-size clastic material, and are glassy in nature. Of particular interest are the dual and tri-coatings of carbon, iron and manganese, partially consumed by accompanying microorganisms observed on the grains. It is probable that the second high Mn coating, originating from environmental leaching, was further built up over time by bacteria feeding on the primary C-rich mat below (Burdige and Kepkay, 1983; Nealson, 1983; Bougerd and de Vrind, 1987). The incidence of shattered quartz, notably with prominent pdfs in the finer silt fractions, psilomelane, monazite, and occasional presence of Rh and Ru indicate a close relationship between this layer and the 'black mat' as described in northern North America (Haynes, 2008). There remain many unanswered questions, particularly those of welding/adhering temperature of the coatings, settling velocities, the frequency of the coatings, and on a larger scale, the size and nature of the ejecta cloud itself. It is our hope that this newly identified 'black mat' in the northwestern Venezuelan Andes will serve as an incentive for the expansion of research efforts beyond sites already studied in Canada and the United States. Newly identified sites should yield additional information to better constrain the YD perturbation and to address possible origins such as impact.

2. Regional geology

The crest of the eastern cordillera of the northwestern Venezuelan Andes (Fig. 1) lies between 8° 30′ and 9° 00′ N and 70° 30′ and 70° 45′ W, at elevations nearly 5000 a.m.s.l. The northern extension of the Sierra Nevada de Mérida, the Sierra de Santo Domingo, trends NE to SW. Underlying bedrock in the area consists of gneiss and granite of the Iglesias Group of Precambrian age (Schubert, 1970). In the Santo Domingo segment, the lithology is divided into two main formations of which the La Mitisus Banded Gneiss is the oldest outcropping in most valleys. The total thickness of the gneiss and minor accompanying schist, which is commonly intruded by granitic and quartz dikes, is unknown (Mahaney and Kalm, 1996).

Most cirques, as in the Upper Mucuñuque Valley, exhibit lagoons carved in bedrock or dammed by moraines. Pico Mucuñuque, at the head of the Mucuñuque Catchment, is the highest summit at 4672 a.m.s.l. The high crest of the range stretches along a narrow ridge with arêtes, horns, and steep walls extending down across talus into bedrock-floored valleys laced with thin, discontinuous ground moraine. A number of cross-valley bedrock bars are spaced ~100 m apart above the Boconó Fault at ~3700 a.m.s.l., forming steps thick with either end moraines/outwash bodies or copious amounts of talus (Mahaney et al., 2007a). The moraine/outwash complex of Late Glacial/Younger Dryas age (Mahaney et al., 2008) situated at 3800 a.m.s.l. contains the sediments described in this report.

3. Geomorphic background

The linear fault-controlled Mucuñuque Catchment (center, Fig. 1), with headwaters on Pico Mucuñuque, trends NW-SE. Bogs are prevalent on the valley floors and provide, along with alluvial fill, ground and recessional/end moraines, which provide the primary source materials for soils, the latter of which belongs to the Histosol, Inceptisol, Mollisol and Entisol orders (NSSC, 1995). The soils have ochric epipedons with lighter than 10YR 5/1 colors. They exhibit udic moisture regimes, which do not record dry periods lasting more than 90 days. All soils, except for the Histosols, key out in the Orthent suborder–suborder Troporthents given the high altitude subtropical locality.

Bogs are shallow and total depth of sediment/organics is <1 m. Prominent amounts of peat are found in alluvial fills, and similar buried peats provide the ^{14}C dates described later in the paper. Some organic carbon from peat beds may follow a pathway into placon beds (Mahaney et al., 2008) similar to the one in MUM7B where the black mat-encrusted material was found. Waterfalls are common wherever bedrock bars are located. No lateral moraines are present above 3700 a.m.s.l. (Mahaney et al., 2008).

4. Methods and materials

The MUM7B Section was dug by hand at 3800 a.m.s.l. elevation to a depth of 2.5 m to expose a fresh cut. Sediment samples, which include the candidate 'black mat' material were collected for laboratory analysis and radiocarbon dating (also see Mahaney et al., 2008). The ^{14}C samples were handled with metal implements, wrapped in aluminum foil, and dated within two weeks at IsoTrace Laboratories, University of Toronto. These samples were washed with double-distilled water and acid treated with 4 N HCl to remove possible carbonate and humic acid impurities. The samples were further extracted using 0.25 N NaOH. The clayey silt sample (TO-9278a; Table 1) was demineralised with hot HCl and HF. All three dates derived from the section (Table 1) were corrected for isotopic fractionation and calibrated using the OxCal v.3.10 calibration programme of Bronk-Ramsey (2005) and the INTCAL04 calibration data for the Northern Hemisphere (Reimer et al., 2004). Uncertainties for each ^{14}C date are given as 1σ with 2σ representing calibrated age ranges.

The section description follows standards set forth by Birkeland (1999), while profile characterizations are based on Soil Survey Staff parameters (NSSC, 1995). Colors were determined in the field and later in the lab using the soil color charts of Oyama and Takehara (1970). The pebbly material, ranging from 2 to 12 mm, was grade sized *in situ*. Particle size analysis was then completed on five air dried samples (MUM7B) following guidelines outlined by Day (1965). Special attention was paid to the prominent black encrustation present on the majority of particles, which was closely examined under the light microscope. Representative grains were then mounted, following procedures outlined by Mahaney (2002) and Vortisch et al. (1987) using silver paint on stubs for analysis under a Field Emission Scanning Electron Microscope (FESEM) and Energy-Dispersive Spectrometer (EDS) at the Department of Metallurgy and Minerals Science at the University of Toronto. The samples were coated with gold-palladium rather than carbon, as carbon was

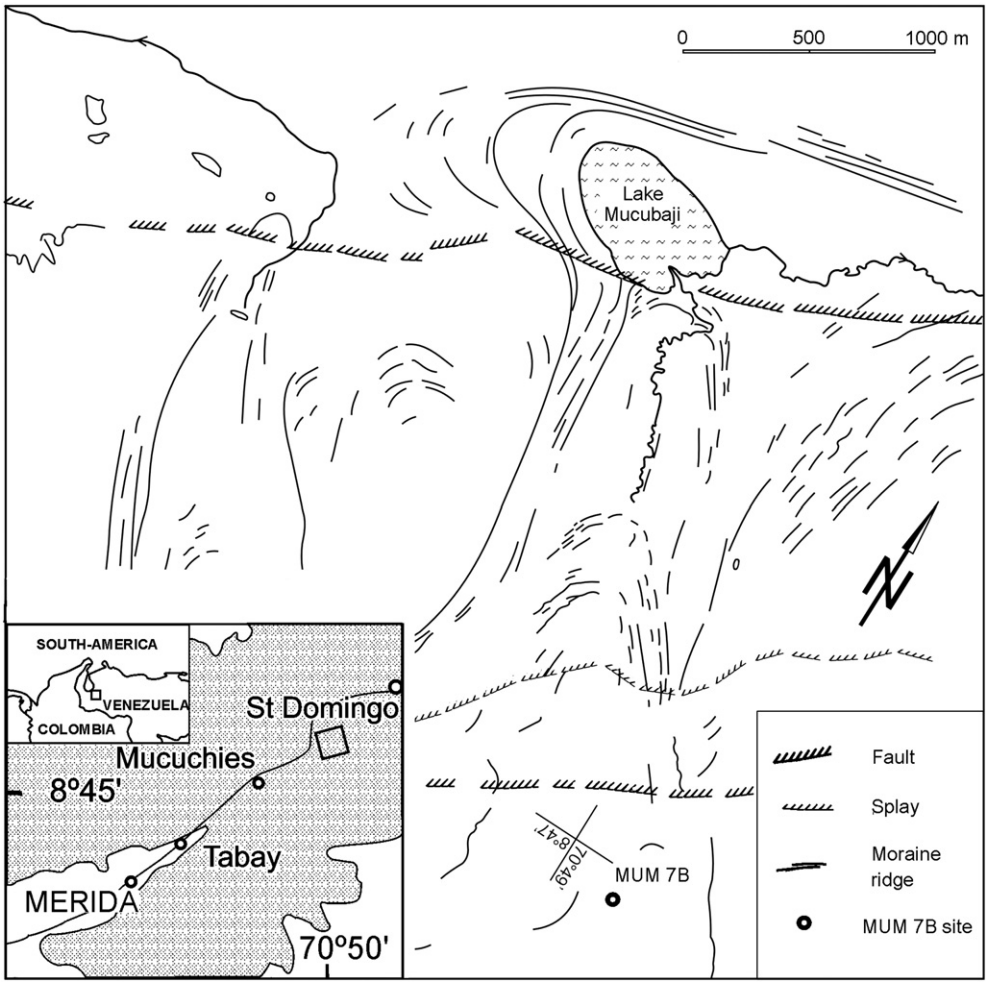

Fig. 1. Location of the 'black mat' site, northern Venezuelan Andes.

a key feature of interest. Photomicrographs were taken at voltages of 4 to 20 keV.

Laser Raman measurements were performed on the black encrustation at the Ecole Normale Supérieure (ENS)-Lyon. We used a LABRAM HR800 double subtractive spectrograph with premonochromator and a nitrogen-cooled SPECTRUM1 CCD detector. The premonochromator was equipped with confocal optics before the spectrometer entrance. The excitation was realized by using a laser beam with a wavelength of 514.5 nm. A microscope equipped with a ×50 objective was used to focus the laser beam and to collect the Raman signal in the backscattered direction. The presence of a confocal pinhole before the spectrometer allows a sampling of about 2 to 5 μm-sized analytical zone. Typical laser power was 400 mW at the sample surface. Acquisition time-span was about 180 s distributed during three accumulating cycles.

Table 1
Radiocarbon dates from the MUM7B Section, Mérida Andes.[a]

Site	Lab no.	Material	^{14}C age	cal BP yrs (2 sigma range)	Median of cal range
MUM7B	TO-9278a	Peaty alluvium	11,440 ± 100	13,510–13,100	13,290
	TO-9011	Peat	11,760 ± 80	13,790–13,420	13,640
	TO-9278c	Peat	11,850 ± 180	14,100–13,300	13,660

[a] See Fig. 1 section location, and Fig. 2 for stratigraphic details.

5. Results

5.1. Stratigraphy

Site MUM7B (Fig. 1) is a uniquely situated location near the base of a prominent bedrock bar at 3800 a.m.s.l. and some 150 m southeast of site MUM7 (see Mahaney et al., 2008 for location of sites). The MUM7B Section (Fig. 2), easily located under an overhanging *Polylepis* (spp.?) tree adjacent to a small glaciolacustrine plain, comprises imbricated outwash, overlying a succession of stratified sand, gravel, and peat, all of YD age (Mahaney et al., 2008). The tree is a common occupant of land adjacent to stream beds above the normal Andean forest timberline (Salgado-Labouriau and Schubert, 1976).

Buried peat and alluvial clay with peat yield calibrated AMS radiocarbon dates of 13.8–13.4 and 14.1–13.3 ka cal BP at 235 cm depth (Table 1) and 13.5–13.1 ka cal BP at 232 cm depth. The sediment stack, including the development of a thin Entisol (A/C/Cu profile at surface) related to ice advances and recession, including outwash, has been reported by Mahaney et al. (2008). This paper discusses the significance of the 3-cm thick C- and Mn-encrusted bed at the 210–213 cm level in the section, as described in the report of Mahaney et al. (2008).

Interpretation of the MUM7B stratigraphy is correlated with the till succession in MUM7 located 150 m down-valley. At the latter site, a series of push moraines overlies a deposit of bouldery-rich sandy gravel interpreted as meltout till (Mahaney et al., 2008, Fig. 2a). The

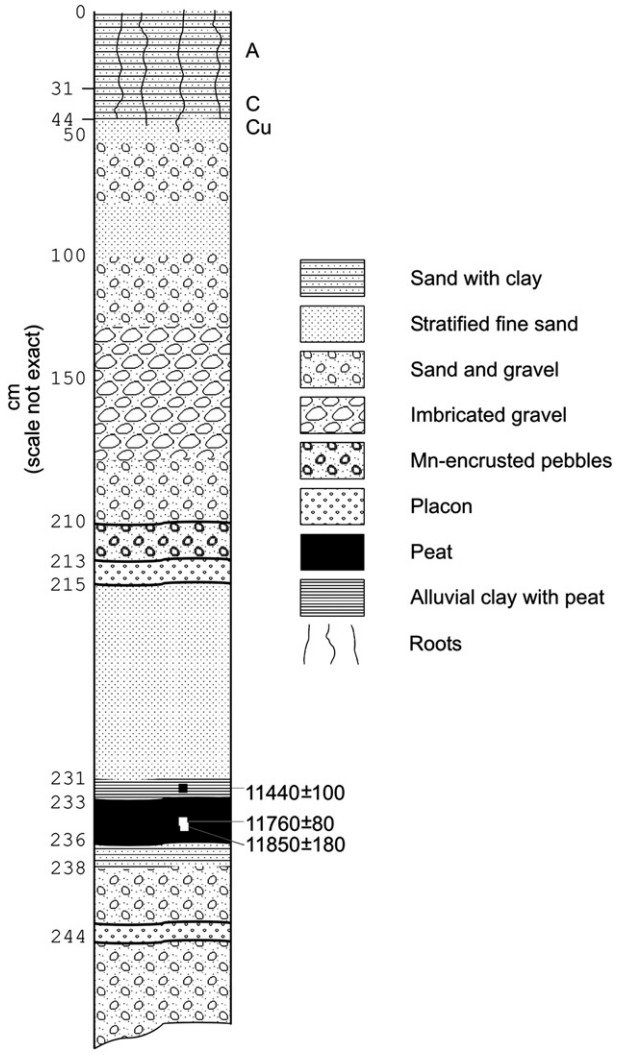

Fig. 2. MUM7B Section at 3800 a.m.s.l. in the Mucuñuque Catchment. Radiocarbon years reported as raw data; see Table 1 for ka cal BP yrs. This section is fully described in Mahaney et al. (2007a,b);
Figure by permission from Elsevier.

upper push moraine in this sequence is considered correlative with the outwash gravel in the upper 210 cm of the MUM7B Section. There is no till in MUM7B; however the preserved alluvial peats record vegetation growth in shallow water with oscillating overlap of glaciolacustrine and glaciofluvial sediment emplacement prior to the advance of the YD ice.

5.2. Color and particle size

Examination of the 3 cm-thick bed of Mn-encrusted pebbles ('black mat' color = 7.5YR 2/1, black; Oyama and Takehara, 1970) yielded clasts ranging from 2 to 64 mm in size, from granules to large pebble grade sizes. Approximately 10% of the total weight of the samples collected consists of sands, mostly coarse (500–1000 μm) to very coarse sand (1000–2000 μm), with small quantities of medium to very fine sand (500–63 μm) interspersed with minor amounts of silt and clay (<63 m). Though a traditional replicated particle size analysis is not possible, even with the gross weight of collected sample, the <2 mm fraction of the material, amounting to about <3% by weight, has been identified from individual samples ($n = 5$) as coarse sandy loam (83% sand, 14% silt, and 3% clay).

5.3. Lithology

The pebble and sand lithology of the host minerals coated with 'black mat' material are almost exclusively of felsic gneissic composition, with sillimanite, andalusite, quartz, and orthoclase. Less than 5% of the studied sample grains consist of biotite and monazite, the latter an accessory mineral comprising La, Ce and Th, which is occasionally encountered in chemical analysis described below.

5.4. Light microscopy

Under low power light microscopy with reflected light, the pebble coating is distinctly black (Fig. 3a), often very glassy and translucent especially on the numerous spheroidal particles which occur on pebbles of all grade sizes and occasionally on very coarse sands. Adjacent to the glassy particles, a thick (up to 1.0 μm) dense black coating or mat is observed welded/adhered to the surface of clasts with variable reflectivity ranging from glossy to flat. Surrounding the 'black mat' surface, a ring-like accumulation of secondary Fe, principally goethite with some hematite (as determined from EDS (Energy-Dispersive Spectrometry) analysis) is present. Much of the surrounding 'black mat' and translucent black spherules have compositions of Fe, Mn, and often with variable amounts of C. In some instances, C encrustations are thick with minor amounts of Fe and Mn, whereas in others, the inverse applies (Figs. 4b and 6b).

5.5. Scanning electron microscopy

The medium to fine sand grains shown in Fig. 3b are nearly all angular to sub-angular in shape, with some (approx 20%) bearing

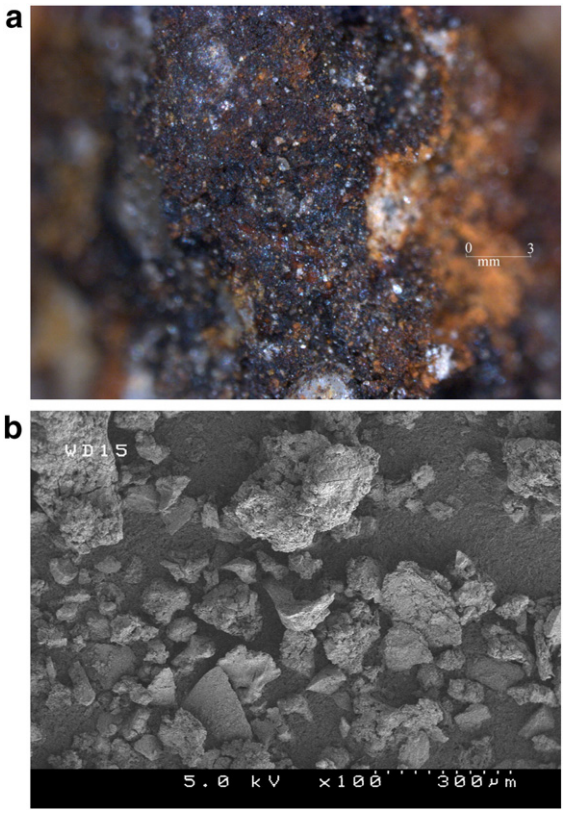

Fig. 3. a, Light microscope image of the black mat cluster on a pebble of felsic gneiss composition. b, General FESEM frame showing the variety of grains observed at low magnification in the MUM7B bed. A cluster of nodular forms is in the upper center and upper left, large shard of quartz in the center low and center right amidst a variety of coated angular grains spread across the remainder.

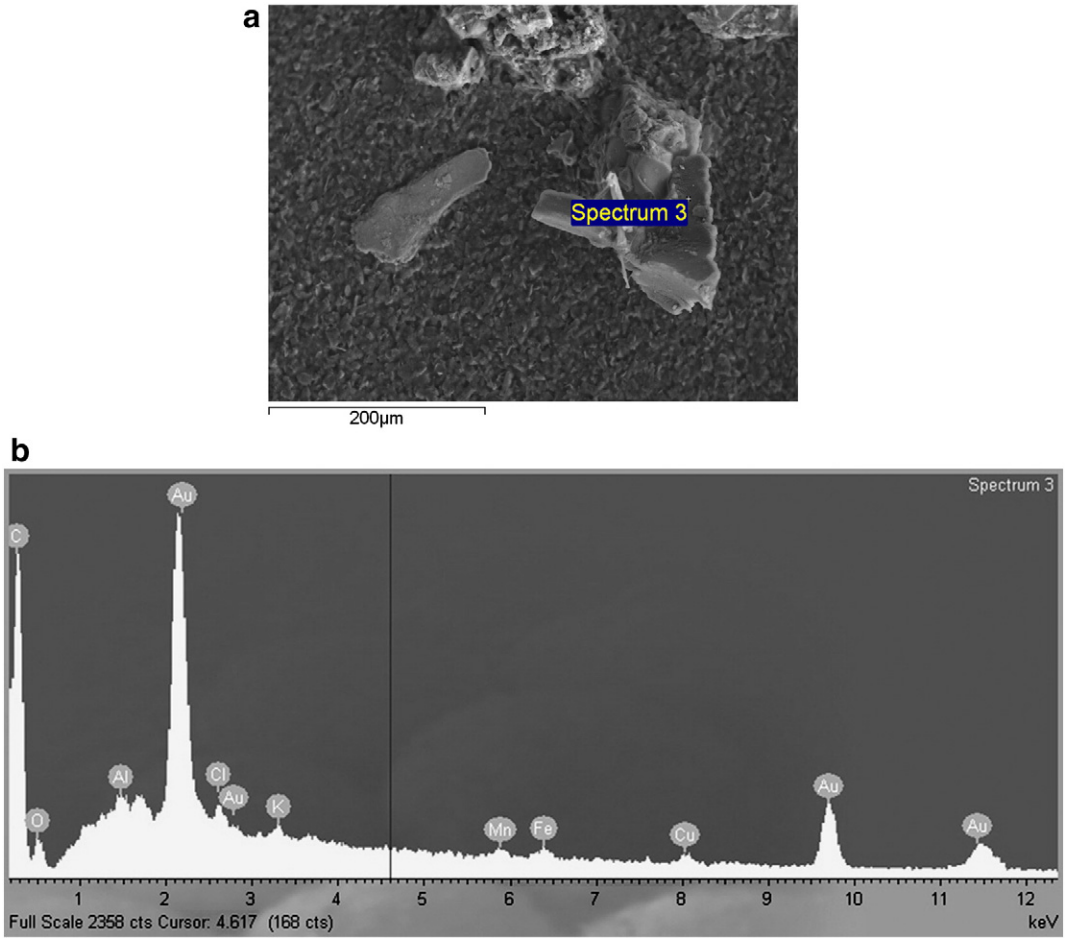

Fig. 4. a, Fragmental grains of carbon mat on quartz in the lower segment. A cluster of nodular forms in the upper center part of the frame. b, Spectrum of the lower right grain in A showing mainly C with O and traces of Si, Al, K, Fe, Mn and Cu. At 20 keV the beam probably penetrated the C coating. The sample is Au coated and the image was photographed at 20 keV.

straight to curved striations, sharp to abraded round edges, and conchoidal and subparallel fractures, interpreted as signs of light glacial crushing (Mahaney, 2002). Other grains carry fracture faces (Mahaney, 2002) indicative of bedrock release without further modification in glacial or fluvial environments.

The 'black mat' shown in Fig. 4a, which is partly protected by a protruding edge of quartz, is welded over much of the fragmental grain. The EDS spectrum in Fig. 4b, taken as a spot in the middle of the 'black mat' shown in Fig. 4a, contains a high concentration of C with much lesser amounts of O, Si, Al, Cl, K, Mn, Fe, and Cu. An enlargement of the lower part of Fig. 4a, shown in Fig. 5a, highlights both the pdfs in the outer quartz rim and the 'welded' character of the 'black mat' residing within protected rims of the mineral. Along a fracture in the quartz, the thickness of the 'black mat', estimated to be approximately ~1 µm, is shown along a fracture in the grain (Fig. 5b).

Fig. 6a displays a representative occurrence of 'black mat' on a fine sand grain of probable sillimanite composition. The EDS spectrum of this occurrence, yielded through an accelerating voltage of 15 keV, shows high C and very low O, Si, Al, Fe, and Cu. The high Au is the coating. The accelerating voltage is 15 keV. A mixed assemblage of C and Fe spherules is shown in Fig. 6c.

A grain coated with Si displays planar deformation features (pdfs; Fig. 7a). A search with the FESEM of three dozen stubs, which collectively comprise about 4000 grains ranging from silt to small pebble-size clasts, revealed frequent pdfs on quartz grains of fine grade size. The pdfs (or planar discontinuities) with planes spaced 1–0.5 µm apart have been interpreted elsewhere to result from impact events (Mahaney, 2002; Suuroja, et al., 2003). Even bent pdfs in quartz parallel to [0001] may reflect continuous bending of the crystal lattice, such as observed in ejecta deposits from the Azuara impact structure in Spain (http://www.impact-structures.com/spain/impact/shockeffects.htm). Gratz et al. (1996) report that pdfs appear as thin lamellae, sometimes filled with amorphous glass (diaplectic glass). While glass was not detected near the pdf planes, TEM investigations may reveal glassy to crystalline, straight and very narrow bands extending deep into quartz.

Sub-samples of the 'black mat' analyzed at KIGAM (Korea Institute Geoscience and Mineral Resources) in a similar fashion, at 15 keV and variable magnification (×100–2500), produced similar results with carbon counts from 200 to 800, variable Si:Al depending on whether quartz or K-feldspar dominated, and extremely variable Mn:Fe. Recent TEM investigations of another set of 'black mat' sub-samples from the same profile show spores and nanobacteria, which help explain the variable Mn detected by SEM and FESEM, since the microbes utilize carbon as an energy source. Both high-resolution NMR analysis of the organic matter fraction and bacterial DNA profiling of the black mat Andean samples are in progress, which may show whether Mn-fixing bacteria are present, and if so, would provide strong evidence for a biological origin of the Mn (Jones and Bish, 2008).

5.6. Raman analysis

The Raman spectrum obtained in the dark area of the black encrustation (Fig. 8a) shows a particular shape with the presence of two large bands respectively between 550–700 cm^{-1} and 1500–1580 cm^{-1}. These two bands are interpreted as the signature of iron

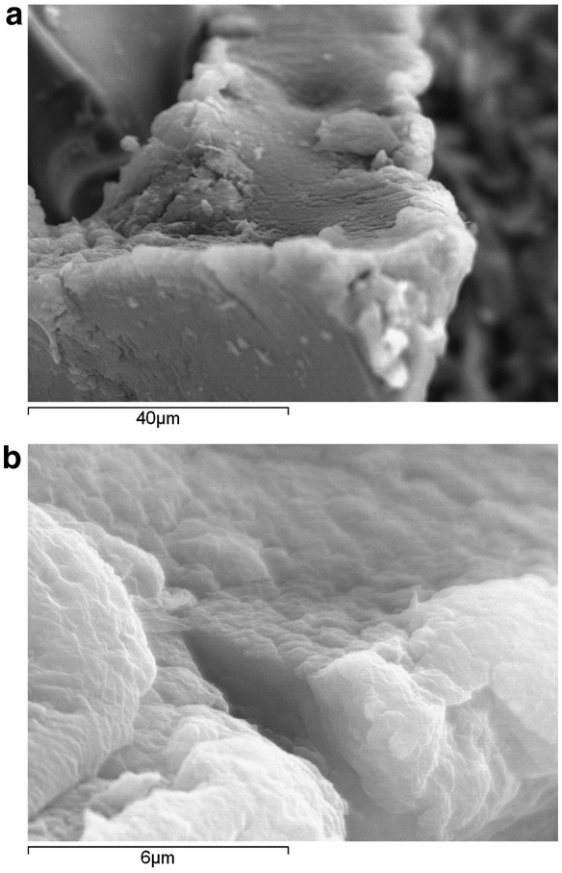

Fig. 5. a, Welded carbon mat with desiccation cracks on carbon mat welded onto quartz shown in Fig. 4a; b, Enlargement showing thickness of the carbon mat (~1 μm).

oxide corresponding to hematite (Fe_2O_3) (de Faria et al., 1997). The 1100 cm^{-1} spectral band corresponds to quartz. On the margin of the dark areas (Fig. 8b), Raman spectra display a broad peak between 1300 and 1600 cm^{-1}, which is interpreted to be a mixture of iron oxide comprising hematite and carbonaceous material. The decomposition of the first-order region of the Raman spectrum shows a thin band at 1597 cm^{-1} (Fig. 8b) that can match the G band characteristic of distorted graphitic structures (Nakamura et al., 1995; Bény-Bassez and Rouzaud, 2002) and a large band at 1360 cm^{-1} that matches the D1 band corresponding to in-plane defects and heteroatoms (Bény-Bassez and Rouzaud, 2002).

6. Discussion

The YD cooling event, often described as an enigma (Kennett et al., 2007), cannot be explained by orbital forcing because Northern Hemispheric insolation was increasing at the time deglaciation was temporarily averted by glacial readvance. This readvance is now known to be widespread stretching into South America (this paper) and possibly Africa (see Shannahan and Zreda, 2000). While the YD cooling is often attributed to major diversion of freshwater outflow into the Arctic Ocean, Gulf of Mexico, Hudson Bay, and Atlantic Ocean (Teller et al., 2002), the event has been controversially tied to an impact event, either over the Laurentide Ice Sheet or possibly the Carolina Bays (Firestone et al., 2007b; Kennett et al., 2007).

Several occurrences of the 'black mat' and relation to the Younger Dryas climatic event are reported on in North America (including Greenland) and Belgium (Quade et al., 1998; Firestone et al., 2007a; Haynes, 2008; Stich et al., 2008; Kennett et al., 2009). Here we unfold the first identification of a candidate 'black mat' deposit in South America with implications on origin. If the impact point is related to the 'black mat' occurrence in North America, assuming the impact occurred over the Laurentide Ice Sheet, the MUM 7B site is within a radial distance (~2500 km) of the impact. Though this finding neither confirms 'black mat' and its potentially greater extent nor its origin through an impact event, it should provoke further investigation south of the United States.

The occurrence of the C-Mn (black) encrusted pebble bed in MUM7B is similar in kind to the *fired* rock outcrop described near the Col du Clapier in the Italian Alps (Mahaney et al., 2007b). However, the graphitic band of the carbonaceous material is always masked by the oxide signal and the graphitization is weak, i.e. the G band determined by Raman Spectroscopy is not well developed. Analyses of the grains and coatings in the MUM7B samples show a black coating welded to (or adhered to) grains without appreciable fracture propagation, as would be expected if the site had experienced a grass fire, as first suspected during field work. While this does not entirely rule out a low temperature alpine grass fire, the extreme desiccation observed on grain coatings (Fig. 6a) supports a hypothesized hot coating material at time zero with cracking occurring upon cooling. In addition, glassy spherules associated with the denser 'black mat' material, as well as the amorphous C (similar to that of impact origin shown by Schüssler et al. (2002)) and the presence of infrequent identification of platinum based metals—Rh and Ru, require further evaluation and explanation. It should be noted that the identification of platinum group metals with the SEM may be a chance encounter given both the limitations of the equipment and that the grains were scanned only under high voltage (20 keV) with electron beam penetration to ~1 μm.

If arguably impact in origin, glassy spherules associated with the denser 'black mat' material could have originated from the release of energy of an incoming extraterrestrial object. A bollide with a velocity of + 15 km/s could produce a force of several tens of gigatons of energy (Hills and Goda, 1999; Hansen and Holsapple, 2003) Using the Chicxulub Impact (Hildebrand, 1993) as a measure of the impact energy, a 1 km-diameter Ni–Fe asteroid, termed a hemispheric impactor, could release 100 Gt of energy, whereas a great impactor (extinctor), the 10 km-diameter Yucatan asteroid for instance, would release 100 million megatons of energy, thereby subjecting the earth to a 'nuclear winter', i.e. soot blanket blotting out sunlight (Stich et al., 2008). If the 'black mat' of North America and the newly identified candidate are correlative in time and origin, this would imply that the proposed Laurentide impact lies somewhere in between a hemispheric and great impactor, perhaps an event akin to, but larger than, the Tunguska Event of 1908 (Phipps and Andronicos, 2008). If the nearly worldwide YD cooling event was indeed impact or airburst generated (Kennett et al., 2009), the so-called North American (Laurentide) air burst impact might more accurately be termed a great impactor.

Given the widespread occurrence of the 'black mat' in North America with azimuths ranging from 270° to ~70° from the Laurentide Ice Sheet, an azimuthal heading toward the Mérida Andes regarding the candidate site, the ejecta from a hypothesized impact event would be radial away from the ice sheet on a heading of ~180°. As such, further identification of the 'black mat' might be expected to the east and west of the Mérida Andes, i.e. Venezuela, Colombia, and within the Caribbean Sea.

The amorphous C shown in Fig. 18 of Schüssler et al. (2002) is similar in kind to what is shown in Fig. 4b herein. The origin of the C-rich encrustations discussed here might have resulted from impact in carbonate-rich rocks which melt at ~3800 °K based on the work of Schüssler et al. (2002).

On the basis of the results and foregoing discussion, four working hypotheses are presented and tested that may be used to explain the origin of the 'black mat' in South America: (1) extraterrestrial impact or airburst with ejecta following vectors to the E and SW of the Laurentide Ice Sheet engendering an inter-hemispheric 'nuclear

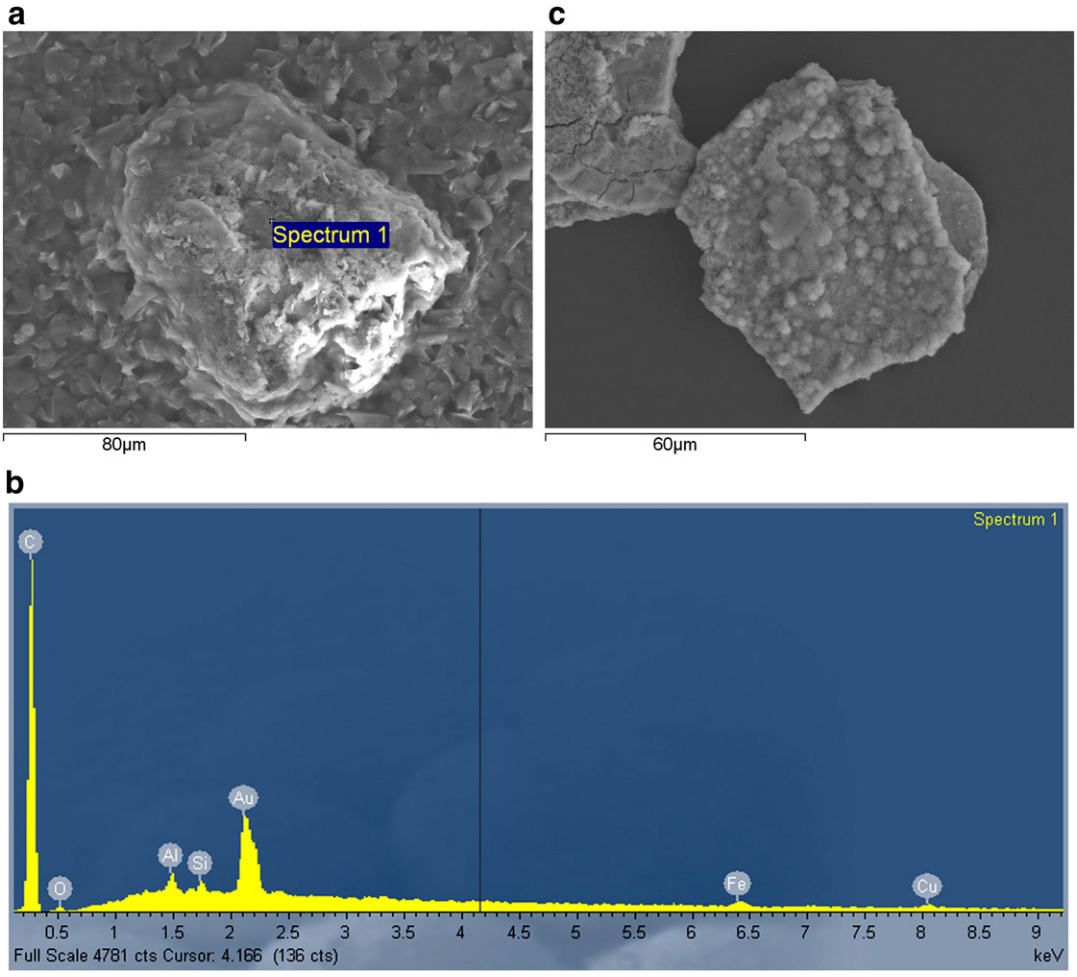

Fig. 6. a, Welded black mat in the center and on the sides of a weakly cemented grain cluster. b, Spectrum showing high C concentration in the center of A with trace amounts of Si. Al and Fe; c, Carbon and Fe spherules representative of the grains in the MUM7B bed.

winter'; (2) leaching and sequestering of high amounts of carbon out of local soils and peat beds into placons as in the MUM7B Section; (3) collection and surface drainage of cosmic dust off the retreating Late Glacial Andean Ice to form encrusted 'black mat' material in coarse glacial gravels; and (4) alpine grass fire. At the time of collection (Mahaney et al., 2008), an alpine grass fire or groundwater phenomena seemed the most logical explanation for the distinctive 1–2 cm-thick black bed.

6.1. Hypothesis 1

An airburst or impact raises the question as to angle of the incoming bolide/comet, its density, and resulting volume and lateral extent of ejecta. The sixty-odd 'black mat' sites in North America, including southern Canada, are spread across the land mass coast-to-coast, a spatial distribution which argues for a large amount of material radially ejected from north to south and east as far as Western Europe. These data indicate either a low-angle bollide trajectory from the north with the emplacement of a greater abundance of ejecta to the south, possibly confined to the troposphere (~10 km height at upper Middle Latitudes) or, alternatively, a higher angle with greater KREEP (K-REEs-P) and larger amount of ejecta reaching higher into the atmosphere, i.e. the stratosphere.

Available dates on the 'black mat' correlate at ~12.9 ka cal BP and suggest a sudden shift from Allerød warming to YD cooling, the black material marking an end to the Clovis Culture in North and Middle America (Firestone et al., 2007a,b). If the density of the bolide/comet was sufficient to fall somewhere between the size of the Yucatan and Meteor Crater asteroids, it may well have put sufficient ejecta into the atmosphere to cause a nuclear winter to sustain the ~1 ka sojurn of the YD readvance (Mahaney et al., 2008). Indeed, the question is not only whether the 'black mat' is extraterrestrial, but also whether such a putative event triggered a major climatic reversal. Is the megafaunal extinction related to it? As this hypothesis continues to be tested, researchers must continue to look for new sites in faraway places such as South America. With the paucity of workers there, as well as the great number of Late Glacial/YD sites, it is likely that other sites of age similar to MUM7B may contain evidence that will help solve the 'black mat' enigma.

6.2. Hypothesis 2

All of the examined 'black mat' sites comprise inordinately high amounts of carbon, consistent with the Andean site described here. As the 'black mat' takes on many different terrestrial forms, including Mollisols with very dark and humic-rich Ah horizons, aquolls, diatomite and alga-rich beds, there is a possibility that some 'black mats' are indeed manifestations of water-transported organic materials that have nothing to do with extraterrestrial impact (Quade et al., 1998). However, there remain the sites that have been analyzed to show the presence of carbon glassy spherules, high content of Ir and other platinum group metals described above, monazite with inordinately high amounts of REEs (Fig. 7b and c), nanodiamonds (Kennett, et al., 2009) and fullerenes with ^{3}He. These assemblages

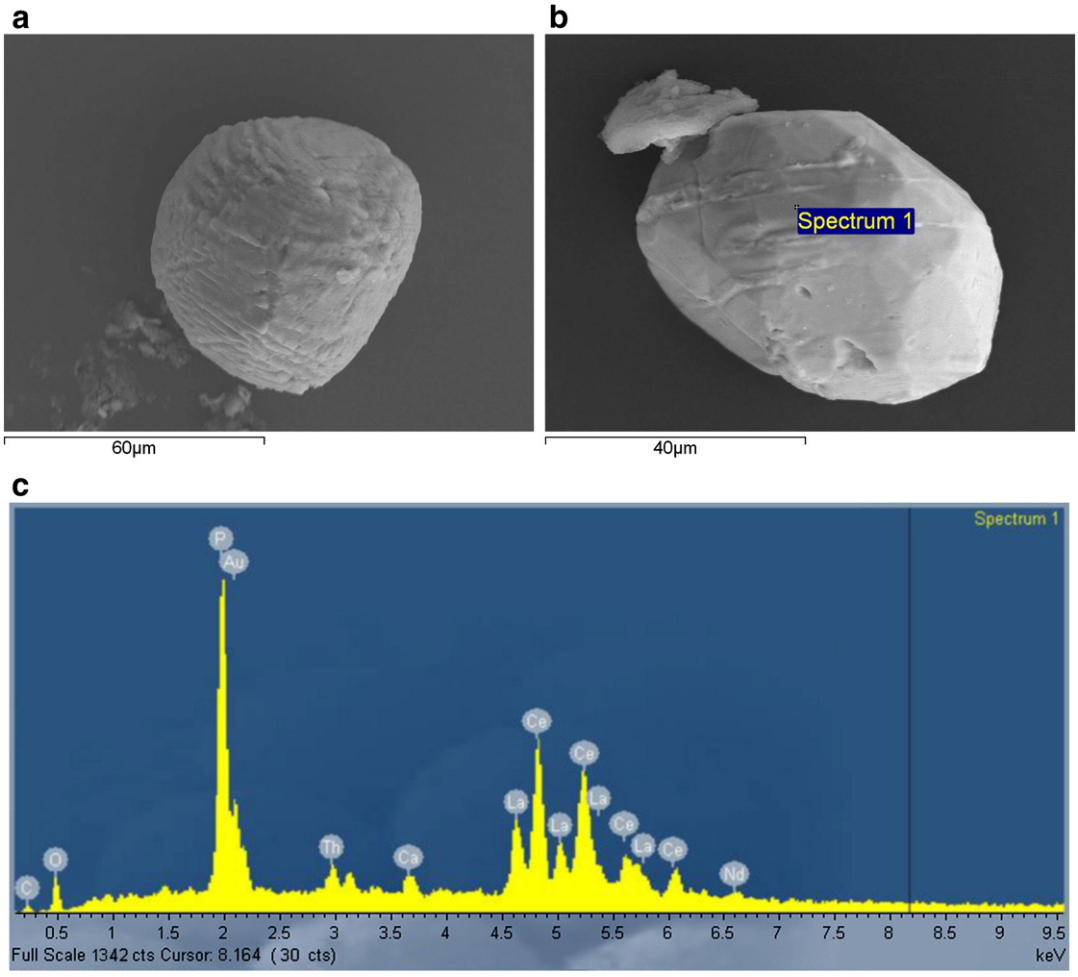

Fig. 7. a, Planar deformation microfeatures on a silt-sized quartz grain with a thin coating in the MUM7B bed; b, Fractured monazite with thin dark carbon coating (upper left); c, Spectrum of B showing REEs (La, Ce, and Nd), and Th.

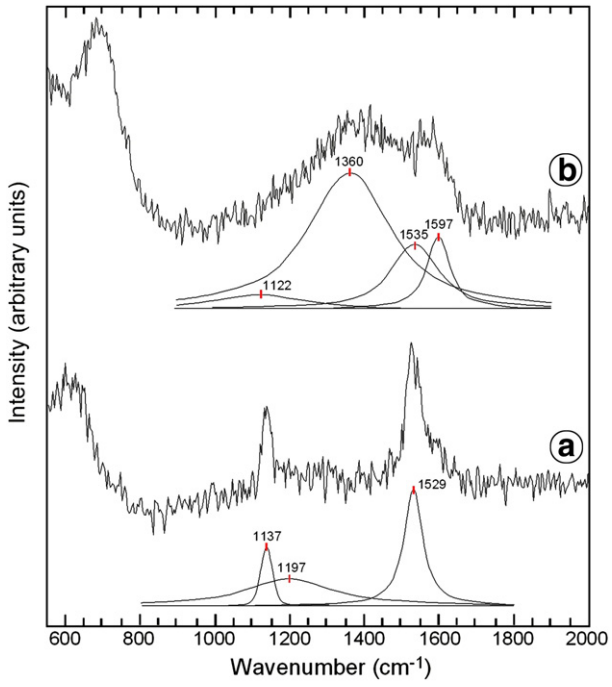

Fig.8. a, The 1100 cm^{-1} spectral band corresponds to quartz. On the border of the dark areas, Raman spectra show a broad peak between 1300 and 1600 cm^{-1} which is interpreted as a mixture of iron oxide (hematite) and carbonaceous material. The decomposition of the Raman spectrum is also indicated.

are difficult to reconcile without an extraterrestrial origin. Though, such sites may contain part but not the total body of evidence, additional evidence including iridium, fullerenes and nanodiamonds are yet to be documented at Site MUM7B.

As some placons are known to have populations of fungi that might add to the bulk organic carbon (Mahaney et al., 2008), and nearby reservoirs of peat and thick Ah horizons resident in Entisols and Histosols dating to the Late Glacial (Mahaney et al., 2007a), it is possible for carbon to accumulate in aquifers associated with outwash gravels such as those that exist in the MUM7B Section. However, the encrusted carbon-rich bed in MUM7B is more than a film of dark material, but rather a cemented and tightly adhered mass of carbon and associated elements firmly fixed to pebble and granule surfaces approximately 2–3 cm in thickness. In all of the nearly four hundred analyzed sections as a part of the Andean (Venezuelan) Research Project from 1993 to 2005, no black bed of encrusted material similar to MUM7B has been identified at other locales. Sites of similar age to MUM7B with mollic horizons exist in several catchments, but none of these are known to comprise distinctly dark bands of material in them, thin beds of which may have resisted downward movement within the wetting depths of the upper two thirds of the soil profile. Though the candidate site may be regarded as a finite occurrence from a local process, we believe that it has not been recognized in other places primarily due to its limited thickness, as well as both insufficient investigation and resurfacing by liquid water and water–ice.

6.3. Hypothesis 3

Cosmic dust, which is known to rain down on Earth from the cosmos, may certainly contain abundant REEs and platinum group metals. This, combined with ablating meteorites, might produce the glassy carbon spherules present at most of the 'black mat' sites. However, the collection and transport of this material on a glacial surface to condense out in one specific bed of material at ambient temperature would produce a film, not an encrustation of black material firmly welded onto granule and pebble surfaces. It is not so much a problem of the process occurring, but rather one of proving the Mucuñuque Catchment has a sufficient surface to collect enough cosmic dust and meteorite fallout to produce the desired effect. From top to bottom of the catchment, taking into account the surface area of the Allerød/YD ice, the collecting surface must be <1.5 km^2, hardly large enough to constrain the necessary amount of material.

6.4. Hypothesis 4

The Venezuelan 'black mat' might in fact relate to a purely terrestrial source, an alpine grass fire. During the late Allerød with the glacier in full retreat, and well above 3800 a.m.s.l., alpine grass would have been *in situ* providing vegetation that could be ignited. No amount of forest growth was possible at the site as at present, since it is well above the timberline at ~2500 m, although with scattered *Polylepis*. Alpine brush and forest ecotone brush fires generate temperatures in the 300–400 °C range, sufficient to leave a carbon film on rock and sediment surfaces (Mahaney et al., 2007b, *cf.* Col du Clapier in the Alps, previously mentioned), but not a welded encrustation and not with high concentrations of C. No human agencies are known in the Venezuelan Andes until late Holocene time (Wagner, 1973). So, if the 'black mat' is purely terrestrial in origin, the igniting agent would have to be lightning. Significantly, an explanation for the presence of platinum group elements, prolific monazite with copious amounts of REEs, pdfs, and glassy carbon spherules found on well over 300 specimens examined with the light microscope require an explanation other than fire.

7. Conclusions

A single occurrence of Mn-encrusted/welded coating and C-glass spherules on a sand/pebble bed in the northwestern Venezuelan Andes prompted an investigation into the composition of the material to determine its origin. The 3 cm-thick bed of material contains infrequent trace amounts of Ru and Rh, glass spherules of C, and a thick and dense mat of C often desiccated with high concentrations of Mn, Fe and Cu. The presence of pdfs, frequently encountered amongst the population of grains studied, along with other attendant information outlined above point to a significant event, ejecta from a major extraterrestrial impact, either an asteroid or a comet.

The immediate occurrence of the candidate 'black mat' bed, ~15 cm above organics dated by AMS to 13.1 to 14.1 ka cal BP, places them well within the YD window. Because the MUM7B 'black mat' sediments are coeval with 'black mat' sites in North America, and since such sites have been arguably modified by an impact event, this raises the question of whether the material is partly impact ejecta. The analysis confirms the presence of trace amounts of platinum group metals, C-spherules, C-dense mat, high amounts of Fe and Mn, and pdfs in some quantity with a frequency higher than chance occurrence. The possible correlations between the candidate site and those of North America have significant implications on what would be a much more expansive deposit, which includes a possible bearing on the controversial Laurentide impact and YD cooling event.

Of all four testable hypotheses, number 3 could be eliminated out of hand because the glacier surface is not large enough to accumulate the necessary material; number 4, while first considered the most plausible explanation, leaves much of the evidence unexplained; number 2 requires additional investigation, especially with regard to surface paleosols dating from Late Glacial time; and number 1, the most likely of all three possible explanations, needs further examination. Other paleosols with thick surface mollic epipedons dating to between 12 and 13 ka, in the general area, may well contain 'black mat' beds that have previously been mistaken for peat and hence not analyzed. However, a perturbation of major proportions occurred, ca. 12.9 ka cal BP, and requires explanation and greater scrutiny. Based on this work, there may be a vestige of a record in South America, one that requires additional work to determine its authenticity and spatial extent. Workers in nearby Colombia and in other ranges in Venezuela need to pay special attention to sections related to the waning phases of the LGM.

Acknowledgements

This research was funded by Quaternary Surveys, Toronto. Financial support to VK by the Estonian State Target Foundation project No 0180048s08 is acknowledged. We thank B. Reynard for his helpful discussion about the Raman spectrum. We thank Vic Baker (University of Arizona) and an anonymous reviewer for a critical review of a draft of the ms.

References

Bény-Bassez, C., Rouzaud, J.N., 2002. Characterisation of carbonaceous materials by correlated electron and optical microscopy and Raman microscopy. In: Reimer, L. (Ed.), Scanning Electron Microscopy. SEM inc, Chicago, pp. 119–132.
Birkeland, P.W., 1999. Soils and Geomorphology. Oxford University Press, Oxford, UK. 430 pp.
Birkeland, P.W., Rodbell, D.T., Miller, D.C., Short, S., 1989. Investigaciones en el Parque Nacional Río Abiseo, San Martin. Boletin de Lima 64, 55–64.
Bougerd, F.C., de Vrind, J.M.P., 1987. Manganese oxidation by *Leptothrix discophora*. Journal of Bacteriology 169, 489–494.
Bronk-Ramsey, C., 2005. OxCal Program v 3.10. University of Oxford Radiocarbon Unit, Oxford. http://www.rlaha.ox.ac.uk/oxcal/oxcal.htm.
Burdige, D.J., Kepkay, P.E., 1983. Determination of bacterial manganese oxidation rates in sediments using an *in situ* dialysis technique, I., laboratory studies. Geochemica and Cosmochimica Acta 47, 1907–1916.
Day, P., 1965. Particle fractionation and particle size analysis. In: Black, C.A. (Ed.), Methods of Soil Analysis. American Society of Agronomy, Madison, WI, pp. 545–567.
de Faria, D.L.A., Venancio Silva, S., de Oliveira, M.T., 1997. Raman microscopy of some iron oxides and oxyhydroxides. Journal of Raman Spectroscopy 28, 873–878.
Firestone, R.B., West, A., Kennett, J.P., Becker, L., Bunch, T.E., Revay, Z.S., Schultz, P.H., Belgya, T., Kennett, D.J., Erlandson, J.M., Dickenson, O.J., Goodyear, A.C., Harris, R.S., Howard, G.A., Kloosterman, J.B., Lechler, P., Mayewski, P.A., Montgomery, J., Poreda, R., Darrah, T., Que Hee, S.S., Smith, A.R., Stich, A., Topping, W., Wittke, J.H., Wolbach, W.S., 2007a. Evidence for an extraterrestrial impact 12, 900 years ago that contributed to the megafaunal extinctions and the Younger Dryas cooling. Proceedings of the National Academy of Sciences 104, 16016–16021.
Firestone, R.B., West, A., Revay, Z., Belgya, T., Smith, A., Que Hee, S.S., 2007b. Evidence for a Massive Extraterrestrial Airburst over North America 12.9 ka Ago. American Geophysical Union Mtg. 07, PP41A sessions, San Francisco, AGU Annual Mtg, 2007, PP41A-02.
Gratz, A.J., Fishler, D., Bohor, B., 1996. Distinguishing shocked from tectonically deformed quartz by the use of the SEM and chemical etching. Earth and Planetary Science Letters 142, 513–521.
Hansen, B.C.S., 1995. A reevaluation of the evidence for a Younger Dryas climatic reversal in the tropical Andes. Quaternary Science Reviews 12, 769–779.
Hansen, K.R., Holsapple, K.A., 2003. Impact cratering in porous asteroids. Icarus 163, 102–119.
Haynes, C.Vance, 2008. Younger Dryas "black mats" and the Rancholabrean termination in North America. Proceedings of the National Academy of Sciences 105, 6520–6525.
Hildebrand, A.R., 1993. The Cretaceous/Tertiary boundary impact (or the dinosaurs didn't have a chance). Journal Royal Astronomic Society, Canada 87, 77–117.
Hills, J.G., Goda, M.P., 1999. Damage from comets–asteroid impacts with Earth. Physica D: Nonlinear Phenomena 133, 189–198.
Jones, Laura K.Z., Bish, D.L., 2008. Mineralogical characterization of manganese oxide dendrites using X-ray powder diffraction—Iron Mountain, Missouri. Geological Society of America, Abstracts with Program 40, 254.
Kennett, J.P., Becker, L., West, A., 2007. Triggering of the Younger Dryas Cooling by Extraterrestrial Impact. AGU Annual Mtg, 2007, PP41A-05.
Kennett, D.J., Kennett, J.P., West, A., Mercer, C., Que Hee, S.S., Bement, L., Bunch, T.E., Sellers, M., Wolbach, W.S., 2009. Nanodiamonds in the Younger Dryas boundary sediment. Science 323 (5910), 94.
Mahaney, W.C., 2002. Atlas of Sand Grain Surface Textures and Applications. Oxford University Press, Oxford, U.K. 237 pp.

Mahaney, W.C., Kalm, V., 1996. Field Guide for the International Conference on Quaternary Glaciation and Paleoclimate in the Andes Mountains. Quaternary Surveys, Toronto. 79 pp.
Mahaney, W.C., Dirszowsky, R.W., Milner, M.W., Harmsen, R., Finkelstein, S., Kalm, V., Bezada, M., Hancock, R.G.V., 2007a. Soil stratigraphy and ecological relationships of a Late Glacial–Holocene fluvial terrace sequence, Sierra Nevada National Park, Northern Venezuelan Andes. Journal of South American Earth Sciences 23, 46–60.
Mahaney, W.C., Milner, M.W., Sodhi, R.N.S., Dorn, R.I., Boccia, S., Beukens, R.P., Tricart, P., Schwartz, S., Chamorro-Perez, E., Barendregt, R.W., Kalm, V., Dirszowsky, R.W., 2007b. Analysis of burnt schist outcrops in the Alps: relation to historical archaeology and Hannibal's Crossing in 218 BC. Geoarchaeology 22, 797–816.
Mahaney, W.C., Milner, M.W., Kalm, V., Dirszowsky, R., Hancock, R.G.V., Beukens, R.P., 2008. Evidence for a Younger Dryas glacial advance in the Andes of northwestern Venezuela. Geomorphology 96, 199–211.
Nakamura, K., Fujitsuka, M., Kitajima, M., 1995. Disorder-induced line broadening in 1st-order Raman-scattering from graphite. Physical Review B 41, 12260–12263.
National Soil Survey Center (NSSC), 1995. Soil Survey Laboratory Information Manual. Soil Survey Investigations Report No. 45. Version 1.00. USDA, Washington, DC. 305 pp.
Nealson, K.H., 1983. The microbial manganese cycle. In: Krumbein, W.E. (Ed.), Microbial Geochemistry. Blackwell, London, pp. 191–221.
Osborn, G., Clapperton, C.M., Thompson-Davis, P., Reasoner, M., Rodbell, D.T., Seltzer, G.O., Zielinski, G., 1995. Potential glacial evidence for the Younger Dryas event in the cordillera of North and South America. Quaternary Science Reviews 14, 823–832.
Oyama, M., Takehara, H., 1970. Standard Soil Color Charts. Japan Research Council for Agriculture, Forestry and Fisheries, Tokyo, Japan.
Phipps, M.J., Andronicos, C., 2008. The Tunguska Enigma: determination and implications of shocked quartz at the site of the Tunguska crypto-explosion. Am. Geophysical Union, Fall Meeting, abstract no. V53A-2147.
Pinter, N., Ishman, S.E., 2008. Impacts, mega-tsunami, and other extraordinary claims. GSA Today 18, 37–38.
Quade, J., Forester, R.M., Pratt, W.L., Carter, C., 1998. Black mats, spring-fed streams, and Late Glacial Age Recharge in the southern Great Basin. Quaternary Research 49, 129–148.
Reasoner, M.A., Osborn, G., Rutter, N.W., 1994. Age of the Crowfoot advance in the Canadian Rocky Mountains: a glacial event coeval with the Younger Dryas oscillation. Geology 22, 439–442.
Reimer, P.J., Baillie, M.G.L., Bard, E., Bayliss, A., Beck, J.W., Bertrand, C.J.H., Blackwell, P.G., Buck, C.E., Burr, G.S., Cutler, K.B., Damon, P.E., Edwards, R.L., Fairbanks, R.G., Friedrich, M., Guilderson, T.P., Hogg, A.G., Hughen, K.A., Kromer, B., McCormac, G., Manning, S., Bronk Ramsey, C., Reimer, R.W., Remmele, S., Southon, J.R., Stuiver, M., Talamo, S., Taylor, F.W., van der Plicht, J., Weyhenmeyer, C.E., 2004. IntCal04 terrestrial radiocarbon age calibration, 0–26 cal kyr BP. Radiocarbon 46, 1029–1058.
Rodbell, D.T., Seltzer, G.O., 2000. Rapid ice margin fluctuations during the Younger Dryas in the Tropical Andes. Quaternary Research 54, 328–338.
Salgado-Labouriau, M.L., Schubert, C., 1976. Palynology of Holocene peat bogs from the central Venezuelan Andes. Palaeogeography, Palaeoclimatology, Palaeoecology 19, 147–156.
Schubert, C., 1970. Glaciation of the Sierra de Santo Domingo, Venezuelan Andes. Quaternaria 13, 225–246.
Schüssler, U., Ernston, T., Ernstson, K., 2002. Impact-induced carbonate-psilomelane vein in the Azuara structure of northeastern Spain, Treb. Museum Geologica Barcelona 11, 5–65.
Shannahan, T.M., Zreda, M., 2000. Chronology of Quaternary glaciations in East Africa. Earth and Planetary Science Letters 177, 23–42.
Stich, A., Howard, G., Kloosterman, J.B., Firestone, R.B., West, A., Kennett, J.P., Kennett, D.J., Bunch, T.E., Wolbach, W.S., 2008. Soot as Evidence for Widespread Fires at the Younger Dryas Onset (YDB; 12.9 ka). Am Geophysical Union, fall meeting abstract no. PP13C-1471.
Suuroja, K., Kirismäe, K., Ainsaar, L., Kohv, M., Mahaney, W.C., Suuroja, S., 2003. The Osmussaar Breccia in northwestern Estonia—evidence of a ~475 Ma earthquake or an impact? In: Koeberl, C., Martínez-Ruiz, F. (Eds.), Impact Markers in the Stratigraphic Record. Berlin, Springer, pp. 333–347.
Teller, J.T., Leverington, D.W., Mann, J.D., 2002. Freshwater outbursts to the oceans from glacial Lake Agassiz and their role in climate change during the last deglaciation. Quaternary Science Reviews 21, 879–887.
Van der Hammen, T., Hooghiemstra, H., 1995. The El Abra Stadial, A Younger Dryas equivalent in Colombia. Quaternary Science Reviews 14, 841–851.
Vortisch, W., Mahaney, W.C., Fecher, K., 1987. Lithology and weathering in a paleosol sequence on Mt. Kenya, East Africa. Geologica et Paleontologica 21, 245–255.
Wagner, E., 1973. The Mucuchies Phase: an extension of the Andean cultural pattern into Western Venezuela. American Anthropologist, New Series 75 (1), 195–213.