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RECENT DEVELOPMENTS IN THE ANALYSIS OF THE BLACK MAT LAYER AND COSMIC IMPACT AT 12.8 KA

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ABSTRACT. Recent analyses of sediment samples from "black mat" sites in South America and Europe support previous interpretations of an ET impact event that reversed the Late Glacial demise of LGM ice during the Bølling Allerød warming, resulting in a resurgence of ice termed the *Younger Dryas* (*YD*) cooling episode. The breakup or impact of a cosmic vehicle at the YD boundary coincides with the onset of a 1-kyr long interval of glacial resurgence, one of the most studied events of the Late Pleistocene. New analytical databases reveal a corpus of data indicating that the cosmic impact was a real event, most possibly a cosmic airburst from Earth's encounter with the Taurid Complex comet or unknown asteroid, an event that led to cosmic fragments exploding interhemispherically over widely dispersed areas, including the northern Andes of Venezuela and the Alps on the Italian/French frontier. While the databases in the two areas differ somewhat, the overall interpretation is that microtextural evidence in weathering rinds and in sands of associated paleosols and glaciofluvial deposits carry undeniable attributes of melted glassy carbon and Fe spherules, planar deformation features, shock-melted and contorted quartz, occasional transition and platinum metals, and brecciated and impacted minerals of diverse lithologies. In concert with other black mat localities in the Western USA, the Netherlands, coastal France, Syria, Central Asia, Peru, Argentina and Mexico, it appears that a widespread cosmic impact by an asteroid or comet is responsible for deposition of the black mat at the onset of the YD glacial event. Whether or not the impact caused a 1-kyr interval of glacial climate depends upon whether or not the Earth had multiple centuries-long episodic encounters with the Taurid Complex or asteroid remnants; impact-related changes in microclimates sustained climatic forcing sufficient to maintain positive mass balances in the reformed ice; and/or inertia in the Atlantic thermohaline circulation system persisted for 1 kyr.

Key words: black mat impact, Younger Dryas boundary, SEM microtextures

Introduction

The black mat beds, originally attributed to a cosmic impact of 12.8 ka (Firestone *et al*. 2007a, 2007b), and found first in the southwest United States have now been found in other interhemispheric localities in South America, Europe and Central Asia (Ge *et al*. 2009; Mahaney *et al*. 2010b, 2011a, 2011b, 2013; Bunch *et al*. 2012; Mahaney and Keiser 2013; Wittke *et al*. 2013). While the origin of the sediment has been disputed vigorously, a key element of the hypothesis is that the impact coincided with the onset of a climatic reversal termed the *Younger Dryas* (*YD*). Hence, the *YD boundary* (*YDB*) has been linked to the climatic reversal at the end of the insolation-induced warming of the Bølling Allerød. Uncharacteristically, the YD glacial event occurred even though insolation was still at its peak, apparently unlike nearly all such previous climatic reversals (Firestone *et al*. 2007a). Still, detractors argue that similar climatic anomalies are normal at the end of glacial periods (Broecker *et al*. 2010) and that some black mat beds may be due to terrestrial processes such as redox fluctuations in aquifers (Quade *et al*. 1998), although these arguments do not preclude an impact. Black mat sediment has been dated to within a few hundred years of the YDB (Mahaney *et al*. 2010b), and arguments have been made that the black mat and the YD are merely coincidental and that a single cosmic impact would be unable to generate climatic forcing sufficient to change the mass balance of glaciers worldwide for

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up to 1 kyr. Recent data supporting a previously fragmented cometary vehicle (Comet Encke) breaking up further over southern Canada at the time frame of the black mat (Napier 2010) may well have spun off fragments radially which generated airbursts over various locales, but some (Higgins *et al.* 2011) still favor an asteroid impact.

Recent analyses of black mat beds in the northwestern Venezuelan Andes (location Fig. 1a, stratigraphy Fig. 1b), to be described here, show conclusive micrographic and chemical evidence of the existence of aerodynamically quenched quartz and chemical signatures that could only be produced by an ET airburst/impact. Add to this the presence of glassy carbon, Fe-rich grains, planar deformation features, occasional platinum metals and carbon welded to partially melted quartz in sediment, associated with and overrun by YD ice, and all this evidence supports an extremely high-temperature event caused by cosmic fragments that produced the YDB layers in South America and in the Alps.

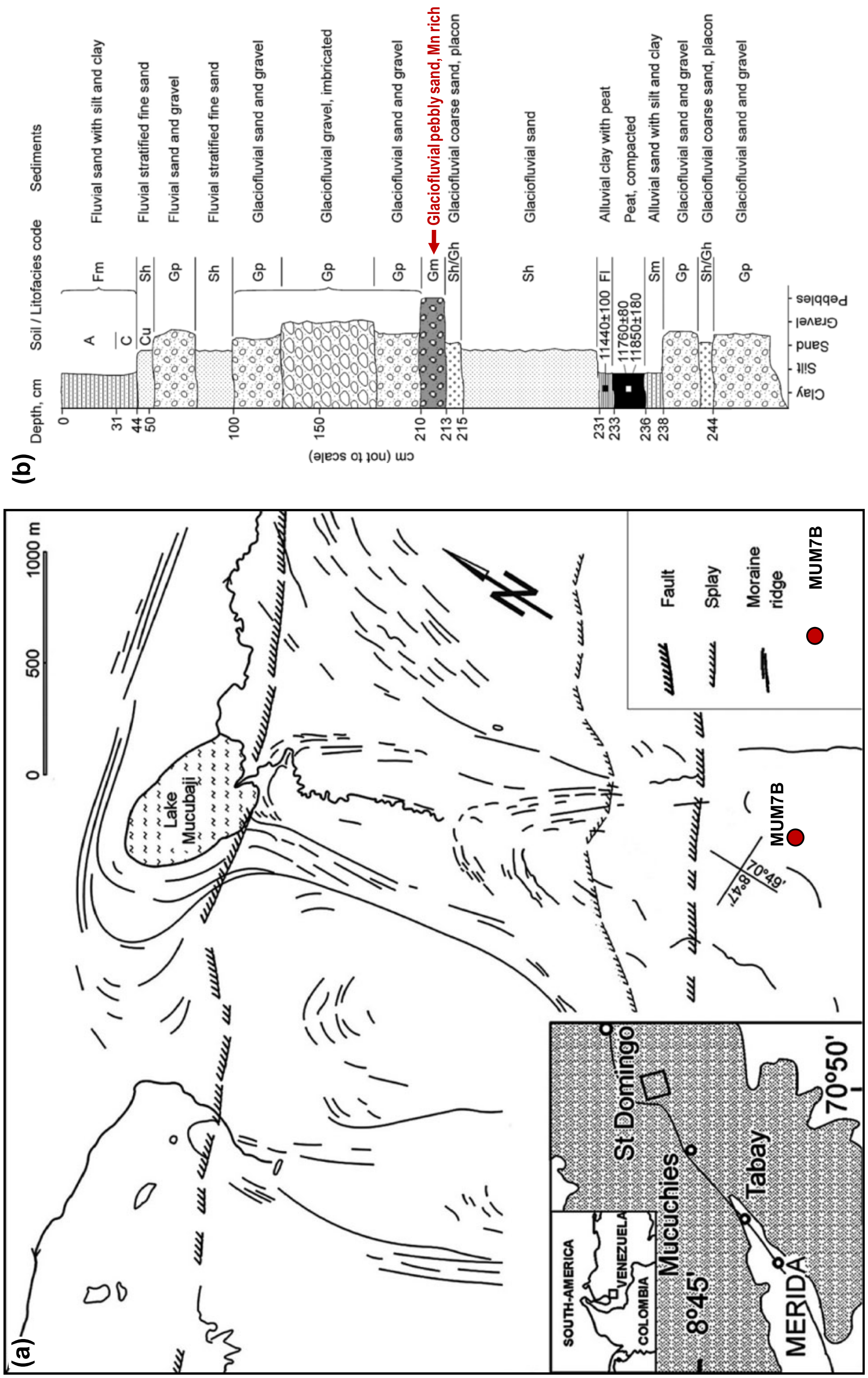
Examination of *Late Glacial* (*LG*) and YD moraines and mass-wasted debris in the Cottian Alps of France and Italy (location Fig. 2a; moraines, Fig. 2b) shows that ice recession during the Bølling-Allerød chronozones was interrupted by the advance of YD ice, followed by moraine emplacement (Mahaney and Keiser 2013). At the sites examined, the impact layer is atypical to that found elsewhere, due perhaps to active glacial and glaciofluvial processes in play. Instead, the impact record at these sites is archived in weathering rinds (Fig. 2c) and in paleosol Ah epipedons (Fig. 2d), the latter similar in kind to signatures described elsewhere by Courty and Federoff (2010), both considered as resulting from an airburst. Weathering rind thickness has been used for relative age determination in postglacial deposit sequences (Sharp 1969; Birkeland 1973; Mahaney 1978; Chinn 1981; Ricker *et al.* 1993; Dixon *et al.* 2002; Laustela *et al.* 2003; Sak *et al.* 2004), for microweathering analysis (Oguchi 2004; Nicholson 2009; Mahaney et al., 2012a and 2012b), and for isotopic dating of penetrating fluids (Pelt *et al.* 2003), but to date, evidence of cosmic impacts in weathering rinds has not been encountered by workers seeking to establish weathering histories and relative ages of glacial deposits. A preliminary search of rock rinds in LG recessional moraines (Guil3 = G3 site, $n = 50$) and mass-wasted debris sheets (Viso9 = V9; $n = 50$) of the Western Alps (Fig. 1) produced evidence of a cosmic impact (Mahaney and Keiser 2013). Cross analysis of rinds in pebbles embedded in younger YD-aged moraine surfaces ($n = 100$) did not produce grains with similar melted microtextures which indicate that the YD moraines postdate a possible airburst.

Regional geologies

The Mucuñuque Catchment (Fig. 1a) drains the northwestern slope of the cordillera Sierra de Santo Domingo in the eastern cordillera of the Mérida Andes (northwestern Venezuelan Andes). As one of the prominent drainages in the area, it contains a record of LG stillstand of retreating ice that was overrun with push moraine deposited during the YD, along with outwash that was emplaced during withdrawal of the glacier (Mahaney *et al.* 2008). Oriented SW–NE, the Mérida Andes extend from the Venezuelan–Colombian border toward the Caribbean Coast, constituting a 100-km-wide mountain belt with summits reaching to 5000 m a.s.l. As a consequence of plate collision (Audemard and Audemard 2002), the mountains formed during an orogeny that began in the Late Miocene. Both the Sierra de Santo Domingo and the Mucuñuque Catchment, located on the northeastern limb of the Boconó Fault, are floored with Precambrian bedrock of gneiss and granite of the Iglesias Group (Schubert 1970).

The SE–NW-oriented Mucuñuque Catchment is a fault-controlled glacially carved valley, which descends from elevations above 4200 m on the western slopes of Pico Mifés (4600 m a.s.l.) and Pico Mucuñuque (4672 m a.s.l.). Debouching into Lago Mucubaji (*c.* 3600 m a.s.l.), the Mucuñuque Valley drains across the MUM7 and MUM7B sites (Mahaney *et al.* 2010b) into the Rio Santo Domingo, eventually emptying into the Orinoco Basin. Upstream of LG recessional moraines (Mahaney and Kalm 1996; Mahaney *et al.* 2008), investigations reveal surface moraine (site MUM7) and outwash fans (site MUM7B), the latter burying alluvial peat dated to within the YDB window. The outwash documents both the advance and retreat of YD-aged ice (see Mahaney *et al.* 2008 for

Fig. 1 (*opposite page*). (a) Location of MUM7B, northwestern Andes; (b) stratigraphy of the site showing the Fe/Mn encrusted bed. Figs 1A and 1B from Mahaney, Krinsley and Kalm, 2011b.


(a)
(b)
0
500
1000 m
Lake Mucubaji
MUM7B
70°49'
8°47'
Fault
Splay
Moraine ridge
MUM7B
SOUTH-AMERICA
VENEZUELA
COLOMBIA
St Domingo
Mucuchies
Tabay
MERIDA
8°45'
70°50'
Depth, cm
Soil / Litofacies code
Sediments
cm (not to scale)
Fluvial sand with silt and clay
Fluvial stratified fine sand
Fluvial sand and gravel
Fluvial stratified fine sand
Glaciofluvial sand and gravel
Glaciofluvial gravel, imbricated
Glaciofluvial sand and gravel
Glaciofluvial pebbly sand, Mn rich
Glaciofluvial coarse sand, placon
Glaciofluvial sand
Alluvial clay with peat
Peat, compacted
Alluvial sand with silt and clay
Glaciofluvial sand and gravel
Glaciofluvial coarse sand, placon
Glaciofluvial sand and gravel
11440±100
11760±80
11850±180
Clay
Silt
Sand
Gravel
Pebbles

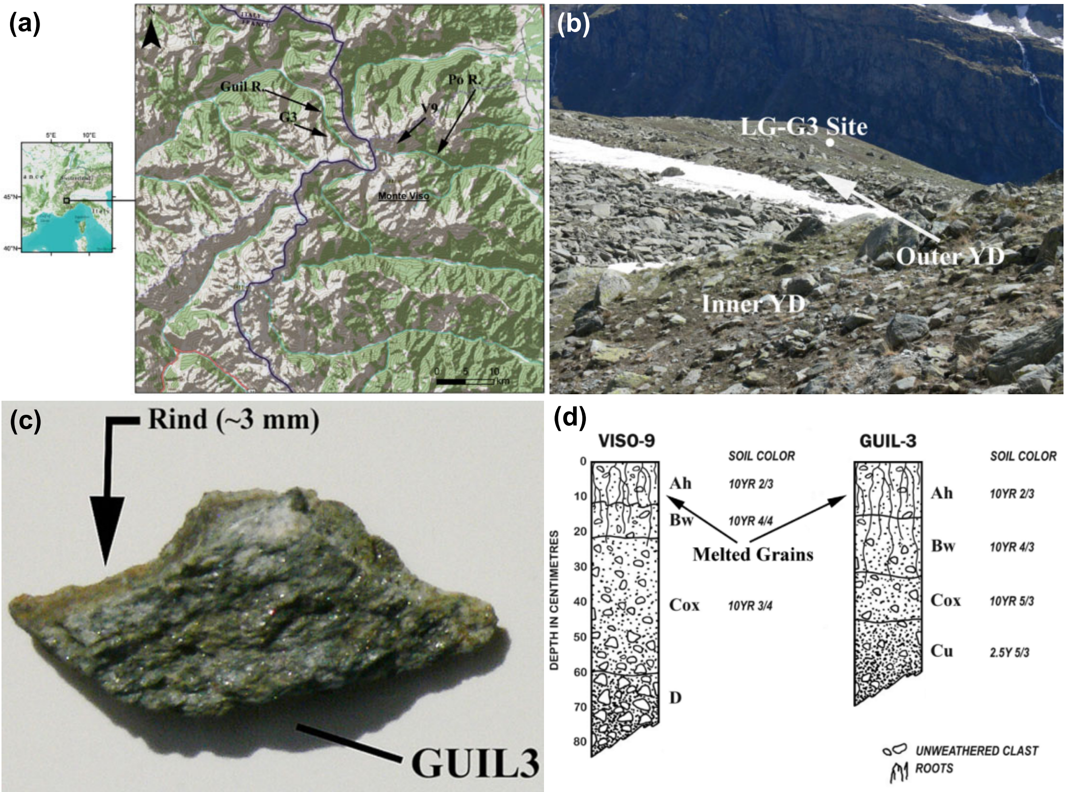


Fig. 2. (a) Location of the black mat sites, western Alps of France and Italy; (b) Late Glacial and Younger Dryas moraines, upper Guil River, France; (c) Macrophotograph of clast rinds, sites G3 and V9 (western Alps) carrying impacted signatures; (d) paleosol profiles G3 and V9 showing surface horizons carrying melted minerals. Figs. 2a, 2b and 2d from Mahaney et al., 2013.

stratigraphy), and the MUM7B section (Fig. 1b), situated at 3800 m a.s.l., contains the YDB black mat sediment with aerodynamically shaped grains described in this report.

The two deposits investigated in the Alps are located at 2300 m a.s.l. (site V9, Upper Po River, Italy) and 2450 m a.s.l. (site G3, Guil River, France) (Fig. 2a). The V9 site is in the outermost lobe of the Traversette Rockfall of LG age (Mahaney *et al.* 2010a), abutting an inner recessional moraine of LG age. The upper G3 site is located by hand-set GPS at 4952235N; 32345383E, on the youngest LG moraine, partially overrun by a YD moraine. The Guil River catchment in the Western Alps (Fig. 1) is a linear fault-controlled glacial basin with headwaters on the western slopes of Mt Viso (3841 m a.s.l.), sourced from the France/Italy border area. While active glacial erosion and postglacial mass wasting is evident on both the north- and south-facing valley slopes, recessional moraines are non-existent below 2400 m a.s.l., which clearly indicates that retreat of LG (Würm/Weichselian) Guil ice from the Durance valley (where it previously joined the larger Durance Glacier) was rapid. Hence, recessional stillstands of LG ice are not recorded in the surface record, if they occurred at all. Soils on the valley floor and sides are in alluvial and mass-wasted deposits and all are thin Entisols (Cryorthents mainly; National Soil Survey Center (NSSC) 1995). Some carbon in the melted pebble clasts embedded in LG moraines may have been sourced from sparse vegetation and associated thin Entisols (NSSC 1995; Birkeland 1999) of the alpine grassland. Encrustation of carbon onto rinds would have occurred when an impact-related, high-temperature cloud, similar in kind to the Andean event described above, descended upon the area producing a wildfire conflagration that destroyed most life, including plants in what was likely a wet tundra in its early developing seral stage (Mahaney and Keiser 2013).

Prominent recessional moraines (Fig. 2b) are found only at the 2400 m a.s.l. contour within the

Guil drainage, located approximately 1 km from the drainage divide at 3000 m a.s.l. The innermost LG recessional moraines, partially overrun by a glacial readvance interpreted to be the YD, exhibit similar weathering characteristics to the LG but lack any melted characteristics which might infer a cosmic airburst. Thus, since paleosol development and weathering properties of coarse clastic debris on LG and YD deposits are similar, they must have an age separation of mere centuries to at most a millennium. Above the LG/YD moraine elevations, steep slopes cross a bedrock bar leading into a prominent cirque (below the Col de la Traversette ~3000 m a.s.l.; Mahaney 2008), the latter floored with Little Ice Age rockfall and talus cover, all lacking ground moraine. While LG ice may have receded into the Traversette cirque prior to the YD, it is unequivocal that the YD ice advanced to 2450 m a.s.l. at a later date, overrunning the upper LG recessional moraine.

Methods

Deposits for both areas were mapped from air photos, and sites selected on the basis of representative deposit and soil expression. Deposits, including MUM7B (Mahaney *et al*. 2010b, 2011a, 2011b), were investigated for LG stratigraphy and radiocarbon controls. The Western Alps sites were similarly studied for differentiation of LG and YD weathering characteristics and paleosol properties. Both the YD and LG deposits were sampled for rinds, and counts with corresponding soil/stratigraphic pits established in each case.

At the Andean site (Fig. 1a), deposit stratigraphy was established in conjunction with a moraine stack of deposits at site MUM7 (Mahaney *et al*. 2008), the attempt being to add radiocarbon control to the withdrawal of YD ice and emplacement of outwash forming a cap on the stratigraphic sequence. In the western Alps, pebbles of uniform lithology were collected from moraine and rockfall surfaces, cracked with a rock hammer, after which exposed rinds (Fig. 2c) were measured to the nearest mm perpendicular to the pebble surface inward to the fresh lithic core. Because rinds indicate the degree to which Fe-bearing minerals have oxidized and discolored the outer periphery of clasts, the rind thickness is used to estimate time since deposition (Birkeland 1973; Mahaney 1990). Since most researchers measure only the maximum thickness of discoloration/alteration, neglecting the irregular rind thickness observed in most specimens, measurements reported here were made for both maximum and minimum rind dimensions on each clast (Mahaney 1990). Normally the maximum rind is in the clast surface in contact with the subaerial atmosphere and biosphere, the minimum rind in contact with the underlying soil/paleosol. Maximum rinds are defined from the maximum thickness measured in the outer surfaces of a population of 50 pebbles of similar lithology at each site. Minimum rind measurements are determined from minimum thickness measurements for the same population of 50 specimens. The populations of maximum and minimum rind thicknesses, subjected to a means test, yield a mean maximum value representative of maximum weathering at a site and mean minimum value representing the lesser penetration of reacting fluids. In this case, however, rind development may have been accelerated by a high temperature conflagration that fractured coarse clastic sediment, producing melted streams of olivine, pyroxene, amphibole and quartz that penetrated inward, post-impact weathering in some cases penetrating to the internal fresh rock core.

Selected grains from rind subsamples (G3 and V9) were mounted on stubs for analysis by normal *scanning electron microscopy* (*SEM*), using secondary electrons (SE), backscattered electrons and *energy-dispersive spectrometry* (*EDS*), following methods outlined by Mahaney (2002). The Andean grains were subsampled and separated with a Nd magnet, the recovered Fe spherules subjected to a similar analysis. Because carbon is important in the analysis, samples were coated with gold paladium (Vortisch *et al*. 1987; Mahaney 2002). Both SEM imagery and x-ray microanalysis (EDS) were obtained at accelerating voltages of 20 keV.

Results

The black mat

The black mat beds thus described from various locations in North and South America, Europe, and Central Asia are normally 2–3 cm thick C-rich or C+Fe+Mn-rich layers found within lacustrine or bog sections or in marginal glaciofluvial sections from Greenland. The Andean locality in Venezuela, described by Mahaney *et al*. (2010b, 2011a, 2011b), consists of a glaciofluvial bed of pebbly sand having a composition of felsic gneiss and granite, fine grained glassy and opaque C, plus Fe-rich spherules welded to quartz and other minerals. Quartz, in particular, appears as contorted and partially melted material. The black mat beds, dated to 12.8 ± 0.2

calibrated ka, have yielded aerodynamically modified Fe spherules that most likely formed in a local airburst, resulting from a fragmented asteroid or comet. As shown with the Andean example, the burnt layer material represented by a high-carbon signature was first thought to result from a lightning strike and resultant fire (Mahaney *et al.* 2008), although the conflagration temperature in a wet Andean tundra undergoing first or second stage succession vegetation growth would not have been of sufficiently high temperature to melt quartz. Also, brushfire temperatures do not produce a temperature high enough to produce glassy C-rich spherules firmly welded to mineral surfaces as occurred with the Andean example (Mahaney *et al.* 2010b, 2011a, 2011b).

Despite the absence in the Alps of the typical black mat bed, weathering rind archives of LG age were found that consisted of associated carbon welded onto pyroxene and quartz, dislocated and partially melted and shocked pyroxene, olivine, amphibole and quartz species, and thick breccia within the outermost ~1 mm of mineral surfaces. Interpreted as the result of the YDB impact, this is a new corpus of data (Mahaney and Keiser 2013) of the black mat event not previously encountered by workers researching LG/YD glacial sequences. The rind archives lead to a testable hypothesis following from previously reported data (Mahaney *et al.* 2011a, 2011b). The high-carbon layer in the rind material of the Alps is similar to burnt material correlated by Mahaney *et al.* (2010b) with black mat beds described elsewhere in North and South America, Europe and Central Asia but with some differences, as described below. For one, the Alps impact was of sufficient intensity to create thick (~1 mm) breccia layers in coarse clasts and to open wide fractures that filled with melted quartz, pyroxene, olivine and plagioclase, all part of the country rock lithology, as well as allochthonous materials, including rutile and zircon. For another, small amounts of Tc and Pt were detected by EDS analyses, although the presence must be confirmed and the origin is unclear. The presence of Tc, in particular, found from chemical mapping of grains, may well be either a false positive or residue from the Chernobyl meltdown of 1986. Along with impacted clast rinds, Ah horizons in associated paleosols contain not only similar impacted relict grains produced by the cosmic impact, they also contain Fe spherules similar to those recovered from the Andean site. All the more important perhaps is the microbiological record in the Ah horizon of one paleosol (G3; Fig. 2d) that yielded a density gradient gel electrophoresis profile dissimilar to genetic profiles obtained from lower horizons in other LG profiles and all horizons in two YD profiles within the same catchment (Mahaney *et al.* 2013). While yet to be proven with a greater population of samples, this microbiological perturbation may result from very small differences in the level of rare isotopes, including radioactive isotopes, released upon impact exerting selective pressure on the microbial population (Melott and Thomas, http://arxiv.org/ftp/arxiv/papers/1102/1102.2830.pdf, 18-Nov-13; Rainey *et al.* 2005).

The analysis of cosmic-impacted grains in Ah horizons of two paleosols under discussion here requires a comparison with black mat grains described in the Northern Andes (Mahaney *et al.* 2008, 2010b). Specific grain microtextures include intense brecciation and internal fracture patterns in both sample suites with a degree of brecciation and fracturing less intense than in the Andean samples. In my opinion (WCM), brecciation in weathering rinds is a unique feature never seen in the thousands of rinds measured over some 45 yr on all continents. The brecciation may be a function of both impact compression and heating, with incoming high speed particulate matter releasing enormous kinetic energy capable of producing disruption of mineral fabric to a rind depth of ~1000 μm with crack propagation reaching even deeper into the rind body in the case of the Alps samples. Microfractures are oriented, both parallel and normal to the surface, and the pattern is related to variable impact energy and resulting energy cone vectors. Microfabric analyses of the Alps samples reported here are similar to those in Mahaney *et al.* (2011b).

The criteria for the YD impact is similar to evidence used to prove the KPg impact (formerly K/T) (Hildebrand 1993), with the exception that the G3 Alps locality is in metamorphic terrane which was under glacier recession at the time of impact. The impact evidence is in pebble size clasts found embedded in the inner LG recessional moraine surface located in front of a doublet cross-cutting moraine of presumed YD age. While ^{14}C dates are not available for the LG at the G3 site and YD moraines (sites G1 and G2), the outer YD moraine buries part of the inner LG recessional, clearly the result of a glacial readvance. The lack of lakes/bogs in LG deposits suitable for coring makes it impossible to find sites with resident impact beds still intact, so that clasts on LG moraine and rockfall deposits and sands in the surface paleosol epipedons are the only repositories of the cosmic impact discovered to date in these two catchments of the French and Italian Alps.

Andean samples

The glassy and opaque carbon and Fe spherules welded to coarse clastic sediment in the Andean site are shown in Fig. 3(a, b). Mixed within these spherules are contorted, partially melted quartz grains, implying temperatures >1730°C (Fig. 3c), mats with quartz welded to carbon, and very coarse sands and granules, all fractured and with many carrying brecciated surfaces (Fig. 3b). The sand fraction in numerous subsamples collected from the black mat bed yielded a magnetic fraction with aerodynamically modified Fe spherules (Fig. 3d) with oxide wt% values (Table 1) for the MUM7B spherules that, although somewhat lower than mean concentrations for other aerodynamically modified grains, closely correlate with widely accepted impact material and previously analyzed YDB material (Bunch *et al.* 2012; Israde-Alcántara *et al.* 2012). There is minor overlap of the MUM7B sediment with cosmic material but the lack of MgO enrichment makes them dissimilar to 95% of

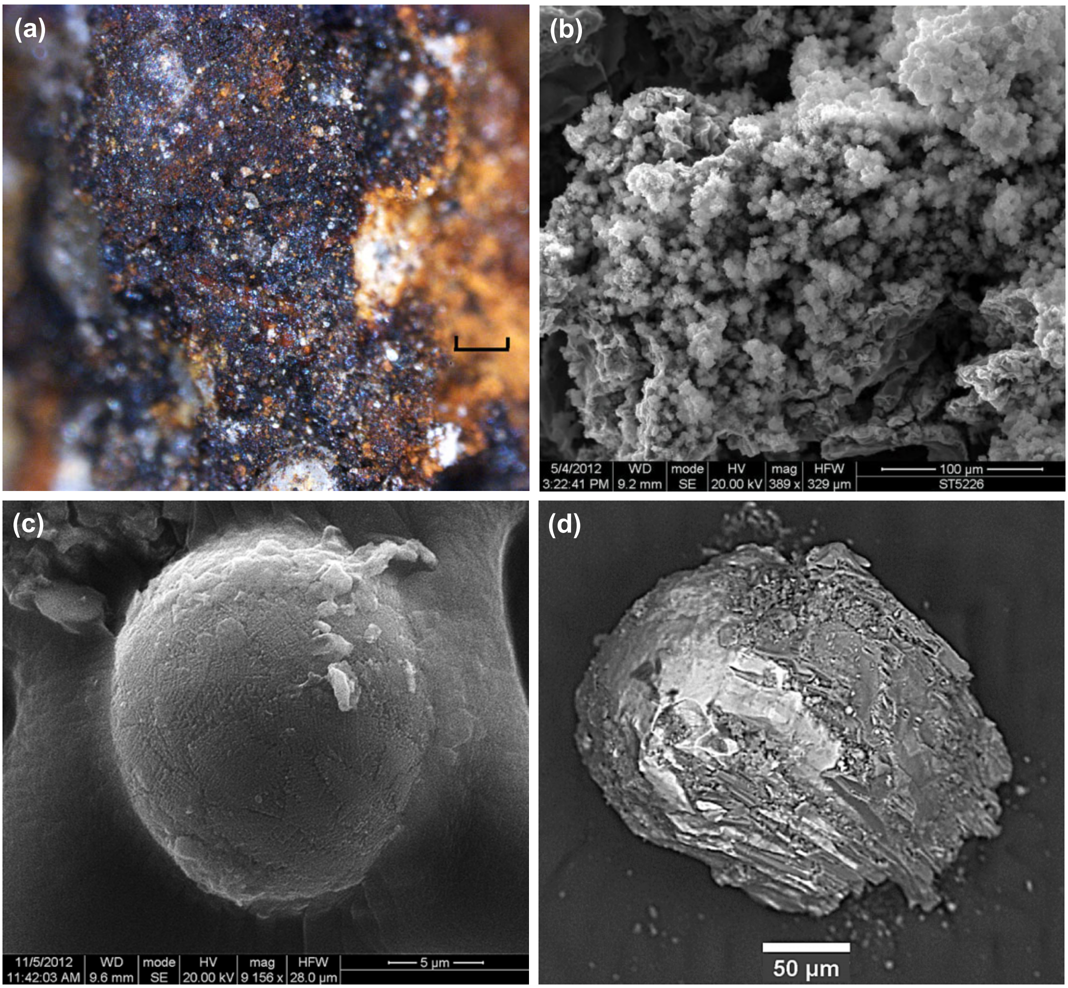


Fig. 3. (a) Light micrograph of impacted sand/spherules in the MUM7B bed northwestern Andes; (b) carbon encrusted spherules on felsic gneissic granule; (c) impacted and partially melted quartz-rich, elongated spherule; (d) melted Fe-spherule with remaglypt aerodynamically shaped microtexture. Fig. 3a from Mahaney et al., 2010b.

Table 1. Chemistry of near full scale silt size spherules in Figure 3, C and D frames of the MUM7B section, northwestern Andes.

Sample	Elements							
	O	Al	Si	K	Ca	Ti	Fe	Mn
C	41.82	6.66	11.23	0.39	0.90	1.21	37.78	–
D	49.82	8.49	12.25	2.58	–	12.73	13.47	0.66

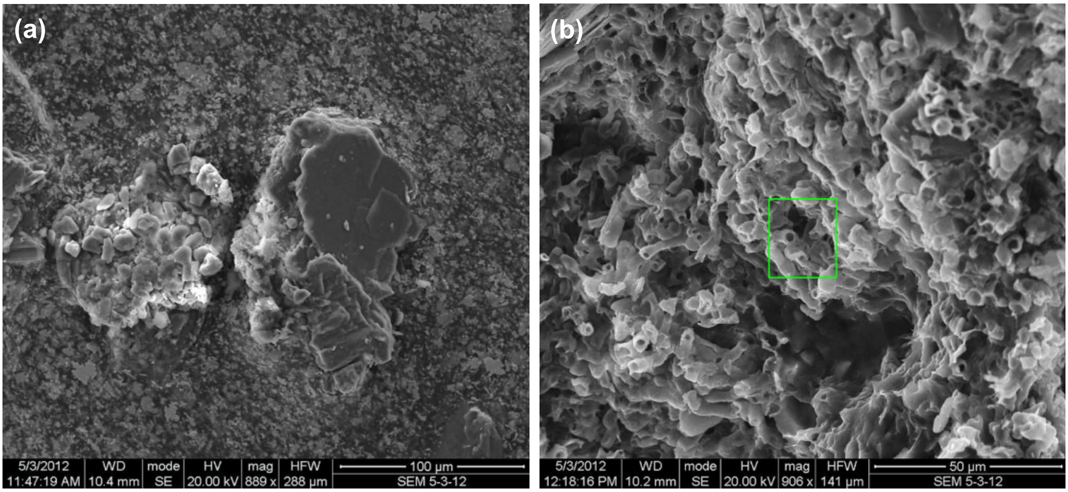


Fig. 4. (a) Contorted and welded pyroxene, plagioclase and quartz grains in two subsamples of the G3 rind, western Alps; (b) melted lithologic mix in the outer G3 Rind, western Alps.

glassy cosmic spherules discussed in Bunch *et al.* (2012). These high-Fe Andean spherules are not volcanic in origin, as demonstrated by Mahaney *et al.* (2013), but all recovered spherules plot within the acknowledged characteristics Evidence was provided previously of terrestrial impact materials, including documented spherules, ejecta and tektites from 12 craters and tektite strewnfields ($n = 1000$), including the Chicxulub crater (Hildebrand 1993), Chesapeake Bay crater, Tunguska, Australasian tektite field, Lake Bosumtwi crater, Ries crater, and more (Bunch *et al.* 2012).

Alps samples

Within the Alps samples from G3 and V9, there are impacted grains, similar to the Andes samples in surface microtexture characteristics, but with different lithologies. They yield fewer Fe and C spherules, but have a greater quantity of near-micron-size grains welded to mineral fabric, as shown in one G3 sample (Fig. 4a). Small particulate matter of largely pyroxene composition, encrusted with carbon (dark tonal contrast is C, light Fe), is frequently found within the outer 1000 µm rind thickness. Carbon mats with opaque thick layers, and soot from wildfires seen elsewhere (Stich *et al.* 2008), are similar to the specimen covering a particle of metabasalt, all welded to the grain surface. The outer rind area shown in Fig. 4(b) is filled with contorted and shocked pyroxene and quartz, many grains of which are the product of immense shock. Some disrupted grain surfaces register as Cl on the EDS, suggesting they might be chloride ion sites in silicate and aluminosilicate glass from an airburst (Stebbins and Du 2002).

A second group of rind samples from site V9 in the upper Po River valley reveal similar fragmental breccia, melted pyroxene, and partially melted and contorted quartz (Fig. 5a). One EDS spot analysis (Fig. 5b), indicates the presence of Tc and Bi in a melted pyroxene spherule, the former element rarely found in nature, so that proof of its presence would require a wider search with high-resolution EDS. Bismuth, common in pyroxene, is unrelated to a cosmic airburst.

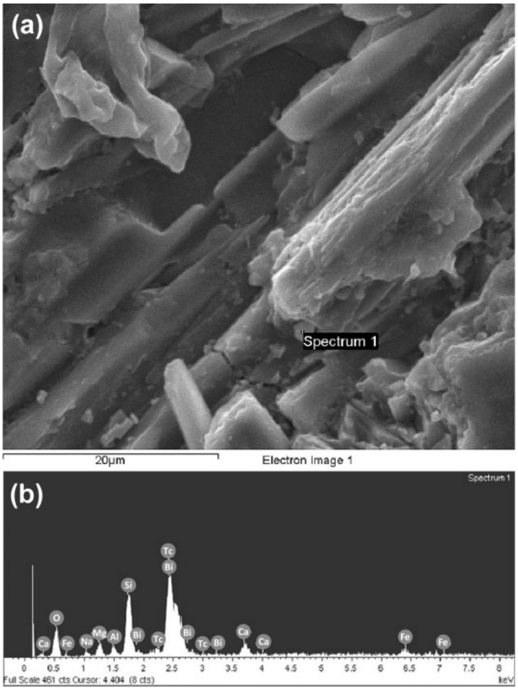


Fig. 5. (a) Brecciated outer rind area of V9 with melted quartz upper left and identified possible transition metal (Tc) composition overlapping with Bi (from Mahaney and Keiser 2013); (b) EDS of (a) (from Mahaney and Keiser 2013 and Mahaney et al., 2013).

Discussion

The G3 site, located on the inner recessional moraine in the upper Guil River valley, is situated such that it received sufficient heat required to melt outer clast surfaces, presumably from the full force of a cosmic airburst covering an indeterminate area of the French and Italian Alps. The exact time frame is unknown due to a lack of ^{14}C controls, but the LG age of the G3 deposit is undeniably correlated with the warming event of the Bølling-Allerød climatic forcing that led to the recession of the Guil Glacier, a feeder system into the massive Durance Glacier. Near the end of the last glaciation, ice was in the final stage of retreat in the upper Guil Valley close to Mt Viso (3841 m a.s.l.) with the main ice sheet separated into two glaciers, one to the north retreating into the Traversette Cirque and the other into an unnamed cirque to the south below the summit of Mt. Viso. It is impossible to reconstruct the positions of these two retreating glaciers after ~12.8 ka, but it is possible to establish that the retreating glacier occupied a stillstand position prior to the cosmic impact and established a moraine system now partly eroded, principally by outwash from later established YD ice. What is certain is that a glacial resurgence, presumably during the YD cooling interval, emplaced a crosscutting end moraine that partially buried the LG moraine creating a small tarn, now filled with coarse clastic debris from talus and debris flows. Close analysis of rinds at the YD and LG sites indicates the impact signature is present only in the LG clasts and paleosol Ah horizon, with such signatures lacking at the YD sites. Because the LG deposit is within the time frame of the black mat sites established elsewhere, and also because the normal black mat grain signature is present within the rinds and the surface paleosol epipedon, it is reasonable to assume that this evidence resulted from the 12.8 ka impact. There is no other proposed impact event that falls into the LG time frame.

The V9 site in the old lobe of the Traversette Rockfall in the upper Po River valley is dated similarly to the LG sites in the upper Guil River. No ^{14}C dates are available for the rockfall, but the deposit is clearly a two-stage system, as originally described by Polybius, a Greek general in antiquity, who followed the invasion route of the Punic Army in 160 BC (Mahaney *et al.* 2010a). We cannot conclusively correlate the rockfall with the LG, but the presence of a cosmic signature, both in rock rinds and in the Ah horizon of the paleosol epipedon of the rockfall deposit, suggests the mass wasting event occurred during the LG.

Following the YDB event, the climatic situation reversed with renewed cooling, the onset of a positive glacier mass balance, and the advance of YD ice. The glacial advance left a wealth of glacial geomorphic and sedimentological evidence, but lacks any cosmic signature, indicating that it postdates the event. The LG stillstand recessional moraines provide coarse clastic debris that acted as host material for weathering rind development, part of which contains evidence of a cosmic impact and resulting wildfire that created soot welded to heated and melted materials. Presumably, the impact was the progenitor of the YD climatic reversal, the latest event in the LG record (Ralska-Jasiewiczowa *et al.* 2001; Gibbard 2004). The YD onset begins at the upper end of a warming trend that began at 14.7 ka (Van der Hammen and Hooghiemstra 1995; Teller *et al.* 2002; Lowe *et al.* 2008) with maximum cooling beginning at 12.8 ka. The hypothesis that a cosmic impact could have generated the YD reversal is still hotly debated in the literature (Haynes 2008; Pinter and Ishman 2008; Ge *et al.* 2009; Kennett *et al*. 2009; Kennett et al., 2007). Recent critical reviews of the YD event by Van der Hammen and Van Geel (2008) and Broecker *et al*. (2010) argue, respectively, that charcoal in paleosols of the Allerød–YD transition were not caused by impact, and that the impact event, by itself, could not have caused a glacial advance lasting 1 kyr. The evidence reported here conclusively contradicts alternative hypotheses for the onset of the YD glacial advance, with the most conclusive evidence coming from aerodynamically modified Fe spherules and microspherules, melted and contorted quartz and other lithologies, and carbon mats welded to various minerals.

The presence of technetium, a rare radioactive byproduct of uranium fission, could be a product of a postulated large scale, if momentary disruption of the atmosphere, sufficient to allow a cosmic ray burst. Technetium (AN 43) occupies a position in the periodic table between Mo (AN 42) and Re (44), the latter platinum element recently detected in melted pyroxene in site G3 weathered rind sediment. As a product of atomic bomb blasts (Yoshihara 2006), and its presence in carbon stars (Bernatowicz *et al*. 2006), Tc might be an undiscovered by-product of a bolide or comet impact. Alternatively, it may be an air-influxed contaminant from nuclear reactors (Istok *et al*. 2004), i.e. Chernobyl, or a false positive, as indicated previously. Tc was found in only one occurrence out of hundreds of grains analyzed, indicating it is not widespread. More work is needed to confirm its presence and determine its origin.

Conclusions

Impacted black mat sediment is present in the Western Alps, where it is found in surface clast rinds embedded in LG moraine/rockfall sediment and in paleosols of the western Alps near Mt Viso on the French/Italian border. The same black mat deposits are also found in the Andes, displaying glassy Fe/C-rich spherules and the presence of high fractures and clast brecciation, complete with melted/quenched and aerodynamically shaped microtextures. The evidence at both sites is consistent with the sediment being the product of cosmic airburst/impact. The relationship with YD till is indisputable, and ^{14}C dates associated with the black mat beds in the Andes, place the impact squarely within the YDB window.

Evidence of cosmic impact in the Western Alps occurs both in weathering rinds and within surface paleosol Ah horizons, all of LG age. We report finding highly fractured and brecciated weathering rinds, complete with multiple impact-related channels filled with melted and contorted grains. These formed from a highly volatile and viscous mass of molten material, now welded together into chains of fused grains and coated with thick opaque carbon, occasionally revealing the presence of Al plus Cl considered to be impact-produced glass.

Although the relationship between the YDB and the YD is still under discussion, it is clear that the black mat extends to the European Alps, and it is also clear that the evidence for it is found both in weathering rinds and in resident grains of Ah paleosol profiles. At the time of impact these Ah horizons were likely C or Cox (ox = oxidized) soil horizons undergoing the initial stage of weathering following deglaciation. This is the first report of black mat archival evidence recovered from weathering rinds and from surface paleosol horizons. The spatial evidence of deposit juxtaposition (the Alps) and superposition (the Andes), strongly indicates cause and effect regarding the black mat as related to the YD. The geomorphological situation in both localities is such that ice withdrawal during the Bølling Allerød was interrupted by a glacial resurgence in two widely separated interhemispheric areas, both with indisputable evidence of a cosmic impact. In the Andes, YDB dated beds were overrun by YD ice while in the Alps cosmic impacted beds were partially overrun and buried by YD moraines. It would seem prudent for other workers to analyze rinds and paleosols in similar venues in both areas to add to the database presented here.

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References

Audemard, F.E. and Audemard, F.A., 2002. Structure of the Mérida Andes, Venezuela: relations with the South America Caribbean geodynamic interaction. *Tectonophysics*, 345, 299–327.

Bernatowicz, T.J., Croat, T.K. and Daulton, T.L., 2006. Origin and evolution of carbonaceous presolar grains in stellar environments. In: Lauretta, D.S. and McSween, H.Y. (eds), *Meteorites and the Early Solar System II*. University of Arizona Press, Tucson, AZ. 109–126.

Birkeland, P.W., 1973. Use of relative age dating methods in a stratigraphic study of rock glacier deposits, Mt. Sopris, Colorado. *Arctic and Alpine Research*, 5 (4), 401–416.

Birkeland, P.W., 1999. *Soils and Geomorphology*. Oxford University Press, Oxford, UK, 430 p.

Broecker, W.S., Denton, G.H., Edwards, R.L., Cheng, H., Alley, R.B. and Putnam, A.E., 2010. Putting the Younger Dryas cold event into context. *Quaternary Science Reviews*, 29, 1078–1081.

Bunch, T.E., Hermes, R.E., Moore, A.M.T., Kennett, D.J., Weaver, J.C., Wittke, J.H., DeCarli, P.S., Bischoff, J.L., Hillman, G.C., Howard, G.A., Kimbel, D.R., Kletetschka, G., Lipo, C.P., Sakai, S., Revay, Z., West, A., Firestone, R.B. and Kennett, J.P., 2012. Very high temperature impact melt products as evidence for cosmic airbursts and impacts 12,900 years ago. *Proceedings of the National Academy of Sciences U S A*, 109, 11066–11075. doi/10.1073/pnas.1204453109.

Chinn, T.J., 1981. Use of weathering rind thickness for Holocene absolute age-dating in New Zealand. *Arctic and Alpine Research*, 13 (1), 33–45.

Courty, M-A. and Fedoroff, M. 2010. Soil morphologic indicators of environmental hazards linked to cosmic airburst. *2010 19th World Congress of Soil Science, Soil Solutions for a Changing World*, 1–6 August 2010, Brisbane, Australia. Published on DVD.

Dixon, J.C., Thorn, C.E., Darmody, R.G. and Campbell, S.W., 2002. Weathering rinds and rock coatings from an Arctic alpine environment, northern Scandinavia. *Geological Society of America Bulletin*, 114 (2), 226–238.

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. and 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 U S A*, 104, 16016–16021.

Firestone, R.B., West, A., Revay, Z., Belgya, T., Smith, A. and Que Hee, S.S., 2007b. Evidence for a massive extraterrestrial airburst over North America 12.9 ka ago. American Geophysical Union Spring Meeting 2007, San Francisco, CA, abstract PP41A-01.

Ge, T., Courty, M.M. and Guichard, F., 2009. Field-analytical approach of land-sea records elucidating the Younger Dryas syndrome. American Geophysical Union Fall Meeting 2009, San Francisco, CA, abstract PP31D-432, 1390.

Gibbard, P.L., 2004. Quaternary . . . now you see it, now you don't. *Quaternary Perspective*, 14, 89–91.

Haynes, C.V., 2008. Younger Dryas "black mats" and the Rancholabrean termination in North America. *Proceedings of the National Academy of Sciences U S A*, 105, 6520–6525.

Higgins M.D., Lajeunesse, P., St-Onge, G., Locata, J., Duchesne, M., Ortiz, J. and Sanfacon, R., 2011. Bathymetric and petrological evidence for a Young (Pleistocene?) 4-km diameter impact crater in the Gulf of Saint Lawrence, Canada. 42nd Lunar and Planetary Science Conference, 7–11 March 2011, The Woodlands, TX, LPI Contribution No. 1608, 1504.

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.

Israde-Alcántara, I., Bischoff, J.L., Dominquez-Vazquez, G., Li, H.-C., DeCarli, P.S., Bunch, T.E., Wittke, J.H., Weaver, J.C., Firestone, R.B., West, A., Kennett, J.P., Mercer, C., Xie, S., Richman, E.K., Kinzie, C.R. and Wolbach, W.S., 2012. Evidence from Central Mexico supporting the Younger Dryas extraterrestrial impact hypothesis. *Proceedings of the National Academy of Sciences U S A*, 109, E738–E747.

Istok, J.D., Senko, J.M., Krumholz, L.K., Watson, D., Bogle, M.A., Peacock, A., Chang, Y.-J. and White, D.C., 2004. In situ bioreduction of technetium and uranium in a nitrate-contaminated aquifer. *Environmental Science and Technology*, 38, 468–475.

Kennett, J.P., Becker, L. and West, A., 2007. Triggering of the Younger Dryas cooling by extraterrestrial impact. American Geophysical Union Annual Meeting 2007, abstract PP41A-05.

Kennett, D.J., Kennett, J.P., West, A., Mercer, C., Que Hee, S.S., Bement, L., Bunch, T.E., Sellers, M. and Wolbach, W.S., 2009. Nanodiamonds in the Younger Dryas boundary sediment. *Science*, 323 (5910), 94. doi: 10.1126/science.1162819.

Laustela, M., Egli, M., Frauenfelder, R., Kääb, A., Maisch, M. and Haeberli, W., 2003. Weathering rind measurements and relative age dating of rock glacier surfaces. In: Phillips, M., Springman, S.M. and Arenson, L.U. (eds), *Crystalline Regions of the Eastern Swiss Alps*. Permafrost, Swets & Zeitlinger, Lisse. 627–632.

Lowe, J.J., Rasmussen, S.O., Björck, S., Hoek, W.Z., Steffensen, J.P., Walker, M.J.C. and Yu, Z.C., 2008. Synchronisation of palaeoenvironmental events in the North Atlantic region during the Last Termination: a revised protocol recommended by the INTIMATE group. *Quaternary Science Reviews*, 27, 6–17.

Mahaney, W.C., 1978. Late Quaternary stratigraphy and soils in the Wind River Mountains, western Wyoming. In: Mahaney, W.C. (ed.), *Quaternary Soils*. Geoabstracts, Norwich, UK. 223–264.

Mahaney, W.C., 1990. *Ice on the Equator*. Wm Caxton, Ellison Bay, WI. 386 p.

Mahaney, W.C., 2002. *Atlas of Sand Grain Surface Textures and Applications*. Oxford University Press, Oxford, UK. 237 p.

Mahaney, W.C., 2008. *Hannibal's Odyssey: Environmental Background to the Alpine Invasion of Italia*. Gorgias Press, Piscataway, NJ. 221 p.

Mahaney, W.C. and Kalm, V., 1996. *Field Guide for the International Conference on Quaternary Glaciation and Paleoclimate in the Andes Mountains*. Quaternary Surveys, Toronto. 79 p.

Mahaney, W.C. and Keiser, L., 2013. Weathering rinds: unlikely host clasts for evidence of an impact-induced event. *Geomorphology*, 184, 74–83.

Mahaney, W.C., Kapran, B., Kalm, V., Tricart, P., Carcaillet, C., Barendregt, R.W. and Somelar, P., 2010a. The Traversette rockfall: geomorphological reconstruction and importance in interpreting classical history. *Archaeometry*, 52 (1), 156–172.

Mahaney, W.C., Keiser, L., Krinsley, D.H., Allen, C.C.R., Dirszowsky, R. and Julig, P., 2013. Weathering rinds as mirror images of Paleosols: examples from the Western Alps. *Journal of the Geological Society.* doi: 10.1144/jgs2012-150

Mahaney, W.C., Krinsley, D.H. and Allen, C.C.R., 2012a. Biomineralization of weathered rock rinds: examples from the lower Afroalpine zone on Mount Kenya. *Geomicrobiology*, 30 (5), 411–421. doi. 10.1080/01490451.2012.705952.

Mahaney, W.C., Krinsley, D.H., Allen, C.C.R., Langworthy, K., Ditto, J. and Milner, M.W., 2012b. Weathering rind: archives of paleoenvironments on Mount Kenya, East Africa. *Journal of Geology*, 120 (6), 591–602.

Mahaney, W.C., Krinsley, D.H., Dohm, J.M., Kalm, V., Langworthy, K. and Ditto, J., 2011a. Notes on the black mat sediment, Mucuñuque Catchment, northern Mérida Andes, Venezuela. *Journal of Advanced Microscopic Research*, 6, 1–9.

Mahaney, W.C., Krinsley, D. and Kalm, V., 2010b. Evidence for a cosmogenic origin of fired glaciofluvial beds in the northwestern Andes: correlation with experimentally heated quartz and feldspar. *Sedimentary Geology*, 231, 31–40.

Mahaney, W.C., Krinsley, D., Langworthy, K., Hart, K., Kalm, V., Tricart, P. and Schwartz, S., 2011b. Fired glaciofluvial sediment in the northwestern Andes: biotic aspects of the black mat. *Sedimentary Geology*, 237, 73–83.

Mahaney, W.C., Milner, M.W., Kalm, V., Dirszowsky, R., Hancock, R.G.V. and Beukens, R.P., 2008. Evidence for a Younger Dryas glacial advance in the Andes of northwestern Venezuela. *Geomorphology*, 96, 199–211.

Napier, W.M., 2010. Palaeolithic extinctions and the Taurid Complex. *Monthly Notices of the Royal Astronomical Society*, 405, 1901–1906.

National Soil Survey Center (NSSC), 1995. *Soil Survey Laboratory Information Manual*. Soil Survey Investigations Report No. 45. Version 1.00. USDA, Washington, DC. 305 p.

Nicholson, D.T., 2009. Holocene microweathering rates and processes on ice-eroded bedrock, Røldal area, Hardangervidda, southern Norway. *Geological Society, London, Special Publications 2009*, 320, 29–49.

Oguchi, C.T., 2004. A porosity-related diffusion model of weathering-rind development. *Catena*, 58, 65–75.

Pelt, E., Chabaux, F., Innocent, C., Navarre-Sitchler, A.K., Sak, P.B. and Brantley, S.L., 2003. Uranium–thorium chronometry of weathering rinds: Rock alteration rate and paleo-isotopic record of weathering fluids. *Earth and Planetary Science Letters*, 276, 98–105.

Pinter, N. and Ishman, S.E., 2008. Impacts, mega-tsunami, and other extraordinary claims. *GSA Today*, 18, 37–38.

Quade, J, Forester, R.M., Pratt, W.L. and Carter, C., 1998, Black mats, spring-fed streams, and Late Glacial Age Recharge in the southern Great Basin. *Quaternary Research*, 49, 129–148.

Rainey, F.A., Ray, K., Ferreira, M., Gatz, B.Z., Nobre, M.F., Bagaley, D., Rash, B.A., Park, M-J, Earl, A.M., Shank, N.C., Small, A.M., Henk, M.C., Battista, J.R., Kampfer, P. and da Costa, M.S., 2005. Extensive diversity of ionizing-radiation-resistant bacteria recovered from Sonoran desert soil and description of nine new species of the genus Deinococcus obtained from a single soil sample. *Applied and Environmental Microbiology*, 71, 5225–5235.

Ralska-Jasiewiczowa, M., Stebich, M. and Negendank, J.F.W., 2001. Correlation and synchronization of Lateglacial continental sequences in northern central Europe based on annually laminated lacustrine sediments. *Quaternary Science Reviews*, 20, 1233–1249.

Ricker, K.E., Chinn, T.J. and McSaveney, M.J., 1993. A late Quaternary moraine sequence dated by rock weathering rinds, Craigieburn Range, New Zealand. *Canadian Journal of Earth Sciences*, 30 (9), 1861–1869.

Sak, P.B., Fisher, D.M., Gardner, T.W., Murphy, K. and Brantley, S.L., 2004. Rates of weathering rind formation on Costa Rican basalt. *Geochimica et Cosmochica Acta*, 68 (7), 1453–1472.

Schubert, C., 1970. Glaciation of the Sierra de Santo Domingo, Venezuelan Andes. *Quaternaria*, 13, 225–246.

Sharp, R.P., 1969. Semiquantitative differentiation of glacial moraines near Convict Lake, Sierra Nevada, Calif. *Journal of Geology*, 77, 68–91.

Stebbins, J.F. and Du, L.-S.hu., 2002. Chloride ion sites in silicate and aluminosilicate glasses: a preliminary study by ^{35}Cl solid state NMR. *American Mineralogist*, 87, 359–363.

Stich, A., Howard, G., Kloosterman, J.B., Firestone, R.B., West, A., Kennett, J.P. Kennett, D.J., Bunch, T.E. and Wolbach, W.S., 2008. Soot as evidence for widespread fires at the Younger Dryas Onset (YDB; 12.9 ka). American Geophysical Union Fall Meeting 2008, San Francisco, CA, abstract PP13C-1471.

Teller, J.T., Leverington, D.W. and 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. and Hooghiemstra, H., 1995. The El Abra Stadial, a Younger Dryas equivalent in Colombia. *Quaternary Science Reviews*, 14, 841–851.

Van der Hammen, T. and Van Geel, B., 2008. Charcoal in soils of the Allerød-Younger Dryas transition were the result of natural fires and not necessarily the effect of an extra-terrestrial impact. *Netherlands Journal of Geosciences*, 87, 359–361.

Vortisch, W., Mahaney, W.C. and Fecher, K., 1987. Lithology and weathering in a paleosol sequence on Mt. Kenya, East Africa. *Geologica et Paleontologica*, 21, 245–255.

Wittke, J.H., Weaver, J.C., Bunch, T.E., Kennett, J.P., Kennett, D.J., Moore, A.M.T., Hillman, G.C., Tankersley, K.B., Goodyear, A.C., Moore, C.R., Daniel, R., Jr., Ray, J.H., Lopinot, N.H., Ferraro, D., Israde-Alcántara, I., Bischoff, J.L., DeCarli, P.S., Hermes, R.E., Kloosterman, J.B., Revay, Z., Howard, G.A., Kimbel, D.R., Kletetschka, G., Nabelek, L., Lipo, C.P., Sakai, S., West, A. and Firestone, R.B., 2013. Evidence for deposition of 10 million tonnes of impact spherules across four continents 12,800 years ago. *Proceedings of the National Academy of Sciences U S A*. doi/10.1073/pnas.1301760110.

Yoshihara, K., 1996. Technetium in the environment. In: Yoshihara, K. and Omori, T. (eds), *Topics in Current Chemistry: Technetium and Rhenium*, 176. Springer-Verlag, Berlin. 17–35.

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