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Evidence for a cosmogenic origin of fired glaciofluvial beds in the northwestern Andes: Correlation with experimentally heated quartz and feldspar

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ABSTRACT

Fired sediment, considered equivalent to the 'Black Mat' impact of 12.9 ka, has been located and analyzed in the Andes of northwestern Venezuela. The 'Black Mat' refers to possible fallout from the *Encke Comet* airburst presumed to have occurred over the Laurentide Ice Sheet, the impact spreading ejecta over large portions of North America and Europe, making it an interhemispheric event of considerable magnitude. These possible equivalent beds in the northern Andes, first considered to result from a lightning-induced conflagration adjacent to the retreating Late Wisconsinan (Mérida Glaciation) ice, are now known to have undergone intense heating upon impact to a temperature much higher than what would occur in a wet, first-stage, successional tundra. Analyses carried out by SEM and FESEM, in SE and BSE modes, show massive micro-disruption on grain surfaces, fractures diminishing with depth toward grain interiors and C welded onto quartz and plagioclase minerals. Bubbles on some grains, possibly the result of exclusion of water-of-crystallization, are seen on some samples, principally quartz. The presence of copious monazite in the carbonaceous coatings is considered part of the incoming ejecta, as it is not a common indicator mineral in the local lithology. Analysis by SEM and FESEM of quartz and plagioclase subjected experimentally to temperatures ranging from 500 to 900 °C shows that intense heating affects resident mineralogies to differing extents, with grain disruption more prevalent along cleavage planes deep into grain interiors. The intergrowth of carbonaceous "black mat" material with thermally disrupted and fragmented quartz and feldspar, a "welded" patina of 100–400 nm thickness could only occur with temperatures in excess of 900 °C, the event interpreted here to be of cosmogenic origin.

1. Introduction

The reversal of global warming during the Alleröd subchron and sudden onset of the Younger Dryas (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; Teller et al., 2002; Mahaney et al., 2007a, 2008; Shannahan and Zreda, 2000). Coinciding with a large-scale Clovis-Age megafaunal extinction, it had far-reaching consequences affecting the geo-ecological environment across North America and Europe (Kennett et al., 2008). Newly discovered sites in Europe indicate the event was indeed interhemispheric and may have affected the entire world (Kennett et al., 2007, 2009).

A variety of hypotheses have been put forth to explain this major perturbation in environmental conditions, including an impact event in North America (Firestone et al., 2007a,b; Haynes, 2008; Kennett et al., 2007, 2009) and breakup of *Comet Encke* (Napier, 2010). Even other possible impact craters such as one in southwestern Nova Scotia (Stevens et al., 2008) and spring seepage and development of reducing environments (Quade et al., 1998) have been invoked to explain the black stratigraphic marker. The available data, compiled primarily from sites within the United States and Canada, centers around the presence of a 'black mat' stratigraphic marker dating to the climatic change at the Alleröd/YD boundary; ~13 ka and argues for the breakup of a vehicle somewhere over the Laurentide Glacier. The sediment within the 'black mat' comprises a thin layer of shocked sediment characteristic of ET impacts, including but not limited to, glassy carbon and/or magnetic spherules, platinum group metals in fine silt, fragmental quartz, orthoclase, monazite and nanodiamond (lonsdaleite). Although clearly contentious as to proof for, and extraterrestrial origin of, the "black mat" (Haynes, 2008; Pinter and Ishman, 2008), the one site location in the northern Andes described herein and new evidence from Patagonia (Kyeong Kim, personal communication, 2009) point tentatively to either an asteroid or comet event that reached far into South America, perhaps even to the

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Antarctic. Previously Firestone et al. (2007a,b) and Mahaney et al. (2010) argued for an asteroid impact but new evidence suggests the impact was cometary in nature (Napier, 2010).

The sheer magnitude of the proposed comet impact (Napier, 2010), an event so cataclysmic that remnants of the comet—the Taurid bodies which occupy near Earth orbits—would have caused a hemispheric-wide shock wave, a major perturbation introducing high-velocity ejecta into the atmosphere (Firestone et al., 2007b), fine ash reaching Venezuela at speeds up to 30 km/s in less than 2 min. A strikingly high percentage of examined sites in N. America (Haynes, 2008) reveal a distinctive horizon of carbon-coated material ('Black Mat'), which supports the theory despite hypotheses advanced for a different origin (Mahaney et al., 2010).

The profile (MUM7B; Mahaney et al., 2008, for stratigraphy) in question, located in the northwestern Venezuelan Andes, is found at 3800 m a.s.l., and dates to within the range of the proposed event. Formed at the base of an outwash fan, 'black mat' beds survived the advance of YD ice, which eventually occupied a stillstand position overlapping slightly older Late Glacial moraines described in Mahaney et al. (2008). The YD till in Site MUM7 (Mahaney et al., 2008) exhibits push-moraine characteristics, the long axes of cobbles and boulders bearing a unimodal azimuth of 320° magnetic. Retreat of the YD ice over the MUM7B site, situated some 100 m up-valley, left no trace of till, only a thin wedge of outwash gravel, approximately 1.0 m in thickness (Fig. 2). Survival of the 'Black Mat' sediment (Fig. 2, arrow for location in section) probably relates to water content, for if the material was saturated as is typical of tropical glaciers, the resulting pressure of the ice would be hydrostatic, shear stress reduced effectively to zero. Alternatively, it could be the material was frozen which would armor the sediments thus preserving them in situ.

Of particular interest regarding the black mat sediment is the composition of thin, dark and spattered glassy coatings of carbon, welded/adhered to sand and pebble size clastic material in the buried alluvial beds, and associated micofractures that are considered to result from the high temperature produced by incoming ejecta. Of even greater interest, perhaps, the dual Fe–Mn–C (tri-coatings), partially consumed by accompanying microorganisms observed on the grains provided an energy source for resident bacteria and fungi. It is probable that a second high Mn coating is the product of a reducing environment and leaching of meteoric-groundwater through the section, a process enhanced over time by bacteria feeding on the primary C-rich ejecta coating below (Burdige and Kepkay, 1983; Nealson, 1983; Bougerd and de Vrind, 1987). The biotic aspect of the black mat will be explored in a later paper but herein we address the

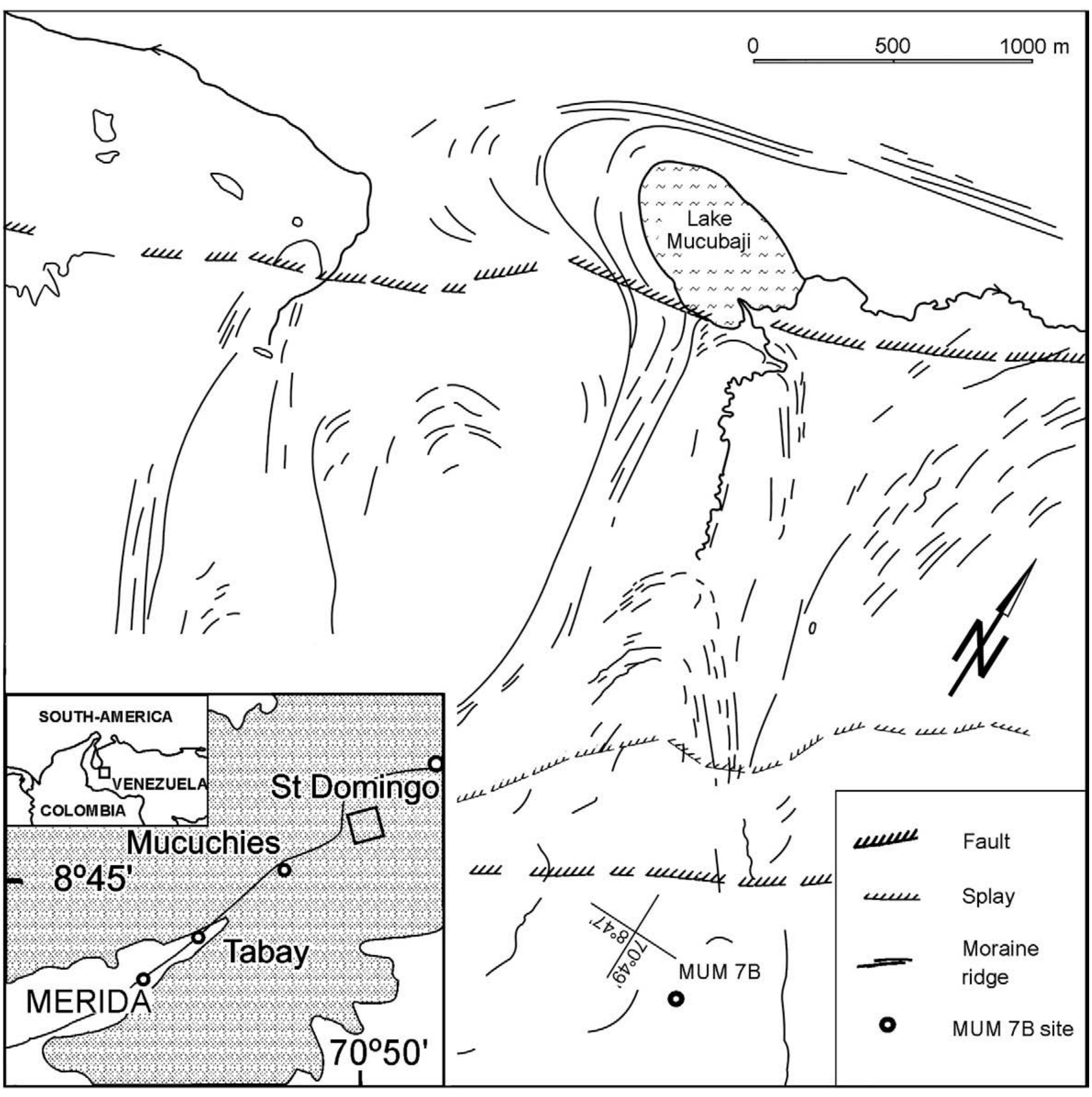

Fig. 1. Location of the MUM7B site in the northwestern Venezuelan Andes.

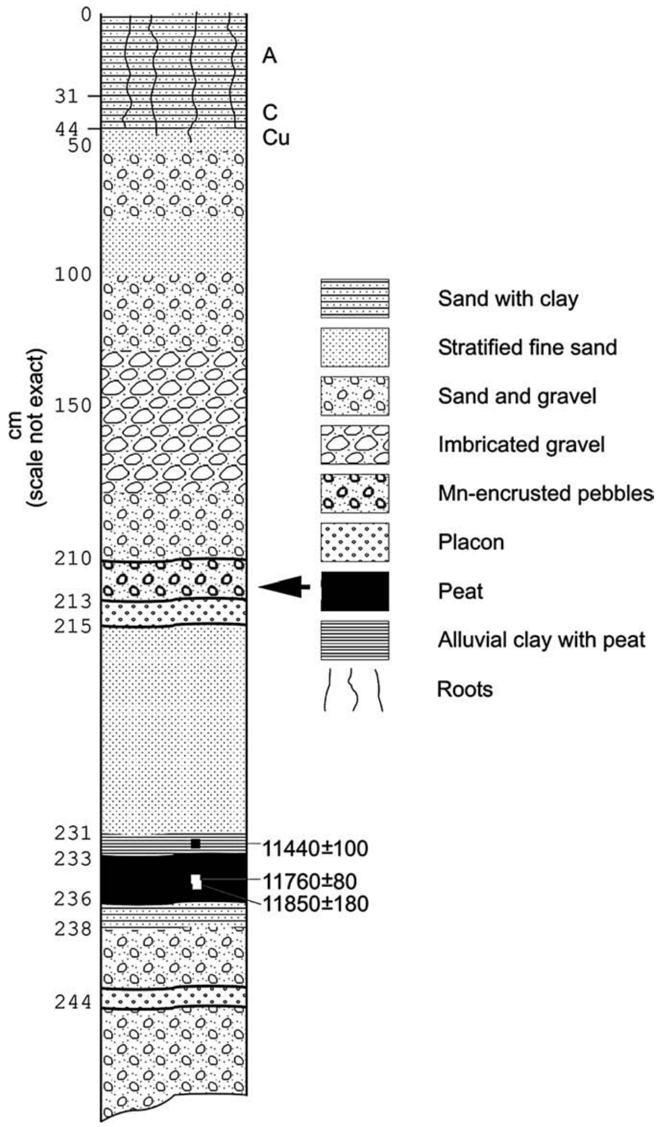

Fig. 2. Stratigraphy of the MUM7B site showing radiocarbon dated beds, position of the black mat beds (arrow) and overlying outwash.

character of the mat itself, its composition and relation to the grains derived from the country rock. There remain many unanswered questions, particularly those of the welding/adhering temperature of

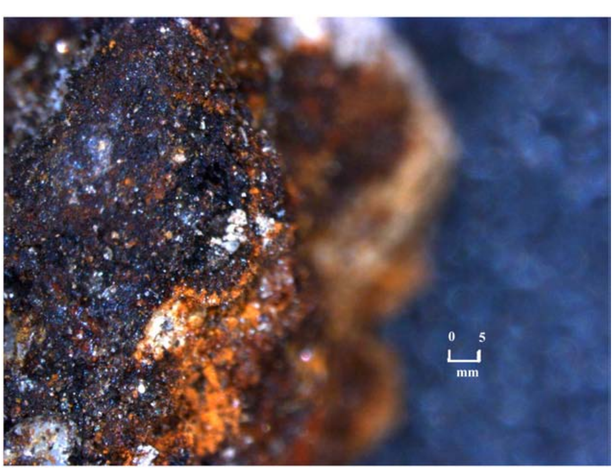

Fig. 3. Light micrograph of the black mat showing carbon glassy spherules.

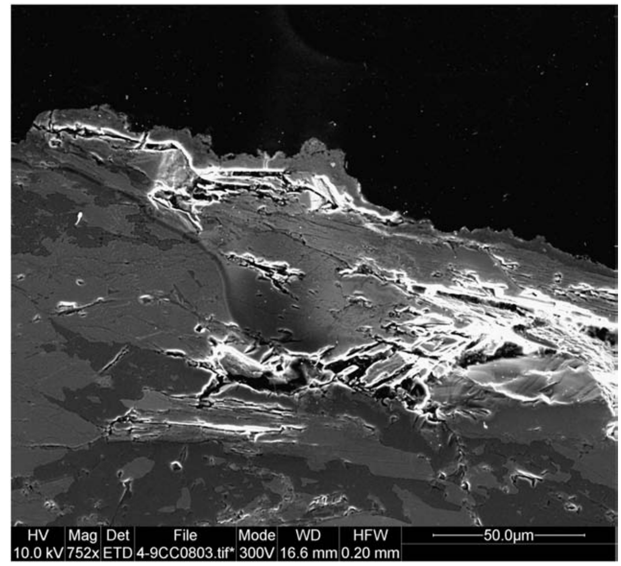

Fig. 4. Quartz grain from black mat showing fragmental edge of quartz grain with very thin coating of black mat (light tone); dark tone is epoxy. Fractures are closely spaced and oriented parallel to the surface.

the coatings, settling velocities, frequency of the coatings across grain surfaces, and on a larger scale, the size and nature of the ejecta cloud itself. To answer some of these questions we compare and contrast the black mat at Site MUM7B with physical changes in quartz and feldspar grains experimentally heated at various temperatures of 500, 700 and 900 °C, the minerals subjected to SEM analysis at each stage.

2. Regional geology

The Mucuñuque Catchment in which the black mat was discovered is shown in Fig 1. The valley is a near linear fault-controlled glacial basin with headwaters on the western slopes of Pico Mucuñuque (4672 m a.s.l.), the major high summit north of the Humboldt Massif. With a SE–NW trend the valley is marked by numerous bedrock bars, each punctuated by 100-m drops in elevation down to the elevation of

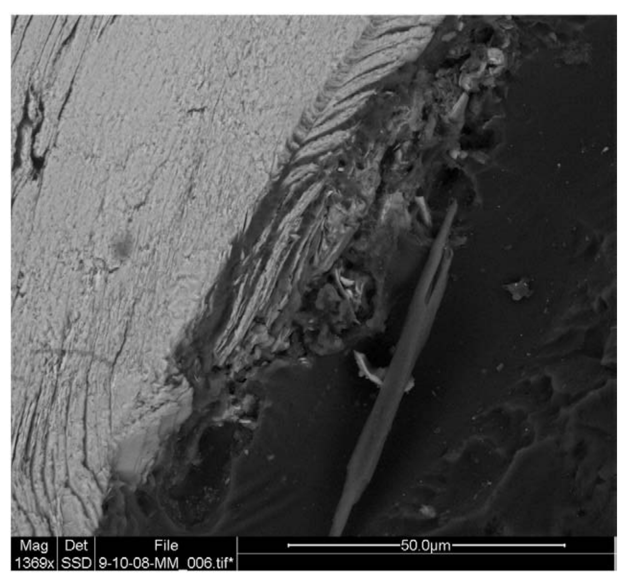

Fig. 5. Andes quartz, narrow frame enlargement, showing very thin C coating, the black mat lighter in tone compared to the epoxy (extreme right). The disrupted mineral edge shows an outer variable fragmented zone 10 µ thick, aligned internally with a coarse fracture zone another 10 µm in thickness, abutting a parallel microfracture zone. Grain damage is interpreted to result from extreme heating upon contact with ejecta.

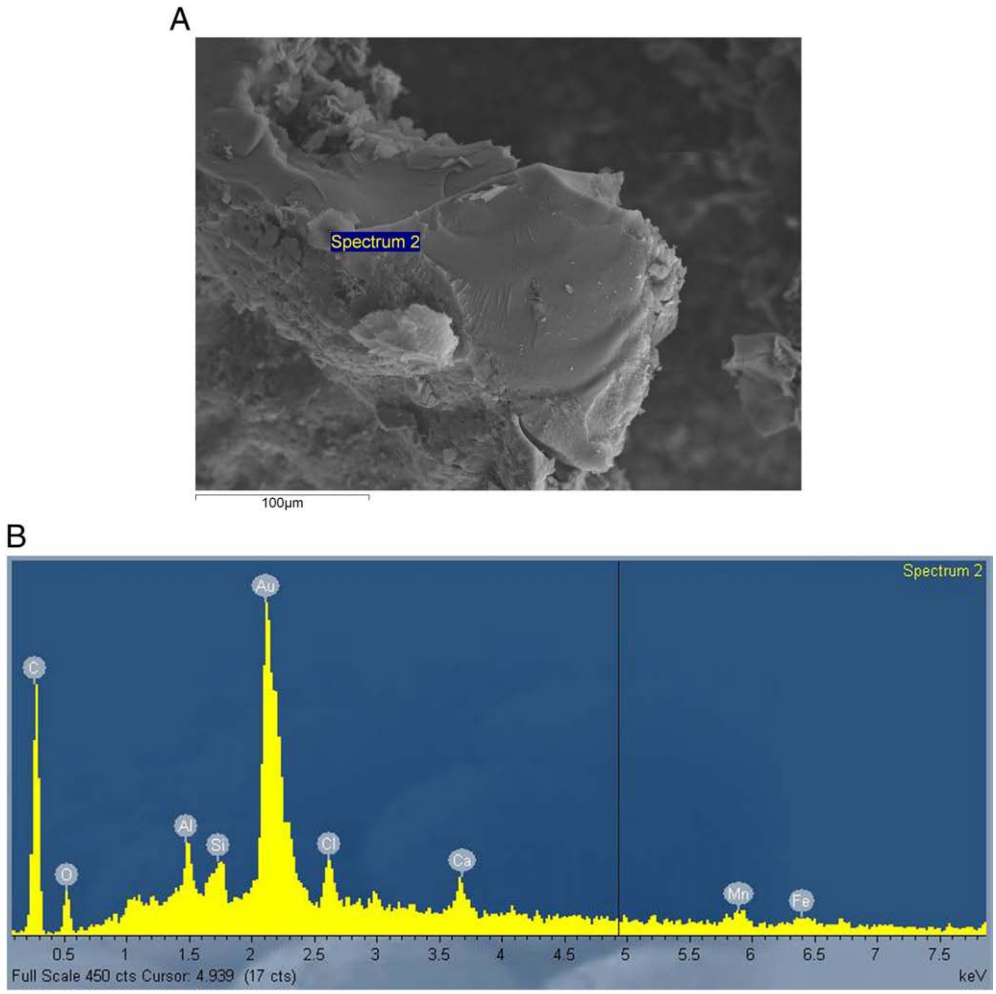

Fig. 6. A, Thick carbon coat on unidentified disrupted silicate showing heavily fractured surface; B, EDS spectrum shows Al:Si at 1.5:1.0, most probably Ca-plagioclase with cosmic Al. The high C is from impact ejecta and ignited terrestrial vegetation. Traces of Mn and Fe are typical components of the black mat. Origin of the Cl is unknown but might originate from comet/meteorite airburst. The Au is conductive coating.

Lago Mucubaji at 3600 m a.s.l. Above 4200 m the valley is floored with bedrock, talus cones dominating the valley sides; below 4200 m bogs dominate and it is from these source materials and associated Mollisols (alpine grassland soils; Mahaney and Kalm, 1996) that some of the carbon in the 'black mat' might have accumulated (see Mahaney et al., 2008). Major bedrock bars have waterfalls present such as the one just above the MUM7B site where the black mat sediment was discovered.

The high summits of the eastern cordillera of the Venezuelan Andes lie between 8°30′ and 9°00′ N and 70°30′ and 70°45′ W, with elevations further south reaching close to 5000 m a.s.l. Ice spilled west from Pico Mucuñuque (Sierra Nevada de Santo Domingo—Fig. 1) during the last (Mérida = Wisconsinan) glaciation (Schubert, 1970, 1974; Mahaney et al., 2007a). The Mucubají Glacier (Fig. 1) left a corpus of glacial geomorphic and sedimentological evidence of Late Pleistocene glacial fluctuations including the Younger Dryas (YD) climatic reversal, the latest event in the Late Glacial (Gibbard, 2004; Ralska-Jasiewiczowa et al., 2001). The valley contains glacial/fluvial outlets, all of which drained across steep gradients (10–35° slopes) into lacustrine basins located between 3000 and 3600 m a.s.l.

Within the Mucubají Valley upstream of the previously documented recessional moraine sites (Mahaney and Kalm, 1996; Mahaney et al., 2008) new investigations reveal geomorphologic and stratigraphic information (including surface moraine and outwash fans burying alluvial peat), which document a resurgence of ice following the breakup and retreat of glaciers in the Late Glacial, the youngest suite of sediments corresponding to the YD. Ice overran older tills, glaciolacustrine, and/or glaciofluvial deposits, leaving buried organic materials dated to between 13.7 and 12.4 ka cal year BP together with reworked peat dating to 18.8 ka cal year BP.

3. The Younger Dryas

The existence of the YD climatic event (11–10 ka; 11.6–12.7 ka cal BP) in tropical South America, as well as its possible timing and/or character, have been the subject of considerable discussion and debate, with most evidence for its existence derived from either palynological/paleoecological or glacial geomorphological/sedimentological studies in Colombia, Ecuador, Peru, and Bolivia (Salgado-Labouriau, 1989; Salgado-Labouriau and Schubert, 1976; Clapperton, 1990; Hansen, 1995; Osborn et al., 1995; Van der Hammen and Hooghiemstra, 1995; Rodbell and Seltzer, 2000). The growing consensus that one or more climatic reversals occurred during overall deglaciation of the Andes (Osborn et al., 1995), the cumulative evidence suggests earlier cooling events (<15.5 ka), less well-defined, possibly longer-lived, and with or without associated glacier advances (e.g., Clapperton and McEwen, 1985; Helmens, 1988; Birkeland et al., 1989; Rodbell and Seltzer, 2000). Sites allowing precise dating of glacial advances coeval with the YD as defined for northwestern Europe are extremely limited (Osborn et al., 1995). In summarizing the rather scanty evidence available for Venezuela, Schubert and Clapperton (1990) suggested that glaciers may not have had time to reform during the YD period

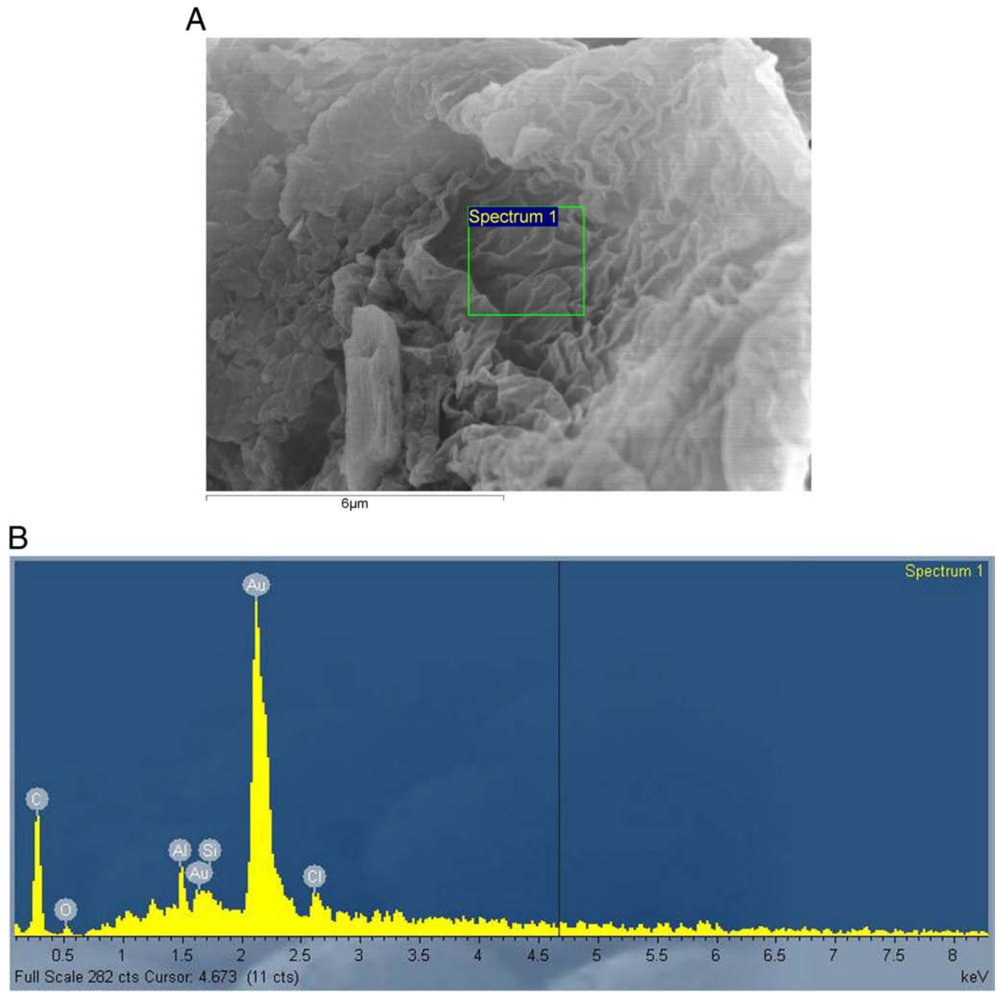

Fig. 7. A, Crenulated coating on undetermined silicate; B, EDS spectrum shows high C with minor Al, possibly sillimanite heated to high temperature. The Cl could have a source in aluminosilicate glass, detection of chloride ion in magma and possibly meteoritic in origin.

following their initial Late Pleistocene retreat/disappearance, particularly at lower elevations. At the time Schubert and Clapperton did not know of the multiple till sections in Mucunuque and in the Humboldt Massif (Mahaney et al., 2010).

In the Venezuelan Andes upstream of Laguna Mucubají (3600 m a.s.l.) and Lago Coromoto (3000 m a.s.l.), a distinct series of recessional moraines located between 3200 and 3800 m a.s.l. (Schubert, 1972, 1974; Salgado-Labouriau et al., 1977) record several stillstands that occurred following the Last Glacial Maximum (LGM). In the Mucubají Valley, these moraines were previously shown to predate 14.9 ka cal BP based on dated peats exposed in river terraces upstream of the uppermost example (Salgado-Labouriau et al., 1977; Mahaney et al., 2007b). An additional ^{14}C date obtained from the base of a core drilled into bog (over lacustrine) sediments just up-valley of the terrace site (Stansell et al., 2005) provides a revised minimum age for glacier retreat of 15.7 ka cal BP. These ages do not account for additional lacustrine sedimentation below sample depths that may have persisted for several centuries (Dirszowsky et al., 2005). While subsequent glacier fluctuations up-valley may have contributed to variation in glaciofluvial/lacustrine sedimentation and peat accumulation at the Mucubají terrace site (Salgado-Labouriau et al., 1977, 1988) as proposed by Stansell et al. (2005), their suggestion that ice readvanced downvalley of the site between 13.8 and 10 ka cal BP is highly improbable given the lack of erosional and/or deformational features in the sediments (Salgado-Labouriau et al., 1977; Mahaney et al., 2007a,b). The terminal position of the YD ice is at 3800 m a.s.l. as explained in Mahaney et al. (2008).

Although several workers, including Schubert (1974), Schubert and Clapperton (1990), Mahaney and Kalm (1996) and Mahaney et al. (2001a,b), have discussed the evidence for punctuated glacier recession following the LGM, glacial landforms in the eastern cordillera of Venezuela have not been subjected to detailed mapping or sedimentologic and geochronologic analysis. The area dealt with in this study, below Pico Mucuñque, witnessed the growth of one of the largest valley glaciers in the entire range during the LGM (Schubert, 1998). The results reported here represent the first terrestrial evidence for resurgence of ice in this area during the YD event complete with bracketing maximum and within-advance radiocarbon ages. The maximum ^{14}C dates bracketing the black mat record an impact of ejecta from the proposed comet airburst that immediately preceded the onset of YD ice in the catchment.

4. Materials and methods

All sections were dug by hand and cut back to expose fresh sediments. Sediment samples were collected for laboratory analysis and peats and organic clayey silts were collected for radiocarbon dating as explained in Mahaney et al. (2008). Samples were handled with metal implements, air-dried, and wrapped in aluminum foil. Laboratory processing of the samples was carried out with speed: the

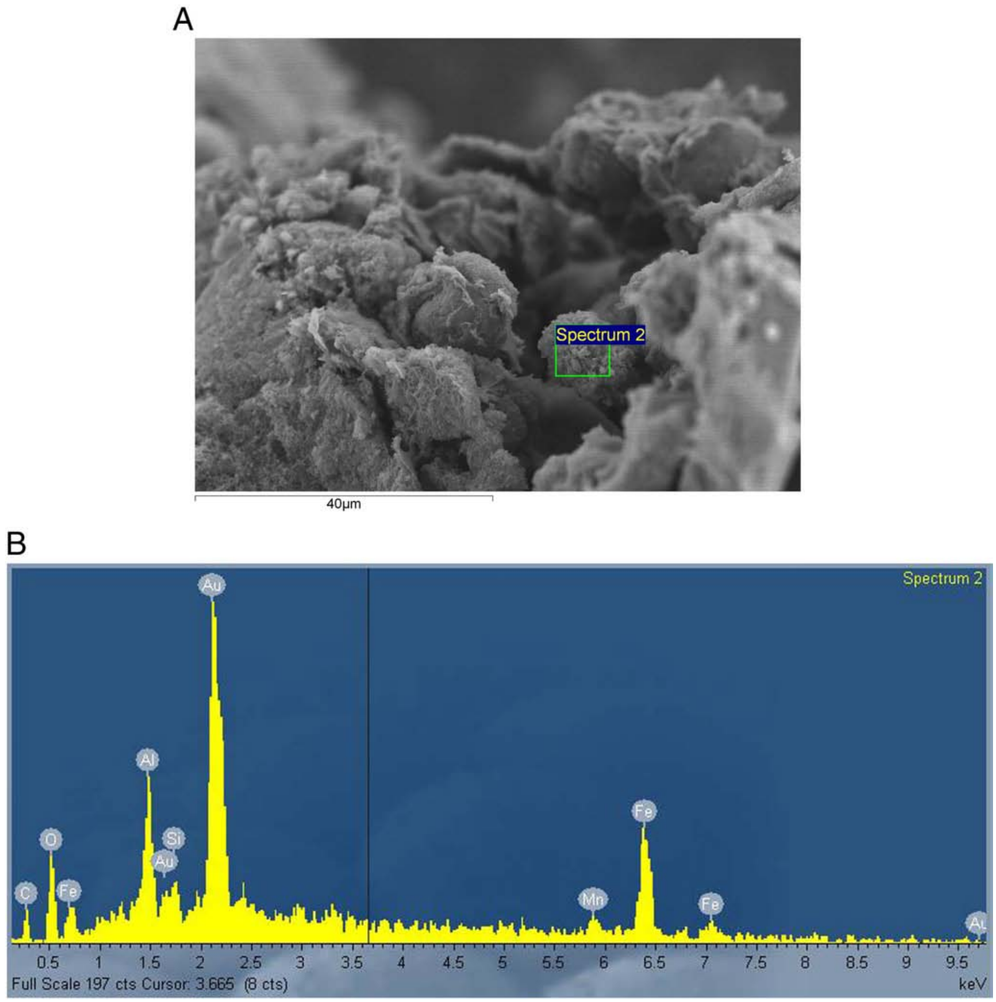

Fig. 8. A, Near spherical grain bearing thick coatings and adhering particles; B, EDS spectrum of C with higher Al either from a cosmic source or melting of sillimanite, minor Si and Mn and higher Fe.

radiocarbon samples analyzed within 1 month of collection. Radiocarbon samples were washed with distilled water and acid treated to remove impurities. Samples were dated by decay counting at the IsoTrace Radiocarbon Laboratory at the University of Toronto. At IsoTrace, samples were treated with hot 4N HCl, followed by extraction with freshly prepared 0.25 N NaOH and acid washed to remove possible carbonate and humic contaminants. As part of pretreatment, the clayey silt sample (TO-9278a) was first demineralised in hot HCl and HF. All dates are corrected for isotopic fractionation and are calibrated with the OxCal v.3.10 calibration programme (Bronk-Ramsey, 2005) using the INTCAL04 calibration data for the Northern Hemisphere (Reimer et al., 2004). In Fig. 2 the uncertainties of the ^{14}C dates are reported as 1σ, whereas calibrated ^{14}C ages were previously reported as 2σ with ranges of 14.1 ka to 13.1 ka with the median of the calibrated dates ranging from 13,290 to 13,640 years.

Sediment/soil samples from the Mucubají sites (MUM7 and MUM7B) were air-dried and subjected to particle size analysis following procedures outlined by Day (1965). Sands separated by particle size analysis and samples recovered from encrustrations on pebbles in an upper placon at MUM7B were dried and subsampled under the light microscope. Selected grains were then mounted on stubs for analysis by field emission scanning electron microscope (FESEM), normal SEM and energy-dispersive spectrometry (EDS) following methods outlined by Mahaney (2002). When analyzing for carbon, samples were coated with gold–palladium; when analyzing silicates samples were coated with C (Vortisch et al., 1987; Mahaney, 2002). Photomicrographs were obtained at accelerating voltages of 10 to 20 keV. X-ray microanalysis was acquired at an accelerating voltage of 10 keV.

Two polished Nimrod granite plugs were placed in a dry oven at ambient temperatures. The plugs were then heated to 400, 700 and 900 °C in platinum boats for 48 h. At ambient temperatures and after each temperature rise, the sections were removed from the furnace and photographed with the SEM. They were then coated with C, which was removed after photography, so that the samples could be readied for the next experimental temperature rise. Scanning electron micrographs were taken in the backscatter (BS) and cathodoluminescent (CL) modes. We will not discuss the features present in the CL pictures, as the details do not apply here.

5. Results

5.1. Black mat samples

The black mat is a 3-cm thick bed of C–Fe–Mn encrusted pebbles and sands (<2–64 mm) with a black color [(7.5YR 2/1), Oyama and Takehara, 1970]. Approximately 10% of the total weight of the bulk sample is sand, mostly coarse and very coarse sand (500–2000 μm), mixed with lesser amounts of medium to very fine sand (500–63 μm) and more minor amounts of silt and clay (<63 μm). Stratification is weak but present, the bed part of a complex of YD outwash, some with placon characteristics indicating the sands serve as aquifers. With the <2 mm fraction of the sample amounting to at most 3% of total weight,

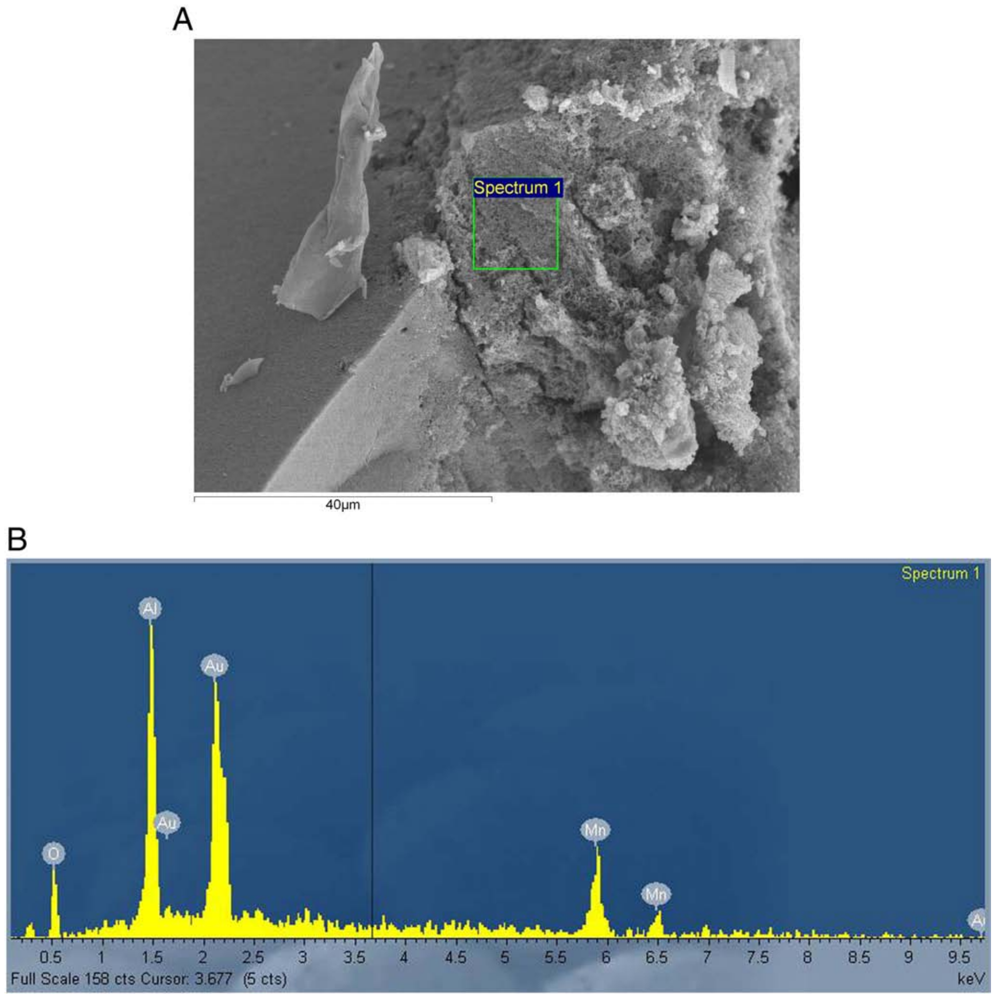

Fig. 9. A, Frothy surface, possibly made ductile from extreme heating; B, EDS spectrum indicates minor C, high Al, mid range Mn, with no Fe. Carbon at .3 keV is unlabeled and high Al could be from melted sillimanite. The trace of Cl at approximately 2.6 has a similar signature to Fig. 7B.

a statistically accurate replicated particle size is not possible but the approximate split of sand–silt–clay is 83–14–3% placing the material in the coarse sandy loam group.

Lithologically, the host rock mineralogy is exclusively felsic gneiss in composition composed of sillimanite, andalusite, quartz and orthoclase. Less than 5% of the sample consists of biotite and monazite, although the proportion of monazite in the black mat is significantly higher than in the country rock and may be part of the incoming ejecta. Chemical analysis of the black mat coating comprises significant concentrations of La, Ce and Th which are associated with monazite grains.

The grain coating under low power magnification (Fig. 3) using the light microscope appears distinctly black, often glassy on translucent spheroidal particles, many welded onto both small and large grains alike. Coatings have mean thicknesses of 500 nm with some reaching 1.0 µm. Other coatings appear dense and distinctly opaque. The micron-thick black mat scale is sometimes C by itself or C encrustations with Fe and Mn, the latter two chemical elements probably resulting from import ejecta or fluctuating redox conditions during diagenesis. Numerous colonies of bacteria and fungi associated with these encrustations are the subject of another report in preparation.

5.2. Scanning electron microscopy

Imagery attained using the SEM provides a database for physical and chemical analyses of the black mat sediment. Images in Figs. 4 and 5 are representative of quartz, presumably resident grains derived from the country rock, which show disarranged surfaces, a micro-brecciated mass. The broken-edge surface up to ~50 µm thick may result from impact with the ejecta mass or from heat release on impact, or both. In the case of Fig. 4 it appears fractured bodies extend

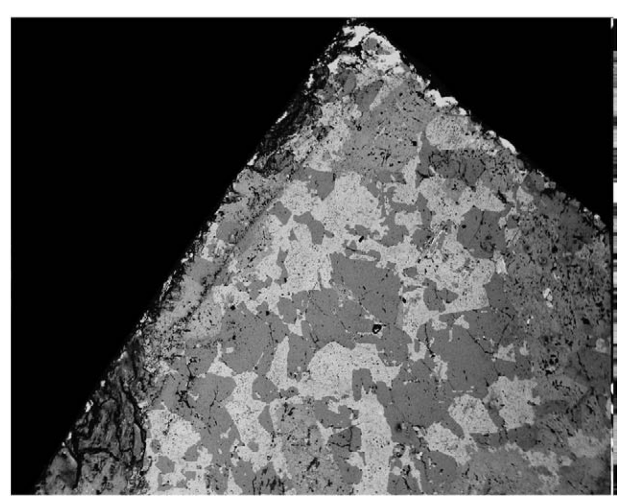

Fig. 10. Scanning electron micrograph taken in the backscatter mode with Z contrast of an area in a standard thin section that has not undergone experimental heating. The large dark grains are quartz and the very light material in between is K, Ca feldspar. Note the lack of cracking (×27).

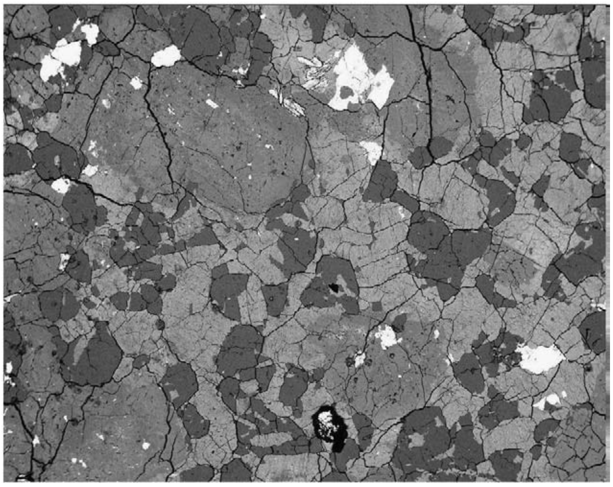

Fig. 11. Image taken under the same conditions as Fig. 10, although the grains in this micrograph were heated to 900 °C as indicated in the text. The area of the thin section in this micrograph was not exactly the same as in Figure 10, but was taken in the same thin section nearby. Note that the feldspar cracking is somewhat different than the same features in quartz, and there is evidence that cleavage is partly responsible for the cracking orientation in feldspar (×27).

normal to the grain edge while in the case of Fig. 5 fractures are parallel adjacent to the disarranged edge. These fracture patterns may be related to pre-existing microfractures in the grains or to various vectors of heat release on impact.

Enlargement (Fig. 6A and B) of the outer surface of impacted quartz shows sharp-edged angular and very fragmental quartz grains, some with conchoidal fractures that may relate to vibration frequency that led to their formation. The micro-sawtooth edges of some of the quartz have never been seen before even on imaged asteroid ejecta (Mahaney, 2002) but may be microfeatures common to cometary impact, a function of impact velocity or heat release. The EDS spectrum for this sample shows a probable Ca-plagioclase composition, minor Fe and Mn coating with high C. Some Al may result from melted sillimanite or andalusite while the Cl may result from incoming ejecta.

Crenulated or scalloped quartz shown in Fig. 7A consists of thick C coating but contains some Al and Cl. The Al could be scavenged from other country rock minerals but the Cl, while unexplained, could be related to aluminosilicate glasses and have an interstellar origin (Stebbins and Du, 2002). Disrupted quartz on a scale such as shown here can only be explained by some combination of impact and heat. Additional imagery (Fig. 8A) shows microfragmental Al, lightly coated with Mn and C, and surrounded by twisted quartz. Some fragmental material, encased in nodules of ~10 μm diameter, also consists of micro-sawtooth forms as seen in Fig. 6A. EDS spectral data indicates the presence of Si, Al, O, and Fe with minor C in this case. An enlargement of Fig. 8A in Fig. 9A shows highly fragmented angular Al-oxide with minor Mn.

5.3. Experimental heating tests

A series of heating experiments were carried out on the Nimrod granite, a small, granitoid stock associated with Oligocene–Miocene deposits in the Western Cascades. The Nimrod (16.3 Ma) at the collection point near Nimrod, Oregon is a medium grained and relatively equigranular rock, and is locally miarolitic (Gustafson and Tepper, 2004).

Cracks were observed at every elevated temperature in both the quartz and feldspar grains (Figs. 10–12). These cracks increased in thickness, density and number as the temperature of exposure increased from 500 to 900 °C. Since the observed grains were surrounded by others, there is not a direct analogy to the cracks found on the surfaces of minerals in the black mat. However, the disruption and cracking observed in the experimental grains is similar in kind but of lower intensity to those photographed in the black mat samples.

With an increase in temperature, dehydration and cracking occurred. Apparently each quartz grain, dependent upon its structure, contained varying amounts of crystalline water. Because the runs were all dry the water must have originated in the individual quartz grains, or possibly from the nearby feldspar grains.

The quartz grains are relatively free of internal spots or possible defects, while the feldspar grain fractures tend to follow lines of defects. In places along the contacts between the central quartz grain and surrounding feldspars, large fractures are present, while in other places they seem to hardly exist at this level. Since the temperature applied to the entire thin section over time is presumed to be the same, there must be a considerable difference between the various contacts, perhaps compositional, crystallographic or defect driven. Note also the lower left corner of the central quartz grain in Fig. 12. In photographs taken of the same grain that was not subjected to temperature increases, this corner is normal quartz. However, at 900 °C in this micrograph (Fig. 12), the lower left area appears dehydrated.

With increasing temperature, the area in question started to crack and the cracks increased with temperature until the final event is as imaged in this figure. This suggests that a portion of the quartz grain contained some water, which when heated, caused cracking while escaping.

There are distinct similarities between the experimental quartz and feldspar grains and the minerals found at the black mat site with respect to internal cracking.

6. Discussion

Similarities between the black mat and the experimental grains include intense brecciation and internal fracture patterns in both sample suites. Degree of brecciation appears more intense in the black mat samples compared with the experimental grains which may be a function of impact rather than heating. Microfracture patterns in the black mat samples are either parallel to or normal from the surface, the pattern possibly related to impact energy or to variable energy

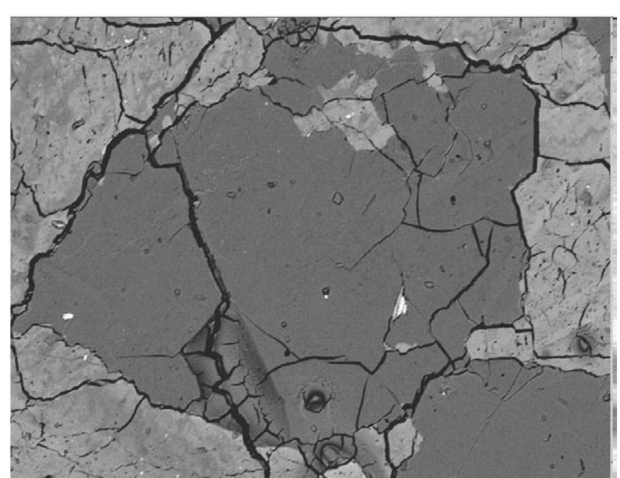

Fig. 12. An enlargement of one of the quartz and feldspar grains in thin section heated to 900 °C. Note the fractures at the edges of the quartz grain. The feldspar grains have somewhat different types of fractures (×300).

cone vectors. Within the experimental grains the brecciated surface is thinner and the internal microfracture pattern either follows crystallographic planes as with the feldspar minerals or is random in the quartz reflecting its poor to indistinct cleavage.

The black mat material ranges from fibrous carbon-rich material with accessory Fe and Mn to glassy C-rich spherules, the latter often welded on grain surfaces and covered with layers of Fe and Mn. Grain surfaces upon which the carbon is fixed are topographically irregular with brecciated microfeatures of some depth radiating out into zones of high frequency microfractures produced either by mass impact, soot release from wildfires (Stich et al., 2008) or heat release. As observed with the experimental grains where heat-induced microfractures are random in quartz and widely spaced, in the black mat samples microfractures are closely packed into high density areas which appear to be vibration-generated microfeatures.

The black mat data available thus far supports a kinetic theory of mass impact for the production of brecciated surfaces and the high frequency of closely spaced microfractures, grain to grain collisions at extremely high velocity although with variable masses involved. The incoming ejecta is expected to be in the fine sand to silt range; the resident grains of small pebble to silt range are part of the country rock. The welded character of C-bonded material argues for extreme heat at temperatures much higher than 900 °C, but apparently not high enough to shock melt quartz. The exact temperature of incoming ejecta is unknown but to weld C to grain surfaces without melting quartz would be between 900 °C and 1670°–1713 °C, of β tridymite and cristobolite the latter estimated melting temperature somewhat higher than α quartz, estimated at <1670 °C (Deer et al., 1966; Frondel, 1962).

Possible alternative hypotheses to explain the black mat might focus on the nature of the placon (aquifer) the black mat resides in at the site. One alternative explanation might be that the black mat forms in place from chemolithotrophic bacteria and alternating redox conditions that favor retention of C, Mn and Fe. This follows the views of a minority that the black mat is simply a subsurface drainage accumulation of organic and associated oxides and hydroxides without any cosmic connection. The null hypothesis for this argument lies in the presence of pdfs, occasional platinum based metals, extraordinarily high monazite and associated concentration of REEs. Admittedly the lack of nanodiamond, Ir and shock-melted quartz softens the cosmic hypothesis but then the distance between primary impact and impact zone of the ejecta leaves open the question of dispersal of impact remnants with increasing distance from the Laurentide Ice Sheet. The spread of ejecta outward from the blast site is hardly expected to be uniformly distributed.

A second alternative hypothesis might question the C spherules as products of mites (faecal pellets) or secondary opaline originating in soils. One might argue the lack of chondrules in the pellets argues against a cosmic origin. Comparison of the C-rich spherules in the black mat in the Andes with similar samples analyzed by Firestone et al. (2007a,b) show more similarities than differences. If one were to consider the C spherules as less dense than those studied by Firestone et al. (2007a,b) one might also argue the Andean specimens could have weathered extensively or suffered from distance traveled. From the data in Fig. 3 there is a preponderance of high density C in the great majority of the spherules and there may likely be micro chondrules within this sediment.

A third hypothesis might challenge our conclusions that the fired rock underwent the extremes of heat without impact which is absolutely correct. However, both the low and high temperature firing produced similar microfracturing around grain edges and along crystallographic planes producing a micro-brecciated effect. With the back mat the fusion of C to mineral surfaces and the twisted/contorted nature of select grains indicate something more than a low grade bush fire occurred at the site. Even with the partial evidence available a cosmic connection offers the best explanation.

7. Conclusion

The database described herein does not conclusively prove an ET impact/airburst at 12.9 ka for the black mat as we have detected no irrefutable pdfs, shock-melted quartz, iridium or nanodiamonds in the samples analyzed thus far. But the data described here highlight a mat of glassy carbon spherules fused/welded onto alluvium firmly dated to within the YD initiation window. The C-rich mat, a nanometer thick coating is encrusted on brecciated/fractured minerals of quartz and feldspar, the disrupted mineral surfaces interpreted to result from mass impact and extreme heat. In eight out of ten occurrences carbon is coated or welded onto mineral grains; in two occurrences out of ten it is coated or welded on pre-existing coatings of secondary Fe and Mn. Most occurrences indicate a tripartite arrangement of coatings of C–Fe + Mn and most often the 3-layer system is prolific with bacteria and fungi. These data indicate the site acted as a placon or aquifer providing water, C and Fe as a medium supporting microbe growth.

Grains of feldspar and quartz, subjected to controlled heating experiments in the laboratory compared with the black mat minerals show similar brecciated surfaces with fractured interiors but with significant differences in depth of ruptured surfaces and densities of microfracture patterns.

Major characteristics of both the black mat and experimental grains include oriented cracks, general disruption of grain surfaces leading to extreme brecciation, dried out appearance of grain surfaces with fractures, and decrease in disruption of mineral grains away from the mat into the mineral structure, the latter more noticeable in the black mat samples.

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