



The Younger Dryas impact hypothesis: a critical review



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ABSTRACT

The Younger Dryas impact hypothesis suggests that multiple extraterrestrial airbursts or impacts resulted in the Younger Dryas cooling, extensive wildfires, megafaunal extinctions and changes in human population. After the hypothesis was first published in 2007, it gained much criticism, as the evidence presented was either not indicative of an extraterrestrial impact or not reproducible by other groups. Only three years after the hypothesis had been presented, a requiem paper was published. Despite this, the controversy continues. New evidence, both in favour and against the hypothesis, continues to be published.

In this review we briefly summarize the earlier debate and critically analyse the most recent reported evidence, including magnetic microspherules, nanodiamonds, and iridium, shocked quartz, scoria-like objects and lechatelierite. The subsequent events proposed to be triggered by the impact event, as well as the nature of the event itself, are also briefly discussed. In addition we address the timing of the Younger Dryas impact, a topic which, despite its importance, has not gained much attention thus far. We show that there are three challenges related to the timing of the event: accurate age control for some of the sites that are reported to provide evidence for the impact, linking these sites to the onset of the Younger Dryas and, most importantly, an apparent age discrepancy of up to two centuries between different sites associated with the proposed impact event. We would like to stress that if the markers at different locations have been deposited at different points in time, they cannot be related to the same event. Although convincing evidence for the hypothesis that multiple synchronous impacts resulted in massive environmental changes at ~12,900 yrs ago remains debatable, we conclude that some evidence used to support the Younger Dryas impact hypothesis cannot fully be explained at this point in time.

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1. Introduction

In 2007, a group of researchers led by Firestone et al. (2007) proposed a unique mechanism for the onset of the Younger Dryas (YD) cold period that followed the Allerød interstadial near the end of the Last Glaciation (Hoek, 2008). According to the YD impact hypothesis (YDIH), one or more extraterrestrial objects hit, or exploded over, the Laurentide Ice Sheet – possibly at a location near the current Great Lakes area – at the onset of the YD, ~12,900 yrs ago (Firestone et al., 2007). Besides initiating several short term cooling mechanisms, the force and extreme heat generated by this impact, according to this hypothesis, would have destabilized the ice sheet, yielding enough meltwater to disrupt ocean circulation and hence initiate the observed long term climate cooling. This

hypothesis (Firestone et al., 2007) thus provides a unique trigger for the generally accepted meltwater re-routing mechanism which was probably responsible for the YD cooling. This meltwater re-routing mechanism includes re-routing of meltwater to the northern Atlantic or Arctic Ocean, disabling the thermohaline circulation and initiating climate cooling (Broecker et al., 1989; Tarasov and Peltier, 2005; Broecker et al., 2010; Murton et al., 2010; Fiedel, 2011). In addition to the rapid climate change, Firestone et al. (2007) also claim that the YD impact accounts for extensive wildfires, Pleistocene megafaunal extinctions and decline of the prehistoric Clovis culture in North America. Evidence presented for the YD impact hypothesis (YDIH) consists of peak concentrations of various markers found in profiles taken across the Allerød-YD boundary at several sites in North America and one in Europe. These markers included magnetic grains and microspherules, charcoal, carbon spherules and glass-like carbon, iridium concentrations, and fullerenes with extraterrestrial helium (Firestone et al., 2007).

Although the YDIH gained further support from a study in 2009 reporting nanodiamonds at the Allerød-YD boundary (Kennett

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et al., 2009a, 2009b), the hypothesis was received with scepticism and is still considered as controversial (Dalton, 2007; Kerr, 2007; Pinter and Ishman, 2008; Dalton, 2009; French and Koeberl, 2010; Kerr, 2010; Jones, 2013). Most reported YD impact markers are not considered diagnostic evidence for impacts (French and Koeberl, 2010). These non-diagnostic markers include different forms of carbon, magnetic grains and spherules and fullerenes. Furthermore, researchers trying to reproduce the work often failed to find nanodiamonds or peaks in magnetic spherule concentration (Surovell et al., 2009; Daulton et al., 2010). Four years after publication of the hypothesis, a review paper titled “The Younger Dryas impact hypothesis: A requiem” argued against all of the evidence presented for the YDIH (Pinter et al., 2011). However, this “requiem” review paper left several questions unanswered: for example, the recent work on a South American site (Mahaney et al., 2010a, 2010b, 2011), although mentioned, is not discussed in any detail and the conclusion that the reported nanodiamonds were probably misinterpreted seems to ignore earlier reports by other independent researchers (Tian et al., 2011). In addition, convincing alternative explanations for the occurrence of these nanodiamonds in the Allerød-YD boundary are lacking.

In this review we address these outstanding questions in the light of the most recent research on the topic (e.g. Andronikov et al., 2011; Marshal et al., 2011; Bunch et al., 2012; Fayek et al., 2012; Israde-Alcántara et al., 2012; Pigati et al., 2012; van Hoesel et al., 2012; Wittke et al., 2013b) and discuss the arguments both in favour of and against the different lines of evidence in detail. The subsequent events supposedly triggered by the impact event and the nature of the event itself are also briefly discussed. Further, we address the timing of the YD impact, a topic which, despite its importance, has not gained much attention thus far. Three main challenges related to the timing of the event are considered: accurate age control for some of the sites that provide evidence for the impact, linking these sites to the onset of the YD and, most importantly, an apparent age discrepancy of up to two centuries between different sites associated with the YDIH. Lastly, we conclude with some recommendations for future studies, with respect to sampling strategies and age control.

2. Summary of data for and against the Younger Dryas impact hypothesis

To substantiate their claim of an extraterrestrial impact at the Allerød-YD boundary, Firestone et al. (2007) report evidence from a wide range of sites, predominantly in North America. Most of their sites contain the so-called Black Mat: a dark grey to black layer with high organic content formed during the early YD (Haynes, 2008). Other samples were taken from the rims of several of the Carolina Bays, elliptical depressions that Firestone et al. (2007) relate to the impact. An impact origin for the bays, however, is unlikely as the bays were not formed instantly, furthermore, there is evidence that the bays were formed before the YD (Brooks et al., 2010; Pinter et al., 2011). Only one of the sites analysed by Firestone et al. (2007) is located outside of North America, namely Lommel (Belgium), where the Usselo horizon was sampled. The Usselo horizon is a buried soil horizon formed during the late Allerød to early YD and is widespread in the European coversand area (Kaiser et al., 2009). Like the Black Mat, the Usselo horizon thus approximately marks the onset of the YD in the sedimentary record. In later studies, sites located in South America and the Middle East were also investigated (Mahaney et al., 2010a; Bunch et al., 2012). Fig. 1 gives an overview of all the sites at which YDIH markers have been reported.

Firestone et al. (2007) report peak concentrations of a wide range of markers across the Allerød-YD boundary. The main markers they report include “magnetic grains with iridium, magnetic microspherules, charcoal, soot, carbon spherules, glass-like carbon containing nanodiamonds, and fullerenes with ET [extraterrestrial] helium”. Of the markers put forward by Firestone et al. (2007), only elevated iridium (Ir) concentrations are commonly used as an impact indicator (Tagle and Hecht, 2006; French and Koeberl, 2010; Koeberl et al., 2012). Fullerenes with extraterrestrial helium on the other hand, are considered controversial and have not been confirmed independently at any known impact site (French and Koeberl, 2010). Charcoal, soot, carbon spherules and glass-like carbon are only indicative of biomass burning, regardless of what initiated the fires. As fullerenes, charcoal or soot cannot be

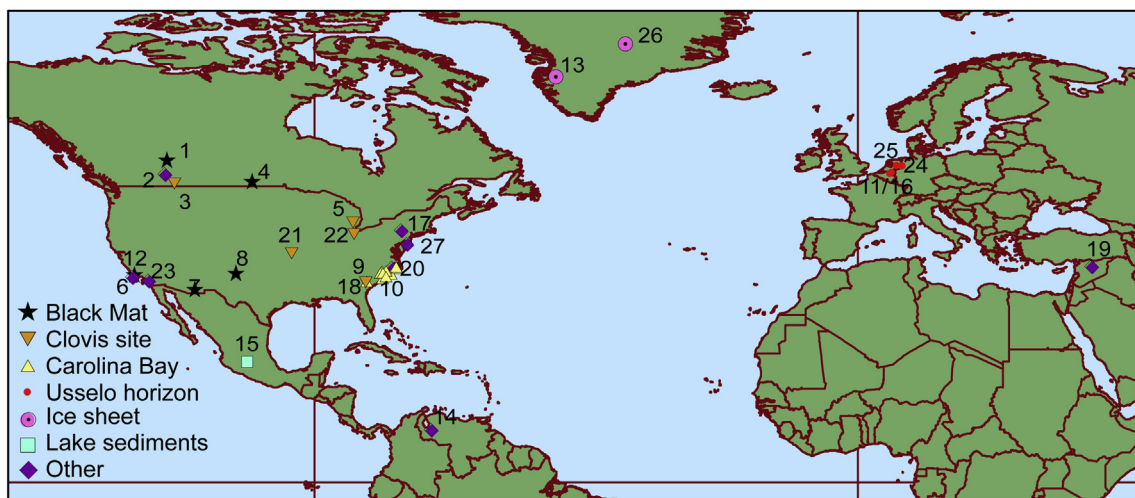


Fig. 1. Overview of all the sites where different YDI markers have been reported. 1. Chobot^{a,b,r} 2. Morley^a 3. Wally's beach^a 4. Lake Hind^{a,b} 5. Gainey^{a,r} 6. Daisy Cave^a 7. Murray Springs^{a,b,c,d,e,f,r,t} 8. Blackwater Draw^{a,g,h,i,r,t} 9. Topper^{a,b,g,h,l,r} 10. Carolina bays^{a,g} 11. Lommel^{a,g,j,r,t} 12. Arlington Canyon^{d,k,l,r} 13. Kangerlussuaq^m 14. Mucubajjiⁿ 15. Lake Cuitzeo^{o,r} 16. Geldrop Aalsterhut^p 17. Melrose^{q,r,t} 18. Blackville^{a,q,r} 19. Abu Hureyra^{q,r} 20. Barber Creek 21^r. Big Eddy^r 22. Sheridan Cave^{r,t} 23. Talega^r 24. Lingen^r 25. Ommen^r. 26. GISP2^s 27. Newtonville^t Different type of sites or sedimentary archives are indicated by different symbols. ^aFirestone et al. (2007); ^bKennett et al. (2009a); ^cHaynes et al. (2010); ^dDaulton et al. (2010); ^eFayek et al. (2012); ^fPigati et al. (2012); ^gPaquay et al. (2009); ^hSurovell et al. (2009); ⁱLeCompte et al. (2012); ^jTian et al. (2011); ^kKennett et al. (2008, 2009b); ^lScott et al. (2010); ^mKurbatov et al. (2010); ⁿMahaney et al. (2010b; 2010; 2011); ^oIstrade-Alcántara et al. (2012); ^pvan Hoesel et al. (2012); ^qBunch et al. (2012); ^rWittke et al. (2013b); ^sPetaev et al. (2013); ^tWu et al. (2013).

used as supportive evidence for an impact, they are not discussed in further detail. Although carbon spherules and glass-like carbon are also not indicative of an impact either, they are briefly discussed as nanodiamonds have been reported to occur in these particles. This review focusses on the proposed impact markers that are currently still part of the debate: magnetic spherules, the recently reported scoria-like objects and lechatelierite, Ir and other platinum group elements (PGEs), shocked quartz, and nanodiamonds. In this section the occurrence of these markers and their relevance as indicators of the YD impact event will be discussed in detail.

2.1. Magnetic microspherules

Spherules, both magnetic and non-magnetic, are known to occur in distal ejecta layers related to extraterrestrial impacts (French and Koeberl, 2010; Glass and Simonson, 2012), they are formed by melting of crustal material heated by an airburst or crater forming impact. Microspherules can, however, also form through volcanism, as meteorite ablation debris (cosmic spherules), and through various sedimentary, diagenetic and artificial processes (French and Koeberl, 2010; Glass and Simonson, 2012). The presence of microspherules is, therefore, not considered diagnostic evidence for an extraterrestrial impact (French and Koeberl, 2010). The impact origin of the microspherules needs to be confirmed by other lines of evidence, such as the presence of meteoritic components, evidence of shock metamorphism or a characteristic composition. Other, non-diagnostic, indications that a spherule-rich layer might be impact related are: the absence of similar spherules in the rest of the sedimentary sequence, the presence of rare splashform shapes indicative of melting, such as teardrops or dumbbells, the presence of vesicles in the spherules indicative of melting, crystallisation structures developed inward from the rim of the spherule, the absence of other volcanic material, a chemical composition similar to the target rock and the absence of exotic compositions (French and Koeberl, 2010; Glass and Simonson, 2012).

Firestone et al. (2007) reported a distinct peak in magnetic grain and microspherule concentrations across the Allerød-YD boundary at most of their sites. Whereas magnetic grains are not reported at known impact layers and quickly left the YD impact debate, the magnetic spherules remain one of the major markers used to support the YDIH (Bunch et al., 2012; Israde-Alcántara et al., 2012; LeCompte et al., 2012; Wittke et al., 2013b). Scanning electron microscopy (SEM) imaging shows that these spherules often have dendritic or polygonal surface patterns. In addition to the patterned spherules, smooth spherules have also been reported as Allerød-YD boundary spherules (Bunch et al., 2012; Israde-Alcántara et al., 2012). The patterned surfaces are interpreted as indicative of melting and rapid quenching, and therefore used to argue in favour of an impact-related origin YDIH (Bunch et al., 2012; Israde-Alcántara et al., 2012; LeCompte et al., 2012; Mahaney et al., 2013; Wittke et al., 2013b).

LeCompte et al. (2012), using SEM, estimated which percentage of the total magnetic spherule count at the Allerød-YD boundary contained quench-like surface microstructures. At the Blackwater Draw site 80% of spherules have quench structures while at the Topper site, where spherule counts were lower, only 25% of spherules have quench textures. The authors do not explain this difference, but it might be just natural variation in spherule abundances. Only these quench-texture spherules in the Allerød-YD boundary were taken into account in the spherule counts for the Allerød-YD boundary by LeCompte et al. (2012). Unfortunately LeCompte et al. (2012) do not report the percentage of quench textured spherules within the sediment layers overlying and underlying the Allerød-YD boundary but instead use the total

spherule count as an upper limit for these layers. Therefore it is not known if the Allerød-YD boundary percentages of quench textured spherules are anomalous for these sites or whether the older and younger layers contain the same percentage of quench-texture spherules and just fewer spherules in total. In order to state that the occurrence of quench texture spherules in the Allerød-YD boundary is anomalous, and possibly indicative of a single event, the relative amount of quench spherules in the rest of the section should also be analysed.

The chemical composition of the magnetic spherules found at the Allerød-YD boundary is another characteristic of the spherules which is used as an argument in favour of an impact related origin (Bunch et al., 2012; Israde-Alcántara et al., 2012; Wittke et al., 2013b). Firestone et al. (2007) argue that geochemical analyses of their Allerød-YD boundary spherules show that the spherules are non-volcanic in origin and suggest an extraterrestrial origin. The other studies (Bunch et al., 2012; Israde-Alcántara et al., 2012; Wittke et al., 2013b) also argue that the Allerød-YD boundary spherules are not of volcanic origin, and show that their spherules have a heterogeneous composition similar to that of impact ejecta. In addition Bunch et al. (2012) show that the rare earth elements (REEs) of the Allerød-YD boundary magnetic spherules are terrestrial. They therefore argue that the Allerød-YD boundary magnetic spherules must consist of crustal material that melted as a result of an extraterrestrial impact or airburst (Bunch et al., 2012; Israde-Alcántara et al., 2012; Wittke et al., 2013b). The data of Bunch et al. (2012) also show that the Allerød-YD boundary objects (including the magnetic spherules) from the Abu Hureyra site differ in composition from those of the Melrose and Blackville site, suggesting a different source for the material.

The combination of microstructural features (quench textures) and composition of the magnetic spherules are thus used as arguments to support the YDIH. Other processes, such as meteorite ablation or volcanism, could, however, also be responsible for the melt and quench features (Weixin et al., 1994; Franke et al., 2007; Itambi et al., 2010; Grebennikov, 2011; Grebennikov et al., 2012). Indeed, magnetic microspherules with dendritic surface patterns have also been found at other locations, in sediments of different ages. These spherules are arguably of volcanic or cosmic origin rather than impact related (Weixin et al., 1994; Franke et al., 2007; Itambi et al., 2010; Grebennikov, 2011). In Fig. 2 we compare the composition of some of these non-Allerød-YD boundary quench spherules to the composition of the Allerød-YD boundary spherules. This comparison shows that some of these older magnetic spherules (Franke et al., 2007; Grebennikov, 2011) have a composition similar to those of the Allerød-YD boundary magnetic spherules (Fig. 2). The marine spherules were found in three cores taken in the Southern Atlantic Ocean from sediments dated to approximately 65,000 and 120,000 yrs ago and are interpreted as volcanic in origin (Franke et al., 2007). No known impacts occurred at these times (Earth Impact Database, <http://www.passc.net/EarthImpactDatabase/index.html>, accessed January 2013). The composition and age of these marine magnetic spherules suggests that the combination of quench textures and composition of the Allerød-YD boundary is not unique to the Allerød-YD boundary spherules or impact spherules and therefore should not be used to argue in favour of an impact origin for the Allerød-YD boundary material. In addition, Bunch et al. (2012) only compared the Allerød-YD boundary spherules to silica-rich volcanic material, while iron-rich spherules have also been related to volcanic activity (Franke et al., 2007; Grebennikov, 2011; Grebennikov et al., 2012). The chemical composition of these ignimbrite spherules overlaps with some of the iron-rich Allerød-YD boundary spherules (Fig. 2). Although there is no known large-scale volcanic activity at the onset of the Younger Dryas, there were two large volcanic eruptions

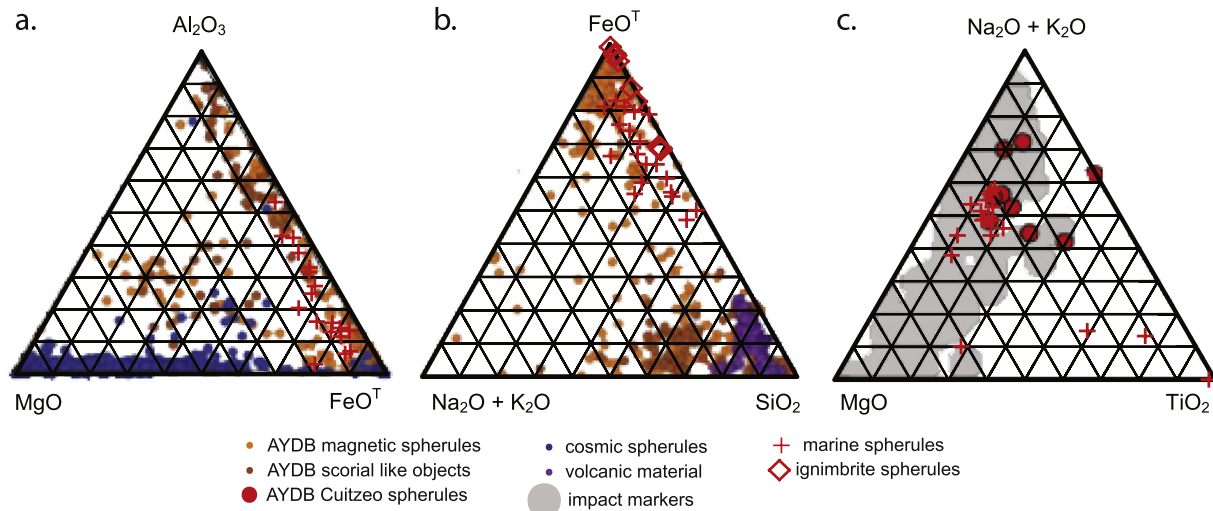


Fig. 2. Comparison of the chemical composition of AYDB magnetic spherules to other types of magnetic spherules: a. cosmic (Bunch et al., 2012, Fig. 3a) b. volcanic (Bunch et al., 2012, Fig. 3c) and c. impact material (Israde-Alcántara et al., 2012, Fig. 6c). We plotted the chemical composition of magnetic spherules from deep sea sediments of non-impact origin (Franke et al., 2007) and spherules found in volcanic ignimbrites (Grebennikov, 2011; Grebennikov et al., 2012) in these diagrams for comparison. This comparison shows that magnesium rich compositions associated with a cosmic origin are not found in spherules from the AYDB, or in older sediments. The spherules from the older marine sediments as well as the ignimbrite spherules have a similar composition to the AYDB magnetic spherules. This comparison shows that the AYDB spherules are not unique to an impact and might have a different origin.

in the centuries prior to the proposed timing of the YD impact event: the Glacier Peak eruption in western North America (Gardner et al., 1998; Kuehn et al., 2009) and the Laacher See eruption in western Europe (Schmincke et al., 1999; Litt et al., 2003). It is possible that some of the volcanic material has been incorporated into the Black Mat, the Usselo Horizon or other sites investigated for YD impact markers (see also section 5), although Wittke et al. (2013b) report that they found no tephra in the Usselo horizon.

Another type of spherule reported as evidence for the YDIH is the framboidal type (Fayek et al., 2012; Israde-Alcántara et al., 2012). Framboids typically consist of spherical clusters of euhedral microcrystals (Sawlowicz, 1993a) and can have a wide range of possible origins, such as algae activity (Pinter et al., 2011) or anoxic conditions (Israde-Alcántara et al., 2012) and are thus not indicative of impacts. The larger framboidal spherules (>400 μm) found by Fayek et al. (2012) were contained in a glassy iron-oxide-rich matrix. Fayek et al. (2012) suggest that the framboids they found at Murray Springs are similar to those found in several types of chondritic meteorites and thus originated from a high velocity impact (Fayek et al., 2012). However, when they plotted in a graph and compared with known impact material (Fayek et al., 2012; Fig. 4), the chemistry of the Allerød-YD boundary spherules does not overlap with that of the plotted impact material, which suggests that the framboids are not impact related.

Pinter and Ishman (2008) argue that the peak concentrations in magnetic spherules at the Allerød-YD boundary found by Firestone et al. (2007) have nothing to do with an extraterrestrial impact and suggested that the magnetic microspherules are consistent with the accumulation of micrometeoritic ablation fallout, or ‘meteoritic rain’, over a longer period of time. A cyclical high input in cosmic dust occurring roughly every 1250 yrs rather than a long accumulation time has also been suggested as an explanation of the peak concentrations in the Allerød-YD boundary (Fiedel, 2010), although this cycle has no known peak at the Allerød-YD boundary (Franzén and Cropp, 2007). The YDIH proponents, however, show that the composition of their Allerød-YD boundary spherules is inconsistent with that of cosmic spherules (Bunch et al., 2008;

Israde-Alcántara et al., 2012; Wittke et al., 2013b). The composition of the Allerød-YD boundary spherules is, however, not unique to impact spherules either (Fig. 2).

Pigati et al. (2012) reported peak concentrations of magnetic spherules across the Allerød-YD boundary. However, the high concentrations of magnetic microspherules were typical for all other black mats they analysed as well, regardless of age. These results strengthen the case of earlier studies, which suggest that the peak in magnetic spherules in the Allerød-YD boundary might be related to the depositional environment rather than to an impact (Surovell et al., 2009; Haynes et al., 2010; Pinter et al., 2011). Bunch et al. (2012), however, suggest that the non-Allerød-YD boundary spherules found by Pigati et al. (2012) are likely to be of volcanic origin as there are several volcanoes in the vicinity of these sites. Unfortunately, since Pigati et al. (2012) analysed their microspherules only for iridium and rare earth elements (see Section 2.3), it is not possible to directly compare the geochemistry and morphology of their spherules to the reported Allerød-YD boundary magnetic microspherules for similarities between magnetic spherules from different black mats.

2.1.1. Reproducibility of the peaks in magnetic spherule concentration

The reproducibility of the peaks in magnetic spherule concentrations was first questioned by Surovell et al. (2009), who investigated seven sites of similar age, including two sites that were also investigated by Firestone et al. (2007). Using the method of Firestone et al. (2007), they were unable to replicate the reported peaks in magnetic spherules but instead found peaks at non-Allerød-YD boundary levels at several sites. Based on their observations, Surovell et al. (2009) argue that the peaks in magnetic spherule as reported by Firestone et al. (2007) are related to changes in the depositional environment rather than an extraterrestrial impact. Two subsequent studies (Haynes et al., 2010; Pinter et al., 2011) also failed to replicate the results of Firestone et al. (2007) and echoed the conclusions of Surovell et al. (2009). LeCompte et al. (2012) investigated the discrepancy between the results of Surovell et al. (2009) and Firestone et al. (2007),

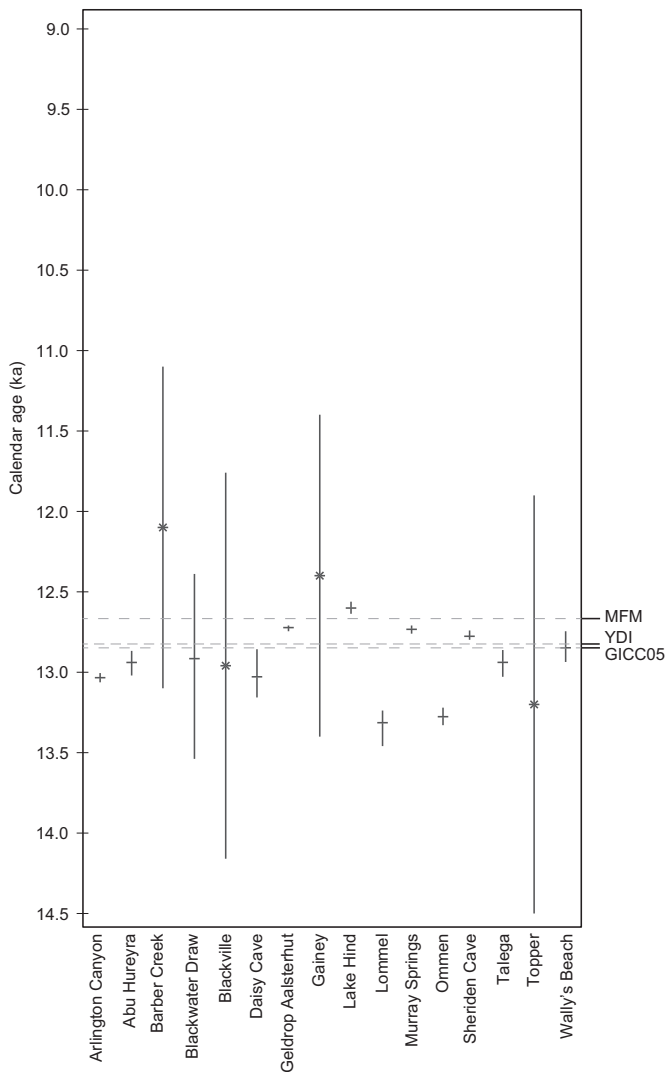


Fig. 3. Calendar age for the different locations investigated in relation to the YDIH where the marker layer has been directly dated (Firestone et al., 2007; Kennett et al., 2009; Bunch et al., 2012; van Hoesel et al., 2012; Wittke et al., 2013b). Ages are given within one standard deviation (OSL/TL; mean indicated with an asterisk) or within the 68% confidence interval (IntCal13 calibrated radiocarbon ages; median indicated with a short horizontal stripe). The proposed age of the YDI (Wittke et al., 2013b) is indicated as well as the onset of the YD according to the Greenland Ice Core Chronology 2005 (GICC05, Rasmussen et al., 2006) and the Meerfelder Maar varved lake record (MFM, Brauer et al., 2008).

conducting a blind study of the magnetic spherule concentrations at three Allerød-YD boundary sites. Two of these sites, Blackwater Draw and Topper, were also investigated by both Firestone et al. (2007) and Surovell et al. (2009). The third site, Paw Paw Cove, was only investigated by Surovell et al. (2009). However, since LeCompte et al. (2012) analysed only one sample from the Allerød-YD boundary at Paw Paw Cove, and no samples from above and below it, it is difficult to compare results for this site. Unlike Surovell et al. (2009), LeCompte et al. (2012) found high concentrations of magnetic spherules in the Allerød-YD boundary, even higher than those reported by Firestone et al. (2007). There thus seems to be a discrepancy in spherule counts between different sites.

In an attempt to explain this discrepancy in magnetic spherule counts, LeCompte et al. (2012) list five major reasons which might have contributed to the absence of peak spherule concentrations at the Allerød-YD boundary as reported by Surovell et al. (2009).

These reasons are summarised in Table 1, which also includes other studies that investigated the magnetic spherule fraction. It is clear from the comparison in Table 1 that there is no consistent trend between the reasons listed by LeCompte et al. (2012) and the discrepancy in spherule counts between studies. In addition, these reasons do not entirely explain why Surovell et al. (2009) or Pigati et al. (2012) found small numbers of magnetic spherules at some other stratigraphic levels. LeCompte et al. (2012) suggest that Surovell et al. (2009) might have found spherules of a diagenetic origin: further SEM work would be necessary to clarify this point. Although size-sorting seems an important factor, as LeCompte et al. (2012) did not manage to find any spherules before applying rigorous size sorting, Pigati et al. (2012), without size sorting report peaks in magnetic spherule concentration at the Allerød-YD boundary. This shows that although LeCompte et al. (2012) failed to find any magnetic spherules without rigorous size sorting, size sorting does not entirely explain the discrepancy in spherule counts between studies. Furthermore, at the Topper site, LeCompte et al. (2012), who used a stronger magnet than the other studies, found three times as many spherules as Firestone et al. (2007). Even though the peak in spherule concentration was reproduced, there is thus still a discrepancy in exact spherule counts between studies. Part of this discrepancy might be related to the method used to extract the magnetic spherules, namely using a hand magnet wrapped in plastic to repeatedly extract the magnetic particles from a slurry until diminishing returns. Although this is an easy method, accessible to most research teams, some researcher consider it as much an art as it is science (Haynes et al., 2010). In addition, different results are obtained when a different magnet is used (LeCompte et al., 2012). To aid reproducibility and comparison between studies it might therefore be better to use an electro-magnetic separator.

It is important to note that even if the discrepancy in spherule count can be explained, the Allerød-YD boundary magnetic spherules are not a unique impact signature. Similar spherules have been found in marine sediments (Fig. 2) and black mats of different ages seem to effectively trap magnetic spherules, explaining the observed peak concentration in the Allerød-YD boundary Black Mat (Pigati et al., 2012).

2.2. Scoria-like objects and lechatelierite

One line of evidence for the YDIH, which was not part of the original YDIH (Firestone et al., 2007), is the presence of vesicular (bubbly) melted siliceous glass, referred to as scoria-like objects (SLOs). These SLOs were found in the magnetic fraction at three sites, two in North America and one in Syria (Bunch et al., 2012), suggesting that these objects also contain some magnetic minerals. Although scorias are volcanic in origin, similar shaped objects are formed during impacts or nuclear airbursts (Bunch et al., 2012). The composition of the scoria-like objects found in the Allerød-YD boundary is similar to the local composition of the sediment cover, suggesting that they consist of molten material of local or regional origin (Bunch et al., 2012). This local origin of the molten material, as well as the large distance between the sites (1000–10,000 km), led Bunch et al. (2012) to adopt at least two impact locations.

Both the SLOs and the magnetic spherules at these three locations are reported to contain lechatelierite (Bunch et al., 2012; Wu et al., 2013), a vesicular form of silica glass containing flow structures (Kieffer et al., 1976; Stöffler and Langenhorst, 1994; Grieve et al., 1996). During an impact, lechatelierite can be formed due to shock-melting of quartz at high pressures (>50 GPa), followed by rapid quenching (Stöffler and Langenhorst, 1994). Inclusions of lechatelierite in tektites (impact related glass) are therefore considered evidence for an impact origin (Glass, 1990; French and

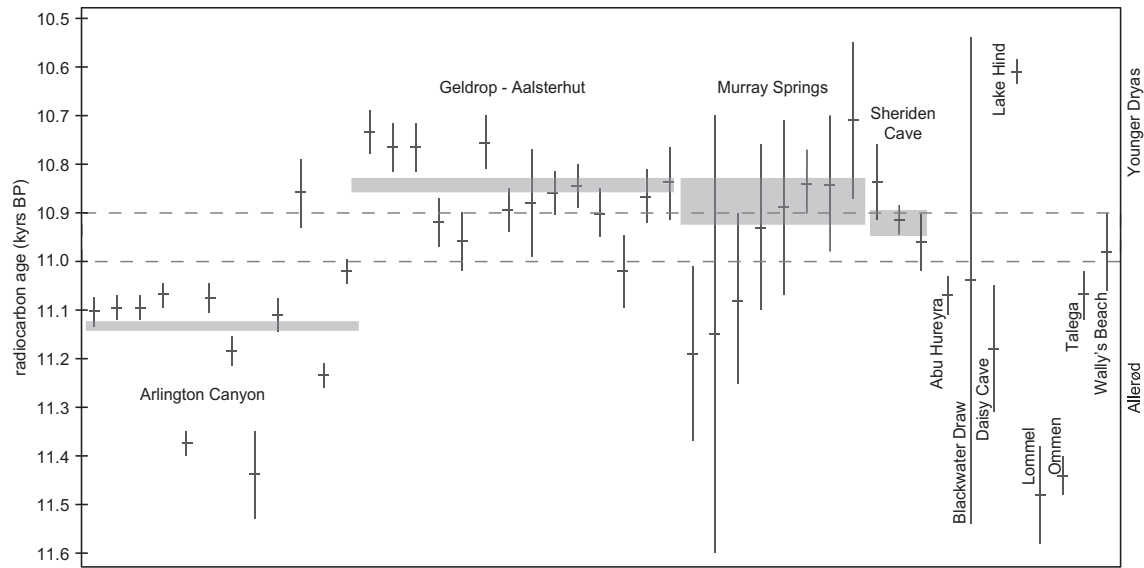


Fig. 4. Reported uncalibrated radiocarbon ages (1σ) for the different locations investigated in relation to the YDIH where the marker layer has been directly dated (Firestone et al., 2007; Kennett et al., 2009; Bunch et al., 2012; van Hoesel et al., 2012; Wittke et al., 2013a,b). Weighted averages (1σ) for sites with multiple ^{14}C ages are indicated as grey bars. The estimated timing for the Younger Dryas onset (11,000–10,900 ^{14}C yrs BP) is indicated with the two dotted lines.

Koeberl, 2010; Glass and Simonson, 2012). However, lechatelierite can also form during lightning strikes, a more local and small-scale phenomenon during which the high temperatures needed to melt the quartz ($>1700\text{ }^\circ\text{C}$) are reached (French and Koeberl, 2010; Bunch et al., 2012). Bunch et al. (2012) argue that at their sites, the SLOs are not confined to a small area but are found over greater distances, and are therefore unrelated to lightning strikes. However, the scoria-like objects containing samples at Abu Hureyra and Blackville came from cores separated by only 4.5 m and 10 m respectively (Bunch et al., 2012). A core taken 2.2 km from the Blackville site, on the other hand, did not contain any scoria-like objects at the Allerød-YD boundary. At Melrose scoria-like objects were also found in samples taken 28 m as well 28 km away from the original site. However, as Melrose contains no visible Allerød-

YD boundary and the two other locations near Melrose were not dated, it is possible that these samples do not date to the Allerød-YD boundary. Exogenic fulgurites, formed when molten droplets are ejected from the soil during a lightning strike, though rare, have been found within a 5 m radius of a lightning strike (Mohling, 2004), suggesting that although it is unlikely that Bunch et al. (2012) found material originating from lightning strikes at three of their sites and only at the Allerød-YD boundary, this is not necessarily impossible. Wittke et al. (2013b) argue that the lack of excess magnetization of the Allerød-YD boundary spherules exclude lighting as a possible formation mechanism. However, none of the lechatelierite-containing spherules or SLOs were analysed in this study.

If the lechatelierite inclusions are correctly identified and indeed unrelated to lightning strikes, this would indicate an impact

Table 1

Overview showing the presence or absence in peak concentration of magnetic spherules for several studies which were published before LeCompte et al. (2012). The methodology used in these studies is summarized in terms of five aspects that might affect the reproducibility of the magnetic spherule analysis according to LeCompte et al. (2012), who looked only at the Firestone et al. (2007) and Surovell et al. (2009) studies. 1. *AYDB sampling thickness*. As the AYDB is a very thin layer (Firestone et al., 2007), LeCompte et al. (2012) suggest that the magnetic spherules are diluted when sampling thickness increases and therefore more difficult to detect. 2. *Aliquot size or amount of investigated material*. As only small numbers of AYDB spherules are present in the samples, it is easy to over, or underestimate the number of magnetic spherules due to natural variation in the sample, especially when looking at small samples. Thus assigning a “peak” concentration to small aliquots is also questionable on this basis. 3. *Size sorting*. At first LeCompte et al. (2012), did not size sort their samples and failed to find any magnetic spherules. Only after they implemented rigorous size sorting to their samples, did LeCompte et al. (2012) find high concentrations of magnetic spherules at the AYDB. 4. *Sphericity*. Surovell et al. (2009) only looked for unfaceted, highly spherical spherules with a smooth glassy surface. However, other studies on the AYDB magnetic spherules used less conservative criteria (Firestone, 2009; Israde-Alcántara et al., 2012; LeCompte et al., 2012), thus including more spherules in the count. 5. *Scanning electron microscopy and chemical analyses*. LeCompte et al. (2012) suggest only quench textured spherules and certain chemical composition should be included in the spherule count. + indicates that peak concentrations of magnetic spherules were found or that the study adhered to a certain part of the methodology. – indicates that peak concentrations of magnetic spherules were not found or that the study used a different methodology.

Study	Peak concentration		Methodology				
	At AYDB	Non-AYDB	1. Sampling thickness	2. nr + size of aliquot	3. Size sorting	4. Perfect sphericity	5. SEM
Firestone et al. (2007)	+	–	2–15 cm	≥ 1 ; 100–200 mg			No images reported
Surovell et al. (2009)	–	+	2–38 cm; most: 5–10 cm	10–40 mg	–	+	–
Haynes et al. (2010)	+		0.5–1 cm	10 mg	+		–
Pinter et al. (2011)		+				+	+
Israde-Alcántara et al. (2012)	+	–	5–10 cm	≥ 1 ; 100–200 mg	+	–	+
Pigati et al. (2012)	+	+	≤ 2 cm	100 g (bulk)	–	+	–
Bunch et al. (2012)	+	–	5–15 cm	nr	+	–	+
LeCompte et al. (2012)	+	–	4–15 cm	10–40 mg	“smaller than recommended mesh size”	–	+

related origin for both the scoria-like objects and magnetic spherules at these three locations, as suggested by Bunch et al. (2012). However, no other inclusions indicative of an impact, such as shocked quartz, other high-pressure polymorphs, or elevated concentrations of projectile-related elements, were reported at these sites. In addition, no lechatelierite has been reported at other sites investigated in the studies reporting lechatelierite (Wu et al., 2013; Wittke et al., 2013b). More work is necessary to establish whether the scoria-like objects and lechatelierite are indeed related to an extraterrestrial airburst and whether they are found at the other Allerød-YD boundary sites as well.

2.3. Iridium and other platinum group elements

Several types of meteorites are highly enriched (up to 1000 times) in the platinum group elements (PGEs) compared to the average continental crust. Following an impact, small amounts of this PGE-rich material are incorporated in the distal ejecta layer, resulting in a typical impact signature (Sawlowicz, 1993b; French and Koeberl, 2010). PGEs are therefore taken as a reliable impact marker (French and Koeberl, 2010). Because of difficulties in measuring very low PGE concentrations, the concentration of Ir (iridium), typically >1–2 ppb in the case of an impact signature, is often taken as representative for all PGEs, as it is the easiest to measure (Kyte et al., 1988; French and Koeberl, 2010). However, small amounts of Ir enrichment can also result from terrestrial processes (Sawlowicz, 1993b; French and Koeberl, 2010), which complicates interpretation. It is therefore more reliable to measure all the PGEs rather than just Ir, which, on its own, cannot be considered a unique marker (Sawlowicz, 1993b; French and Koeberl, 2010).

Firestone et al. (2007) initially found elevated concentrations of Ir in the Allerød-YD boundary layer at half of their sites (in bulk samples: <0.5–3.8 ppb with ± 50 –90% uncertainty; in the magnetic fraction: up to 117 ppb with ± 10 % uncertainty). However, upon retesting subsamples from the same sites only half of the elevated Ir concentrations were confirmed (Firestone et al., 2007). Different studies also report different Ir concentrations for the same site, for example at the Murray Springs site (see Table 2). Ir concentrations thus not only vary between sites, but also within the same site. These varying results do not exclude an extraterrestrial origin, as impact signatures vary as well (Sawlowicz, 1993b). However, at Murray Springs, Haynes et al. (2010) showed that the background concentration at the site is variable as well, including Ir concentrations as high as those found in the Black Mat (33–72 ppb). The Ir concentrations at Murray Springs are therefore variable and not anomalous when compared to the background concentrations. The reported Ir concentrations at Murray Springs thus cannot be taken as evidence for an extraterrestrial source of the material.

Pigati et al. (2012) report peaks in magnetic spherules and Ir concentrations (bulk and magnetic) of different magnitudes at, or near, the base of several Allerød-YD boundary Black Mats, as well as

Black Mat like deposits of different ages. They suggest that the peaks in magnetic spherule and Ir concentrations at the bottom of the Black Mat must therefore be inherent to the depositional environment in which Black Mat like layers are formed. These inherent peak concentrations (Ir and magnetic spherules) in Black Mat like deposits show that unless there were impacts at all these sites at different times, a peak in Ir concentrations (regardless of the exact amount) at the bottom of the Black Mat does not immediately imply that an extraterrestrial impact occurred, as suggested by Firestone et al. (2007) and Bunch et al. (2010). Moreover, Pigati et al. (2012) found high Ir concentrations of >1–2 ppb, not only in one of the Allerød-YD boundary Black Mats but also in several black mats of different ages (>40 ka–5.6 ka), both in the American Southwest and in Chile. This is consistent with the idea that isolated Ir analysis are not strong evidence for an impact and that other related elements, such as the rest of the PGEs, should be analysed in order to get a reliable indication of an impact (French and Koeberl, 2010). In addition, Petaev et al. (2013) found no Ir anomaly at the Allerød-YD boundary in the GISP2 ice core, but found a peak in Pt concentrations. Their results suggest that the Ir concentrations found in some black mats might indeed have terrestrial origins, as suggested by Pigati et al. (2012). Based on the combination of high Pt with low Ir and Al concentrations, Petaev et al. (2013) suggest that the source of the Pt peak in the GISP2 ice core most likely has an extraterrestrial source, possibly a magmatic iron meteorite.

An extensive study on the bulk sediment PGE concentrations within the Allerød-YD boundary at several sites was conducted by Paquay et al. (2009). At all sites, the bulk PGE concentrations, including those of Ir, were similar to average continental crust values and lower than those reported by Firestone et al. (2007) or Haynes et al. (2010). Although at some sites the Ir concentrations reported by Paquay et al. (2009) peaked in the Allerød-YD boundary, the values (max 0.117 ppb at Lake Hind) are still well below the >1–2 ppb threshold used to identify impact signatures (Kyte et al., 1988; French and Koeberl, 2010). In response, Firestone (2009) argues that Paquay et al. (2009) sampled without using the proper microstratigraphy, thereby diluting the Ir signal. However, Paquay et al. (2009) claim to have used subsamples of the Murray Springs samples that were used by Firestone et al. (2007). It therefore seems unlikely that the lack of evidence reported by Paquay et al. (2009) is entirely the result of the wrong sampling strategy. Furthermore, Paquay et al. (2009) also looked at the bulk Os isotope ratio, which has an even greater potential to identify small amounts of meteoritic material compared to the PGE method (Paquay et al., 2009; French and Koeberl, 2010). All measured $^{187}\text{Os}/^{188}\text{Os}$ ratios in the Allerød-YD boundary were too high (mostly >1) to be consistent with the input of extraterrestrial material (Paquay et al., 2009). Another argument put forward against the work of Paquay et al. (2009) is that they only analysed the PGE and Os-isotope ratios in the bulk sediment rather than in the magnetic fraction (Bunch et al., 2010). The largest peaks in Ir have indeed been reported in the magnetic fraction rather than in the bulk sediment (Firestone et al., 2007; Haynes et al., 2010; Pigati et al., 2012). If the magnetic grains are the carriers of the Ir signal (Bunch et al., 2010), eliminating the Ir poor non-magnetic parts of the samples by only analysing the magnetic fraction, would increase the measured Ir relative to measurements of the bulk samples. In addition, analysing the magnetic fraction might concentrate any cosmic spherules present in the sample. As cosmic spherules may contain Ir concentrations of >1000 ppb (Sawlowicz, 1993b), concentrating this material by only looking at the magnetic fractions will increase the measured Ir concentration in the total magnetic fraction. Pigati et al. (2012), however, showed that the rare earth elements (REE) of the total magnetic grain fraction found at the Allerød-YD boundary has a typical terrestrial profile,

Table 2

Ir concentrations of the AYDB at Murray Springs (Arizona) within both the magnetic fraction and the bulk sediment as reported by different research teams.

Study	Ir concentration in magnetics (ppb)	Ir concentration in bulk sediment (ppb)
Firestone et al. (2007)	<0.1–<11	<0.5–2.2
Paquay et al. (2009)	Not reported	0.077
Haynes et al. (2010)	64 ^a	nr
Pigati et al. (2012)	1.03–129 ^b	0.06–0.66

^a Similar Ir concentrations were reported in the non AYDB sediments as well.

^b The highest concentration of Ir in the magnetic fraction (200 ppb) was reported 10 cm below the AYDB.

suggesting that cosmic spherules concentrations might be low. In addition, Wu et al. (2013) investigated the Os-isotope ratio in both bulk and magnetic fractions and reported no Os-isotope anomaly at most of their sites. They report low Os-isotope ratios in the bulk sediment at Lommel and Melrose. Total Os concentrations at these sites are however low and Wu et al. (2013) therefore suggest the Os might have a terrestrial source.

In summary, although Firestone et al. (2007) report peaks in Ir concentration at some of their sites, other researchers were not always able to reproduce these results (Paquay et al., 2009). Furthermore, it has been shown that the peaks in Ir concentration do not necessarily indicate an impact event (Haynes et al., 2010; Pigati et al., 2012) and analysis of other elements indicate a terrestrial origin of the material (Paquay et al., 2009; Pigati et al., 2012). Although Petaev et al. (2013) suggest that the Pt peak they found in the Greenland ice sheet is related to a meteorite impact, no Pt has been reported at other sites yet. There is thus no unambiguous geochemical evidence that the YD impact event took place.

2.4. Microstructures in quartz

Planar deformation features (PDFs) are thin (<1 µm), closely spaced (<10 µm), straight, parallel deformation planes in crystals which form during shock deformation and are sometimes referred to as ‘shock lamellae’ (Langenhorst, 2002; French and Koeberl, 2010; Hamers and Drury, 2011). They are most well known for their occurrence in quartz (also referred to as ‘shocked quartz’), where they are oriented parallel to specific crystallographic planes. As PDFs are distinct and unique features, they are widely used as a diagnostic indicator of high shock pressures following an impact (Langenhorst, 2002; French and Koeberl, 2010; Hamers and Drury, 2011). Nevertheless, some non-shock lamellae in quartz have occasionally been misidentified as PDFs (Langenhorst, 2002; French and Koeberl, 2010). It is therefore important that the correct identification techniques and criteria are used in identifying PDFs. The only completely reliable method to distinguish PDFs from non-shock lamellae is transmission electron microscopy (TEM), but orientation measurements using a U-stage microscope or analysis using scanning electron microscopy (SEM) cathodoluminescence (CL) imaging also give good results (Boggs et al., 2001; French and Koeberl, 2010; Hamers and Drury, 2011).

In 2010, Mahaney et al. reported the occurrence of “shattered quartz, notably with prominent PDFs in the finer silt fractions” in a ~13 ka Black Mat-like layer in the Venezuelan Andes. Their interpretation was based on SEM observations of planar surface features, spaced 0.5–1.0 µm apart. Although the spacing of the features is consistent with PDFs, only one set of features was observed and none of the other features indicative of PDFs were reported. Further analysis, such as SEM-CL or TEM, is thus necessary to establish whether these features are indeed PDFs (e.g. French and Koeberl, 2010; Mahaney et al., 2010a; Hamers and Drury, 2011). In a follow-up paper, Mahaney et al. (2010b) stated that they found no irrefutable PDFs. Instead, Mahaney et al. (2010b) focus on the presence of closely spaced fractures oriented parallel to the surface of the quartz grains, as well as highly disrupted grain surfaces leading to extreme brecciation (Mahaney et al., 2010b). (Mahaney et al., 2010b)(Mahaney et al., 2010b)These features are however not considered as indicative of an extraterrestrial impact (French and Koeberl, 2010). As Mahaney et al. (2010b) have shown, these fractured and disrupted grain surfaces can form as a result of heating and are thus not necessarily the result of an impact. Even though Mahaney et al. (2010a) show no conclusive evidence for the occurrence of shocked quartz and Mahaney et al. (2010b) conclude that they find no irrefutable evidence for the occurrence of PDFs, the first paper (Mahaney et al., 2010a) has been cited by proponents

of the YDIH to substantiate their claim that a large impact event occurred (Mahaney et al., 2011; Bunch et al., 2012; Israde-Alcántara et al., 2012; Mahaney et al., 2013).

2.5. Nanodiamonds

Nanodiamonds have been found in meteorites and in relation to impact craters (Hanneman et al., 1967; Carlisle and Bramant, 1991; Daulton et al., 1996; Hough et al., 1997; Koeberl et al., 1997; Gilmour, 1998; Masaitis, 1998; Karczewska et al., 2008; French and Koeberl, 2010). In meteorites, several polymorphs of diamond have been reported, namely: the diamond cubic polymorph (3C diamond, spacegroup 227 – Fd₃m; hereafter referred to as 3C diamond), the most common form of diamond found on Earth and often referred to simply as cubic diamond; a relatively new form of diamond called n-diamond (structure uncertain, often thought to have a face centre cubic (fcc) structure, see also (Konyashin et al., 2006; Dadsetani et al., 2010)); a hexagonal form of diamond named lonsdaleite (2H diamond, space group 194 – P6₃/mmc). The different crystal forms can be recognised using transmission electron microscopy (TEM) on the basis of their crystal structure and d-spacing (Table 3), which are visible in high resolution images and diffraction patterns, or their electron energy loss spectrum (EELS) (Qin et al., 1998; Phelps, 1999a; Daulton et al., 2010). Other, non-diamond forms of carbon include: graphite, the most common form of carbon on Earth; graphene, single one-atom thick sheets of carbon which form turbostratic carbon when disorderly stacked; graphane, a modified structure of graphene; carbon onions, spherical nanoparticles consisting of concentric graphite shells (Banhart and Ajayan, 1996; Daulton et al., 2010).

The occurrence of nanodiamonds in the Allerød-YD boundary was first reported by Firestone et al. (2007), who found a peak in a nuclear magnetic resonance (NMR) spectrum of glass like carbon which they interpreted as nanodiamond. However, according to Kerr (2008) and Pinter et al. (2011) the peak is too broad for diamond and at the wrong location, at 38 ppm rather than at 34 ppm (Fig. S11 in Firestone et al. (2007) and Fig. 4 in Cody et al. (2002)). Two years later, Kennett et al. (2009a), using TEM and selected area electron diffraction patterns (SADP), reported the occurrence of nanodiamonds in the Allerød-YD boundary layer at several locations in North America. These nanodiamonds were found within, or adhered to, carbon spherules, as well as in the bulk sediment of the Black Mat. Two polymorphs of diamond were reported: 3C diamond and the relatively new structure called n-diamond. In a different study of the Black Mat at Arlington Canyon (Santa Rosa Island, California, USA), Kennett et al. (2009b) found not only 3C diamond and n-diamond, but also the hexagonal polymorph

Table 3

Interplanar spacings, or d-spacings, for the different carbon crystal structures found in the AYDB (Hirai and Kondo, 1991; Qin et al., 1998; Phelps, 1999a,b; Daulton et al., 2010).

Cubic diamond 3C diamond	n-diamond fcc-carbon (?)	Lonsdaleite 6H diamond	Graphite	Graphene	Graphane
			3.35		
2.06	2.06	2.18	2.13	2.13	
		2.06	2.03		2.02
		1.93			
			1.68		
	1.78		1.80		
		1.50	1.54		
1.26	1.26	1.26	1.23	1.23	
		1.16	1.16		1.17
		1.09	1.12		
1.08	1.08	1.08		1.07	
1.03	1.04	1.06			1.01
0.89		0.83		0.81	0.76

lonsdaleite in 'carbon elongates' and carbon spherules. Lonsdaleite can be formed through shock metamorphism and is therefore often considered as an indicator for shock (Hanneman et al., 1967). However, lonsdaleite can form through non-shock mechanisms as well (Frenklach et al., 1989; Daulton et al., 1996; Erlich and Hausel, 2002) and the utility of nanodiamond as an impact indicator is still debated because the relationship between nanodiamonds and impact events is still unclear (French and Koeberl, 2010).

Daulton et al. (2010), however, failed to find any nanodiamonds in samples from the Black Mat. Instead, they identified graphene and graphene/graphane aggregates within microcharcoal, carbon spherules, and glass-like carbon from the Black Mat as well as in older and modern samples. Moreover, Daulton et al. (2010) note that the diffraction patterns reported by Kennett et al. (2009b) do not show the unique 1.5 and 1.93 Å atomic spacing's found in the lonsdaleite structure (Phelps, 1999a). Daulton et al. (2010) therefore conclude that Kennett et al. (2009b) must have mistaken graphene/graphane aggregates for lonsdaleite and graphene aggregates for polycrystalline 3C diamond. Daulton et al. (2010) also report finding nanocrystalline copper, which they suggest might have been misidentified as n-diamond. In contrast, two groups working on European Allerød-YD boundary sections report the occurrence of nano to microscale diamonds (Tian et al., 2011; van Hoesel et al., 2012). These diamonds include rounded nanodiamond and flake-like microdiamonds (both 3C diamond) in bulk samples from the Usselo horizon at Lommel (Belgium), and flake-like polycrystalline microdiamonds (3C diamond) in glass-like carbon from the Usselo horizon at Geldrop Aalsterhut (The Netherlands), 25 km from Lommel. No lonsdaleite or n-diamond structures were identified in these studies. Only the Usselo horizon was sampled in these two studies, the underlying and overlying sediment was not investigated and it is thus unknown whether the 3C diamonds found are ubiquitous in the sedimentary record or limited to the Allerød-YD boundary. Nano- and microdiamonds have been identified in carbon spherules from modern European forest soils (Yang et al., 2008), but these came from different locations namely Burghausen (Germany) and Spa (Belgium). The origin of these nanodiamonds is still unknown, the possibility of an impact event was suggested but has not been confirmed (Yang et al., 2008).

Both lonsdaleite and n-diamond have been reported in the Greenland ice sheet at Kangerlussuaq (Kurbatov et al., 2010) and in lacustrine sediments from Lake Cuitzeo, Central Mexico (Israde-Alcántara et al., 2012). Both of these studies included high-resolution TEM images that show the unique 1.93 Å lattice spacing corresponding to the (101) plane of lonsdaleite, but no corresponding diffraction patterns. Daulton (2012) suggests that the high-resolution image given by Kurbatov et al. (2010) is inconsistent with lonsdaleite and that the images in Israde-Alcántara et al. (2012) are also consistent with other materials. Kurbatov et al. (2010) state that the lonsdaleite and n-diamond they found in the Greenland ice are "morphologically and analytically indistinguishable" from those found in the Black Mat layer. The rounded lonsdaleite particles as reported in the Greenland ice (Kurbatov et al., 2010), however, are dissimilar to the "stacked diamond clusters" from the Black Mat layer at Arlington Canyon (Kennett et al., 2009b). Furthermore the particles are freely dispersed in the ice layer rather than found within carbon spherules. This dissimilarity suggests that if the Greenland Ice Sheet particles are indeed nanodiamonds, these might yet still have a different origin.

Pinter et al. (2011) note that the electron energy loss spectrum (EELS) given by Kurbatov et al. (2010), Fig. 8) as evidence for n-diamond is similar to the spectrum of amorphous carbon with sp^2 bonded components rather than that of n-diamond. However, when compared to the spectra published by Konyashin et al. (2001, Fig. 3), the spectrum in Kurbatov et al. (2010) looks more similar to

the spectrum of fcc-carbon (n-diamond) then to the spectrum of amorphous carbon. The EELS pattern of the Lake Cuitzeo nanodiamonds (Israde-Alcántara et al., 2012 Fig. 9), on the other hand, appears closer to that of amorphous carbon. In both cases, however, high-resolution TEM and SADP analysis on other n-diamond particles as reported in the papers clearly show that those particles are polycrystalline (Kurbatov et al., 2010; Israde-Alcántara et al., 2012). Assuming both particles consist of carbon, the similarity of the EELS spectra of the reported nanodiamonds to the spectra of amorphous carbon in both cases is thus likely due to the relatively small size of the nanodiamonds compared the amorphous carbon coating on the thin film grid used to support samples resulting in a low signal to noise ratio. The particles reported might thus still be nanodiamonds, even though there is no clear EELS signal.

In summary, the proponents of the YDIH have claimed to have found 3C diamonds and n-diamonds in several North American Black Mats, the Greenland ice sheet and Central Mexico (Kennett et al., 2009a, 2009b; Kurbatov et al., 2010; Israde-Alcántara et al., 2012) as well as a possible Allerød-YD boundary in the Greenland ice sheet (Kurbatov et al., 2010). In addition they report lonsdaleite at some of those sites, which is known as the hexagonal shock polymorph of diamond. Another group of researchers trying to reproduce the work on the North American Black Mats failed to find any nanodiamonds and suggested that Kennett et al. (2009a; 2009b) had misinterpreted the nature of the particles (Daulton et al., 2010). Two other groups working on the European Usselo horizon did report the occurrence 3C diamond, while failing to find n-diamond or lonsdaleite (Tian et al., 2011; van Hoesel et al., 2012). Although the occurrence of 3C diamond in the Allerød-YD boundary seems confirmed, the occurrence of n-diamond and lonsdaleite is still questioned (Daulton, 2012). In addition, although there are similarities, there are also differences in morphology of the nanodiamonds reported by the different groups, suggesting that the reported nanodiamonds might have different origins. In order to use the occurrence of the 3C diamonds and possibly lonsdaleite, it is thus important to discuss the possible origin of these nanodiamonds.

2.5.1. Origin of the nanodiamonds

Although micrometre to millimetre-sized shock-produced diamonds in craters have been used to establish an impact origin, no distal ejecta layers have been diagnosed based on nanodiamonds (<5 nm) alone. Instead, the use of these nanodiamonds as a definite impact criterion is still debated since their formation mechanisms are still not always clear (French and Koeberl, 2010). Within the YD impact debate lonsdaleite was presented as a clear impact proxy as lonsdaleite is mostly known in relation to meteorites or impact craters, and it is often seen as a shock indicator (Kennett et al., 2009b). However, lonsdaleite can also be formed through other, non-shock, processes, such as carbon vapour deposition (Frenklach et al., 1989; Daulton et al., 1996; Erlich and Hausel, 2002) and is found in a number of other environments on Earth (Shibata et al., 1993; Erlich and Hausel, 2002; McCall, 2009; Dubinchuk et al., 2010). Furthermore, the occurrence of lonsdaleite in impact craters has been challenged (Koeberl et al., 1997; Gilmour, 1998; Masaitis, 1998).

Because the exact formation mechanisms for nanodiamonds, including lonsdaleite, are still unclear, in order to establish whether the nanodiamonds found in the Allerød-YD boundary sediments are evidence for an impact, it is also necessary to look at other hypotheses for the origin of these nanodiamonds. The nanodiamonds could either be extraterrestrial in origin (1), arriving at Earth through continuous meteoritic rain or as part of an impacting body. They could also have been formed during an impact (2), either through shock deformation of carbon-rich target rock or during a carbon vapour deposition (CVD) mechanism following an

airburst or 'atmospheric impact'. Finally, a terrestrial origin should be considered (3).

- (1) Certain types of meteorites, micrometeorites and interplanetary dust particles are known to be carriers of nanodiamonds (Hanneman et al., 1967; Dai et al., 2002; Aoki and Akai, 2008; Ferroir et al., 2010). Shortly after the YDIH was proposed, Pinter and Ishman (2008) suggested that the evidence put forward by Firestone et al. (2007) was not related to an impact but the result of the accumulation of meteoritic rain over time. Although this is a plausible mechanism to explain the nanodiamonds found in sediments (Kennett et al., 2009a; Kurbatov et al., 2010; Tian et al., 2011; Israde-Alcántara et al., 2012), meteoritic rain does not explain how nanodiamonds ended up within carbon spherules, carbon elongates or glass-like carbon (Kennett et al., 2009b; van Hoesel et al., 2012). Furthermore, accumulation of meteoritic rain would result in a continuous background concentration, rather than the clear peak in nanodiamond concentration found in the Greenland ice sheet or Lake Cuitzeo (Kurbatov et al., 2010; Israde-Alcántara et al., 2012). This peak in nanodiamond concentration could be explained if the nanodiamonds had arrived in a larger impacting body. However, other traces of an impactor are absent and the nanodiamond concentrations reported are too large to have come from a small impactor body (French, 1998). Furthermore, Tian et al. (2011) show that the carbon isotope and C/N ratios of the bulk material from the Usselo horizon at Lommel are more indicative of a terrestrial origin for the carbon material. Considering the above, it seems unlikely that the nanodiamonds arrived in an impactor body or through meteoritic rain
- (2) Diamonds (up to mm-sized) occur in impact craters (Hough et al., 1995; Koeberl et al., 1997; Masaitis, 1998; Smith and Godard, 2009) and in distal ejecta layers (Carlisle and Bramant, 1991; Gilmour et al., 1992; Hough et al., 1997). Impact diamonds can form in two ways: through the shock transformation of graphite in the target rock, in which case they are associated with a crater, and during a carbon vapour deposition (CVD) process in the fireball following an airburst or atmospheric impact similar to the Tunguska event (Svetsov and Shuvalov, 2008). A CVD-like process, in which the nanodiamonds grow from a carbon rich vapour, is also consistent with the rounded shape and non-linear twins found in some of the round Allerød-YD boundary nanodiamonds (Daulton et al., 1996; Tian et al., 2011; Israde-Alcántara et al., 2012), but might be less consistent with the plate-like diamonds reported by others (Tian et al., 2011; van Hoesel et al., 2012), or the occurrence of large amounts of lonsdaleite (Kennett et al., 2009b; Tian et al., 2011; van Hoesel et al., 2012)
- (3) On Earth, diamond is often associated with kimberlitic volcanic settings or metamorphic rocks in, for example, Norway. Sub-micron diamonds have also been found in a xenolith within Hawaiian tuff as well as in fluid inclusions in alkaline lavas (Wirth and Rocholl, 2003; Frezzotti and Peccerillo, 2007). The Hawaiian magmas are relatively similar to the volcanic region in the Eifel, suggesting a hypothetical regional source for the European nanodiamonds. However, nanodiamonds in the (older) volcanic rocks would be rare and if eroded and transported they are not expected to occur in a distinct layer. An eruption, on the other hand, would allow for the dispersion of nanodiamonds in a single layer. Nanodiamonds, however, would still be rare and likely to be locked up in xenoliths. In addition, Israde-Alcántara et al. (2012) failed to find any nanodiamonds in samples of tephra from the Laacher See volcanic eruption

Another, more common, process that might hypothetically create nanodiamonds is wildfire. Some of the Allerød-YD boundary nanodiamonds have been found in carbon spherules and glass-like carbon (Kennett et al., 2009b; van Hoesel et al., 2012), both of which are considered wildfire products (Hunt and Rushworth, 2005; McParland et al., 2010; Scott et al., 2010). Paquay et al. (2009) speculated that high temperatures, low oxygen levels and a source of carbon, all necessary conditions for diamond formation through CVD, can also be present in natural wildfires. Indeed, artificial nanodiamonds have been grown using low pressure CVD at temperatures as low as 450 °C (Frenklach et al., 1989; Daulton et al., 1996; Cowley et al., 2004). Moreover, nano-particles with a 3C diamond structure have been found in wood that was experimentally charred at 700 °C and subsequently cooled in a nitrogen atmosphere (Ishimaru et al., 2001). In addition, carbon onion structures, which can serve as nanoscopic pressure cells for diamond formation (Banhart and Ajayan, 1996; Banhart, 1997; Tomita et al., 2000), have been observed in charcoal (Hata et al., 2000; Ishimaru et al., 2001; Cohen-Ofri et al., 2007) and in the Allerød-YD boundary layer (Tian et al., 2011; Israde-Alcántara et al., 2012). These observations all suggest that it might be possible for nanodiamonds to have formed through wildfire.

3C diamonds (<5 nm) have recently also been discovered in a candle flame as well as in a natural gas flame (Su et al., 2011). Although most of these nanodiamonds burn up in the candle flame, this discovery suggests it might be possible for nanodiamonds to form during a combustion-type process under normal atmospheric conditions. Although Daulton et al. (2010) do not report any nanodiamonds in carbon spherules of different ages, 3C diamonds have been found in carbon spherules from present day forest soils (Yang et al., 2008). The origin of these nanodiamonds in present-day carbon spherules is unclear, both a volcanic and an impact-related origin have been proposed (Yang et al., 2008). Morphologically, these recent carbon spherules, like the Allerød-YD boundary carbon spherules, are similar to the charred fungal sclerotia reported by Scott et al. (2010), suggesting that they might have formed during wildfires as well. Israde-Alcántara et al. (2012) argue that since nanodiamonds combust at temperatures above 600 °C and as typical wildfire temperatures are 900–1200 °C, nanodiamonds could not have formed during wildfires. However, wildfire temperatures can be lower, even within a single wildfire (McParland et al., 2009; Stoof et al., 2012). At the Geldrop Aalsterhut site, for example, where nanodiamonds have been reported in the Usselo horizon, reflectance measurement of charcoal indicated a wildfire temperature of ~420 °C (van Hoesel et al., 2012). In addition, nanodiamonds formed within carbon spherules or glass-like carbon might be protected from combustion at higher temperatures by the surrounding particle. Although this is still hypothetical, it could be validated as a possible origin when more nanodiamonds would be found in charcoal or other wildfire products. If, on the other hand, it can be shown that widespread occurrence of nanodiamonds occur only at specific points in time (see also Section 5), wildfires or erosion of diamond-rich source material would be unlikely.

3. Events associated with the Younger Dryas impact hypothesis

3.1. Extensive wildfires

Based on the presence of charcoal, soot, and polycyclic aromatic hydrocarbons (PAHs) at many Allerød-YD boundary sites, Firestone et al. (2007) argue that a fireball and superheated ejecta following the YD impact resulted in continent-wide (Kennett et al., 2008) wildfires, possibly even reaching Europe. The environmental

destruction brought by these wildfires would have affected the human and animal populations, while the soot in the atmosphere would have had a short term cooling effect (Firestone et al., 2007). Although soot and PAHs have been reported at the K/T boundary (Wolbach et al., 1985), the presence of extensive wildfires at a boundary reveals nothing about how the fire was ignited. Regional fires caused by small impacts do not differ much from natural fires (Svetsov, 2008) and wildfires frequently occurred during the Late Glacial, either naturally or initiated by humans (Pinter and Ishman, 2008; van der Hammen and van Geel, 2008; Daniu et al., 2010).

Marlon et al. (2009), using 35 charcoal records located across North America, found neither evidence for a charcoal peak at 12,900 yrs ago nor any continent-wide wildfire episode during the Last Glacial–Interglacial transition (15,000–10,000 yrs ago). Kennett et al. (2009), argue that multiple ^{14}C -dating errors led Marlon et al. (2009) to miss the continent-wide charcoal peak and that this peak is present in other records as well. Yet other groups also failed to find charcoal peaks at 12,900 yrs ago (Gill et al., 2009; Daniu et al., 2010). Haynes et al. (2010) also report that they found no evidence for extensive biomass burning at any Clovis site in the San Pedro Valley of Arizona. In addition Haynes et al. (2010) argue that the peak in charcoal, vitreous carbon and vitrinite as reported by Firestone et al. (2007) at Murray Springs came from a sample located near a Clovis hearth and that three other samples from Murray Springs did not contain any charcoal.

Firestone et al. (2007) further argue that ammonium and nitrate spikes in the GISP2 ice core (Mayewski et al., 1993), as well as a major ammonium spike in the GRIP ice core (Führer et al., 1996) are evidence for impact related biomass burning. Mayewski et al. (1993), however, attributed this brief (100 yr) increase in the ammonium flux during the early YD to the destruction of the Bølling–Allerød biomass. In the GRIP ice core, ammonium actually increases steadily during the Bølling–Allerød, reaching a maximum concentration during the early YD (Führer et al., 1996). Führer et al. (1996) suggest that this trend in ammonium concentration parallels the build-up of biomass during the warming climate followed by plant material released during deglaciation. This increase of ammonium and biomass during the warming climate is in line with the worldwide charcoal records analysed by Daniu et al. (2010), which show a significant peak in biomass burning corresponding to the warming events, lagging the peak of the warm period by 100–200 years, then dropping during the cold periods. The high ammonium concentration in the ice cores therefore seems consistent with natural wildfires and does not indicate the occurrence of an extraterrestrial impact. In addition, Melott et al. (2010) argue that the nitrate spike at the Allerød–YD boundary in the GISP2 record is smaller than for the Tunguska event and thus too small for the hypothesised YD impact event. Furthermore, the Pt peak found in the GISP2 ice core predates the ammonium and nitrite peaks by 30 years (Petaev et al., 2013). If the Pt peak is directly caused by a YD impact event, as suggested by Petaev et al. (2013), the wildfires are not.

3.2. Climate change

The cause of the YD cold period is still not entirely clear (Broecker et al., 2010; Fiedel, 2011). In the past, it was thought that the YD cooling might have been related to the eruption of the Laacher See volcano (11,063 ± 13 ^{14}C yrs BP; 12,995–12,890 cal yrs BP¹), but research on varved lake sediments showed that the

eruption actually occurred 180–200 years prior to the onset of the YD in Europe (Schmincke et al., 1999; Litt et al., 2003). The current main hypothesis for the cause of the YD was first proposed by Broecker et al. (1989). This hypothesis involved rerouting of drainage from the pro-glacial Lake Agassiz to the northern Atlantic Ocean, rather than the Gulf of Mexico, causing a shutdown of the thermohaline circulation, resulting in cooling of the region (Broecker et al., 1989, 1990). More recently, it has also been proposed that meltwater flow into the Arctic ocean was responsible for the cooling (Tarasov and Peltier, 2005, 2006; Bradley and England, 2008; Condron and Winsor, 2012). The exact size and origin of the freshwater discharge resulting in the Younger Dryas cooling is however still debated and we refer to Carlson and Clark (2012) for a detailed overview of the current hypothesis for the cause of the Younger Dryas. Alternative hypotheses for the YD cooling include a decrease in summer insolation or a displaced jetstream (Renssen et al., 2000; Fiedel, 2011).

With the extraterrestrial impact hypothesis Firestone et al. (2007) offered a new alternative explanation: they note that in addition to the known short-term cooling effects of impacts, the YD impact event would have destabilized the ice sheet, suddenly releasing meltwater into the North Atlantic. In effect, the YDIH provides a unique trigger for the generally accepted meltwater hypothesis. However, conceptual models have shown that YD-like cold periods could be inherent to the climate system (Schulz et al., 2002; Sima et al., 2004) and more recently, evidence for YD-like cooling events during other glacial terminations have been found in Antarctic ice cores and Chinese stalagmites (Carlson, 2008; Cheng et al., 2009; Broecker et al., 2010; Denton et al., 2010). The existence of these similar events during earlier terminations indicates that the YD cooling might not have been as unique as originally thought and would have happened with or without the interference of an extraterrestrial object. Furthermore, extraterrestrial impacts do not necessarily induce climate change, so even if an extraterrestrial object hit Earth at the onset of the YD, this does not immediately imply that it accounted for the YD cooling.

3.3. Megafaunal extinctions

During the end of the Last Glaciation, most of the megafaunal species became extinct. These extinctions occurred at different times in different continents: first in Australia around 45,000 yrs ago, after humans arrived at the continent, and finally in South America when climate started to change to interglacial conditions. The Eurasian extinction happened in two events, approximately 48,000–23,000 yrs ago and 14,000–10,000 yrs ago, the second interval roughly coinciding with the Allerød–YD periods. Africa seems to have been little affected by the Late Pleistocene extinction episodes (Barnosky, 2008). The degree of abruptness, timing, and cause of the megafaunal extinctions are still under debate. Explanations for the megafaunal extinctions include human overkill, competition for resources, climate change, pandemic disease, or even a combination of several triggers (Barnosky, 2008; Haynes Jr., 2008; Fiedel, 2009; Ruban, 2009). Early proponents of the YDIH argued that the YD impact was responsible for the megafaunal extinctions (Firestone et al., 2007; Kennett et al., 2008, 2009b). However, Gill et al. (2009) show that a decline of *Sporomiella* (dung fungus) spores suggests that the major collapse of the North American megafauna happened between 14,800 and 13,700 cal yrs BP (calibrated using Calib 5.0.2), well before the proposed YD impact. Others, however, do not consider the use of *sporomiella* spore abundances as a percentage related to the pollen sum is the most appropriate method to investigate megafaunal abundances (Baker et al., 2013; Wood and Wilmshurst, 2013). Although the exact timing of the megafaunal extinctions in North America is still

¹ All uncalibrated radiocarbon years are presented as ^{14}C yrs BP. Unless otherwise specified, calibrated radiocarbon ages (cal. yrs BP) are calibrated using the IntCal13 calibration curve (Reimer et al., 2013) and the OxCalv4.2 calibration software (Bronk Ramsey, 2009).

uncertain, it is not likely that the proposed YD impact was the major cause of the extinctions (Ruban, 2009). Most likely, a combination of different factors, such as ecosystem changes associated with the Last Glacial Termination and human hunting, are the causes of megafaunal extinctions.

3.4. Disappearance of the Clovis culture in North America

Firestone et al. (2007) argue that major adaptive shifts in human culture, including the disappearance of the Clovis culture and an inferred population decline in North America, occurred at the onset of the YD as a result of the YD impact event. However, some regions show evidence of overlap between Clovis and post-Clovis cultures (Hamilton and Buchanan, 2009) and no population decline (Buchanan et al., 2008; Hamilton and Buchanan, 2009; Fiedel, 2010). Other studies however showed a population decline near the Allerød-YD boundary (Anderson et al., 2008; Jones, 2008; Kennett and West, 2008). Whether or not there was a population decline at the onset of the YD is thus still debated. Furthermore, if there was a population decline, other possible causes, such as climate and environmental change or disappearance of prey, must be ruled out before the population decline can be conclusively related to an impact event.

A recent study reporting evidence in support of the YDIH from the Abu Hureyra site in Syria (Bunch et al., 2012), however, puts the effect of the proposed YD impact on the human population into question. Abu Hureyra was inhabited almost continuously from 13,400 to 7500 cal yrs BP (IntCal09) (Colledge and Conolly, 2010). The scoria-like objects found at the site (Bunch et al., 2012) suggests that the proposed airburst must have happened relatively close to Abu Hureyra, seemingly without a large effect on the local population. The continuing population at Abu Hureyra is inconsistent with the suggestion that a similar airburst or airbursts caused a population decline over the North American continent.

4. Nature of the event

Based on the evidence they found, Firestone et al. (2007) suggested that a fragmented body, likely a comet (an icy body), colliding with Earth was responsible for the peak concentrations in certain markers and environmental changes. According to the original YDIH (Firestone et al., 2007) the comet fragments (<2 km) either obliquely hit the 2 km thick Laurentide ice sheet, thereby disrupting the ice sheet but not producing a crater in the crust below, or exploded in the atmosphere above the ice sheet, resulting in an airburst much larger than the Tunguska event in 1908 (Svetsov and Shuvalov, 2008; Napier and Asher, 2009; Mignan et al., 2011), which devastated over 2000 km² of forest in Central Siberia during an explosion with an estimated equivalent energy of 5 Mton TNT (Mignan et al., 2011). It has also been suggested that the Corossal structure, a possible impact crater in the Gulf of Saint Lawrence (Higgins et al., 2011), is related to the YD impact event (Israde-Alcántara et al., 2012). The uncertainty in the age of the Corossal structure is currently however quite large, ranging from 12.9 ka to 450 Ma. The lower limit of 12.9 ka is based on dates from a core through the crater infill. However, the core did not extend to the crater floor, so the crater could be older than 12.9 ka. The Corossal structure thus cannot be related to the YD impact event with any certainty until better age control is established. The two other Canadian craters mentioned by Wu et al. (Wu et al., 2013) can also not be tied to the YD impact event. The age of the Bloody Creek structure, Nova Scotia (Canada), has not yet been determined (Spooner et al., 2009) and the Charity Shoal structure, Lake Ontario, is most likely of Ordovician age (Holcombe et al., 2013). No other craters of possible Allerød-YD boundary age have been found thus

far and it is considered unlikely that all evidence of an Allerød-YD boundary impact crater would be completely erased in only ~13,000 years (French and Koeberl, 2010). The most recent papers on the YDIH, however, seem to favour the airburst model over an actual impact, although the type of impactor is not specified (Bunch et al., 2012; Israde-Alcántara et al., 2012; Wittke et al., 2013b). In addition, Bunch et al. (2012) suggest that there must have been at least three airbursts rather than just one, one in Syria and two in North America. Wittke et al. (2013b) suggest a comet that broke up in multiple fragments before encountering Earth, which further disintegrated when travelling through the Earth's atmosphere. This idea is similar to one of the original hypothesis in Firestone et al. (Firestone et al., 2007), except that multiple impact sites are involved.

Pinter and Ishman (2008) argue that even for a very high fireball, the thermal radiation is zero below the horizon, making it impossible for an impact over North America to have ignited forests in Europe. In addition, large impactors are required to ignite continent-wide (>8 km diameter impactor) or global (>15 km impactor) wildfires (Durda and Kring, 2004; Svetsov, 2008). However, the total damage of small impactors can greatly increase when fragmentation occurs in the atmosphere (Svetsov, 2008). If multiple impacts or airbursts were spread over the globe, as suggested by Bunch et al. (2012), this would greatly increase the directly affected burn area, which could include the flight path and region beneath any airburst exposures. However, small impacts and airbursts do not necessarily ignite wildfires. For example, the Chelyabinski event (February 15, 2013), which had a total energy equivalent to 440 kton TNT, was only accompanied by shock wave, and the Carancas impact event (September 15, 2007), which had an estimated energy of 0.015–3 ton of TNT and left a small 13.5 m diameter crater (Kenkmann et al., 2009; Tancredi et al., 2009), also did not result in wildfires. In addition, there is no evidence for increased biomass burning or continent-wide wildfires at the onset of the Younger Dryas (see Section 3.1).

Several researchers have also challenged the YDIH based on the type of impactor. Pinter and Ishman (2008) argue that the combined lines of evidence are incompatible with any single impactor or known impact event. Paquay et al. (2009), after eliminating the presence of increased concentrations of platinum-group elements (PGEs) in the Allerød-YD boundary, suggested that the impactor might have been a PGE-poor type of achondritic meteorite. However, the probability of such an achondritic meteorite hitting Earth is low, and such meteorites are not known to contain nanodiamonds (Paquay et al., 2009). Nanodiamonds formation may have occurred in an impact related airburst through a CVD mechanism (Israde-Alcántara et al., 2012), thus excluding the need for a nanodiamonds rich impactor. Petaev et al. (2013) agree that the impactor could not have been a chondritic meteorite, but, based on the Pt anomaly they found, they suggest a highly differentiated, possibly iron-poor, meteorite.

French and Koeberl (2010) note that in order to avoid visible surface deformation, any impactor fragments hitting the Laurentide ice sheet would need to be clustered in a size range of 30–50 m in diameter; such clusters are unknown in the solar system (French and Koeberl, 2010). Boslough et al. (2012) agree with French and Koeberl (2010) that the Younger Dryas impact event as originally put forward in Firestone et al. (2007) is physically not possible and add that it is also “statistically impossible”. Napier (2010), on the other hand, argues that it is theoretically possible for Earth to have encountered a swarm of debris from a fragmenting comet large enough to have caused a catastrophe around 12,900 yrs ago.

Bunch et al. (2012) proposed multiple impact epicentres near the three sites where they found lechatelierite (Abu Hureyra, Middle-East; Blackville and Melrose, North America) and possibly

at other locations. The available dates for these three sites, however, have large uncertainties (see also Section 5): the layers in which the lechatelierite was found could have been formed centuries to millennia apart. Even if the layers formed at different times, this does not necessarily imply that the sites are not impact related. Tunguska-sized airbursts are fairly common, occurring roughly every 220–1000 years, depending on the study (Revelle, 1997; Brown et al., 2002; Bland and Artemieva, 2006). Impacts on land by iron meteorites large enough to form 100 m diameter craters occur every 500 years (Bland and Artemieva, 2006). Craters this small might be easily obscured by erosion and sedimentation processes over several thousand years. If Bland and Artemieva (2006) are correct, the occurrence of several airburst and/or small impacts occurring decades to centuries apart might prove a plausible explanation for some of the markers found.

5. Timing of the Younger Dryas impact event

One important part of the YDIH that has not gained much attention in the literature so far is the timing of the event. In order to claim that a single impact event (be it multiple airbursts or just one impactor) caused the YD, all sites at which impact markers have been found must be synchronous and date to the onset of the YD. This synchronous-site requirement presents five challenges to the YDIH, which are discussed below.

Firstly, the exact timing of the YD onset is still uncertain (Fiedel, 2010, 2011). The originally proposed YD impact age of $12,900 \pm 100$ yrs ago (Firestone et al., 2007) fits relatively well (within uncertainties) with the onset of the Younger Dryas according to the Greenland ice cores and the Cariaco record (Table 4). Many terrestrial European records, on the other hand, place the onset of the Younger Dryas up to two centuries later (Goslar et al., 2000; Brauer et al., 2008; Hajdas and Michczyński, 2010). It must be noted here that Wittke et al. (2013b) propose an age of $12,800 \pm 150$ cal yrs BP (IntCal09 calibrated) for the YD impact event. They obtained this date by calibrating (using IntCal09) a radiocarbon age of $10,900 \pm 145 \pm^{14}\text{C}$ yrs BP, which they suggest was the date originally reported for the impact event (Wittke et al., 2013b), although we did not find this age in Firestone et al. (Firestone et al., 2007). Using the recently published IntCal13 calibration curve (Reimer et al., 2013), the radiocarbon age cited by Wittke et al. (2013b) for the age of the YD impact event is calibrated to $12,950$ – $12,700$ cal yrs BP (68% confidence interval, median $12,830$ cal yrs BP) or $12,820 \pm 130$ cal yrs BP. Compared to the age proposed by Wittke et al. (2013b) the latest radiocarbon calibration curve thus reduces the uncertainty in the calendar age for the YD impact event and increases it by two decades.

Secondly, many of the terrestrial sites where YD impact markers have been found have been dated using radiocarbon (^{14}C) dating (Table 5), which can introduce additional uncertainties. For instance, when dating charcoal, the “old wood” or “inbuilt age” effect arises when that the wood was burned months or decades after it was grown (Schiffner, 1986; Gavin, 2001). Additional uncertainties arise when calibrating the radiocarbon ages to calendar years or when comparing ages calibrated using different calibration curves van Hoesel et al. (2013). These additional uncertainties are introduced because of uncertainties in the ^{14}C calibration curve, especially when calibrating ages beyond the dendrochronologically calibrated part of the curve (0–12,550 cal yrs BP, Reimer et al., 2009; Blockley et al., 2012). The latter uncertainties can be avoided by directly comparing radiocarbon ages rather than calibrated values, although age differences will not be directly comparable to calibrated years. When looking at radiocarbon ages of the YD onset in terrestrial records, most dates are in the range of 11,000–10,950 ^{14}C yrs BP, although ages as young as 10,900 ^{14}C yrs BP are also considered a possibility (Table 4). It is considered unlikely that the YD started before 11,000 ^{14}C yrs BP, as the Laacher See eruption, which probably took place two centuries before the onset of the YD (Brauer et al., 1999), is dated to $11,063 \pm 13$ ^{14}C yrs BP (Stuiver et al., 1995; Litt et al., 2003). The range of 11,000–10,900 ^{14}C yrs BP adopted in this review for the timing of the YD onset, roughly corresponds to the timing of the YD impact event as adopted by Wittke et al. (2013b).

Thirdly, not all sites have been directly dated or their dates have a high uncertainty. Of the ten Clovis sites reported by Firestone et al. (2007), six have been directly dated, sometimes with a large uncertainty in their age (Table 5). In addition, the age Firestone et al. (2007) use for the Usselo horizon at the Lommel site, does not appear in the literature they cited (van Geel et al., 1989; Hoek, 1997). However, recent optical stimulated luminescence (OSL) dates at Lommel give an age of $12,400 \pm 900$ yrs ago (Derese et al., 2012), which, within uncertainty, is still consistent with the proposed age for the YD impact. Wittke et al. (2013b) acquired an age of $11,480 \pm 100$ ^{14}C yrs BP on charcoal from the Usselo horizon at Lommel, older than age they proposed for the YD impact ($10,900 \pm 145$ ^{14}C yrs BP).

The identification of the Allerød-YD boundary in the Greenland ice sheet at Kangarlussuaq was based on a visible dust layer (Kurbatov et al., 2010) and Pinter et al. (2011) argue that the oxygen isotopes given by Kurbatov et al. (2010) are more typical for Holocene values than for Younger Dryas values. Although Pinter et al. (2011) do not give any information about the records on which their argument is based, their observation is consistent with the GISP2 and NGRIP ice core oxygen isotopes (Stuiver et al., 1995; Steffensen et al., 2008). On the other hand, Kurbatov et al. (2010, Table 1) show

Table 4
Timing of the onset of the Younger Dryas according to different records.

Record	Type of record	Calendar age (yrs ago)	Radiocarbon age (^{14}C yrs BP)	Reference
GICC05 (Greenland)	Ice core (GRIP, NGRIP)	$12,846 \pm 138$ (max)		Rasmussen et al., 2006
GISP 2 (Greenland)	Ice core	$12,890 \pm 260$ (max)		Meese et al., 1997; Stuiver et al., 1995
Cariaco varves (Venezuela)	Marine sediments	$12,820 \pm 30$		Lea et al., 2003
Hulu Cave (China)	Stalagmites	$12,823 \pm 60$		Wang et al., 2001
Meerfelder maar (Germany)	Varved lake	12,679		Brauer et al., 2008
Holzmaar (Germany)	Varved lake	12,606		Brauer et al., 2008
Lake Gosciarz/Perespilno (Poland)	Varved lakes	12,650	~ 11,000	Goslar et al., 1995, 2000
Soppensee (Switzerland)	Varved lake	$12,593 \pm 93$		Hajdas and Michczyński, 2010
Swedish time scale	Varved lakes	12,500–12,700		Wohlfarth, 1996
Original YD onset (Scandinavia)	Biostratigraphy		11,000	Mangerud et al., 1974
The Netherlands	Biostratigraphy		$10,950 \pm 50$	Hoek, 1997
North American Black Mats			$10,900 \pm 50$	Haynes, 2008
Late Glacial Pine (LGP) record	Tree rings (floating)	12,950	10,950	Kromer et al., 2004
LGP + Huon Pine	Tree rings	12,760	10,950	Hua et al., 2009
Radiocarbon cliff	Multiple records		~ 11,000	Fiedel, 2011

that the oxygen isotope values vary greatly between different records. In addition, (Kurbatov et al., 2010) argue that the record should be compared to the Dye-3 ice core instead, which has a similar accumulation area as Kangarlussuaq (Kurbatov et al., 2010) and values more consistent with their own record. The age of the 'Black Mat' at the Mucubají site, Venezuela, has also not been dated directly. The correlation to the onset of the YD is based on stratigraphy and radiocarbon ages of a peat bed 20 cm below the black mat (Mahaney et al., 2010a). Some of the sites presented by Wittke et al. (2013b), namely Kimbel Bay and Lingen, were also only indirectly dated.

At Lake Cuitzeo, Central Mexico, the proposed Allerød-YD boundary layer has been directly dated to $27,360 \pm 130$ ^{14}C yrs BP, which is considerably older than the Allerød-YD boundary (Israde-Alcántara et al., 2012). According to the authors, however, the radiocarbon dates are erroneously old as a result of reworking of organic material. Using an age-depth model based on a known tephra layer and several radiocarbon ages, excluding the anomalously old dates, the peak in markers was dated to approximately 12,900 cal yrs BP (calibrated by Israde-Alcántara et al., 2012 using IntCal04). However, if the organic matter in the layer is reworked, it is also possible that the markers in the layer are also reworked and thus from a different moment in time. In addition, Blaauw et al. (2012) find no reason to assume that the dates from the Lake Cuitzeo Allerød-YD boundary layer are anomalously old. In the age model of Blaauw et al. (2012), which includes all dates of the section, the marker layer is placed $> 16,000$ cal yrs BP (IntCal09). Considering the above, the markers found at Lake Cuitzeo might not be related to the Allerød-YD boundary.

Bunch et al. (2012) investigated the Allerød-YD boundary for markers at 18 sites in North America, Europe and the Middle East, eight of which have been reported in earlier studies and three of which, where lechatelierite was found, are discussed in depth in their supporting information. For seven sites, no information on dating, stratigraphy or sampling is presented at all, except for their approximate location, although information on these sites was recently published (Wittke et al., 2013b). Age control at two of the three sites where lechatelierite was found (Bunch et al., 2012) also raises some questions. OSL dating of the Allerød-YD boundary at Blackville gave an age of $12,960 \pm 1200$ yrs ago, almost right at the proposed timing of the impact (Bunch et al., 2012). However, one of the other two OSL dates from the same site, taken 30 cm above the Allerød-YD boundary, has a much older age of $18,540 \pm 1680$ yrs ago. Bunch et al. (2012) reasoned that this older OSL age should be excluded from their age-depth model "because of the large magnitude of the age reversal, i.e., older sediments lying stratigraphically higher than younger sediments" (Bunch et al., 2012). This reasoning can however easily be inverted: why not exclude the OSL date at the Allerød-YD boundary because younger sediments cannot lie stratigraphically lower than older sediments? In that case, linear interpolation of the two other OSL dates would yield a much older age ($>20,000$ yrs ago) for the layer containing the markers. At Melrose, only one OSL age, from 5 cm below the Allerød-YD boundary, is reported. Based on linear interpolation between the OSL date and the surface, assuming a modern age for the surface, Bunch et al. (2012) date the layer to exactly the time of the proposed impact. No validation for the assumption of a linear model and modern age of the surface are presented. In addition, for the other two sites investigated for the occurrence of scoria-like objects, 28 m and 28 km from Melrose, no age control is presented at all. Instead, even though the sediment consists of colluviums and there is no clear marker horizon visible, the same depth interval was sampled. There is thus no guarantee that these different locations near Melrose where scoria-like objects are reported, are of the same age.

Fourthly, at several sites the sampling thickness or the thickness of the peak in markers leads to a large uncertainty in sample age. For example, Bunch et al. (2012) present an age of $12,900 \pm 1600$ yrs ago for the Allerød-YD boundary at Melrose. From Fig. S5 in their work, assuming their age-model is correct, it can however be inferred that the top of the 10 cm thick layer marked as the Allerød-YD boundary is 9000 yrs old while the bottom of the Allerød-YD boundary is 14,000 yrs old (Bunch et al., 2012), a 5000 year range. At Lake Cuitzeo, the 10 cm wide peak in markers (Israde-Alcántara et al., 2012) might reflect almost 5900 yrs of deposition (Israde-Alcántara et al., 2010). Given these wide age ranges, any markers at these three sites could have been deposited well before or well after the onset of the Younger Dryas.

In addition, many of the other Allerød-YD boundary sites which have been investigated featured either a Black Mat or, in the case of the European sites, the Usselo horizon. The Black Mat is generally considered to be a wet paleosol or algal mat deposited during the Younger Dryas. The sediment directly below the Allerød-YD boundary, the 'Clovis surface', would have been at the surface for several decades near the end of the Allerød (Haynes, 2008) before the Black Mat was deposited during the Younger Dryas. There is thus a small hiatus between the top of the Clovis surface and the bottom of the Black Mat. Compared to the Black Mat, the Usselo horizon (a Late-Glacial paleosol formed in the dry aeolian sandbelt in North-Western and Northern-Central Europe during the late Allerød to early YD) comprises a longer lasting hiatus in sedimentation, probably lasting several centuries (Kasse, 2002; Kaiser et al., 2009; Jankowski, 2012). Any material found in the Black Mat and especially the Usselo horizon could thus come from a large interval of time, and increased values of cosmic material are expected due to relative enrichment as a result of non-deposition of sediments. Unless markers are related to dated material such as charcoal, it is thus difficult to pinpoint the exact time of deposition.

Lastly, there is an age discrepancy between different sites related to the YDIH (Table 5). Fig. 3 shows the different age estimates for all sites investigated for YD impact markers. Although some of the locations clearly overlap in time, others show a significant difference. Due to the radiocarbon cliff and additional uncertainties introduced through calibration, as well as the large scale range needed to present all the data in Fig. 3, some of the differences in age are more clearly visible in the radiocarbon ages, as shown in Fig. 4. Four main age-groups can be distinguished in Fig. 4. According to the ^{14}C ages, Daisy Cave, Abu Hureyra, Talega and Arlington Canyon cluster just before the early limit for the onset of the YD (Fig. 4). Lommel and Ommen, two sites containing the Usselo horizon, are even older. Murray Springs and Geldrop Aalsterhut, on the other hand, likely date to the early YD. Lake Hind is a single younger outlier. Only Sheriden Cave, Wally's Beach and Blackwater Draw date to the approximate time of the YD onset, the latter, however, has a very high uncertainty. The marker horizons dated using OSL or thermoluminescence (TL) - Barber Creek, Blackville, Gainy and Topper - all have large uncertainties and overlap with most radiocarbon dated sites (Fig. 3). As the marker horizons found at different sites have ages that differ by up to two centuries, these markers may not be related to the same event.

Some caution must, however, be taken into account when interpreting the age data. As mentioned in our second point, the "old wood" effect plays a role in interpreting radiocarbon ages. Kennett et al. (2008; 2009b) left out some of the older radiocarbon dates for Arlington Canyon, attributing them to old wood. Interestingly, these older dates were obtained from a carbon spherule, a glassy carbon particle and a carbon elongate (Kennett et al., 2008), all particles in which nanodiamonds have been reported and which are said to have formed within the fireball following the impact (Firestone et al., 2007; Kennett et al., 2009b). Fiedel (2010) argues

that the age of these particles shows that the event must have occurred 100 or even 500 years before the onset of the YD. Wittke et al. (2013a) even suggest that the radiocarbon ages of Arlington Canyon should not be used to date the nanodiamonds because of the old wood effect, even though the radiocarbon was used to date the layer in the original studies (Kennett et al., 2008, 2009b). Although the older dates at Arlington Canyon may have originated from the pith of very old trees, similar reasoning should apply to all other radiocarbon-dated sites. It can, for example, easily be argued that the YD impact layer at Murray Springs must be up to a century younger than indicated by the average radiocarbon ages, as the impact supposedly happened after the Clovis occupation, which was dated (Waters and Stafford, 2007), and the Clovis people could have burned older re-used wood. Invoking the old wood effect might therefore even increase the age discrepancy, rather than reducing it. Some of the age discrepancy could be explained by the occurrence of hiatuses or large sample intervals, as discussed earlier. However, this explanation only applies to some sites and only when the markers are not related to the dated material. Hiatuses, or large sampling intervals, therefore cannot eliminate the age discrepancy for all sites.

In short, there are several problems posed by the timing of the YDIH. Part of the problem is that the onset of the YD is not precisely known and the reported markers are generally not accurately dated, which makes it difficult to link the markers exactly to the onset of the YD. This problem is further amplified by uncertainties in dating the different locations where YDIH evidence is detected. One solution to this problem would be to look for markers in continuous varved lake records spanning a large period of time, such as found in Europe (e.g. Brauer et al., 1999). Although sample sizes might be relatively small in lake cores, it would be possible to take a sample from the period right at the YD climate change. These varved records enable sampling material from several decades to centuries before and after the YD climate change to accurately establish the timing of the YD impact relative to the Allerød-YD boundary. The age discrepancy between different sites is potentially a greater challenge. If impact markers from different sites have different ages, they clearly cannot relate to the same event.

6. Summary/Conclusions

The Younger Dryas impact hypothesis (YDIH) consists of two essential parts, (1) an extraterrestrial impact occurring $12,820 \pm 130$ yrs ago that (2) resulted in continent-wide or world-wide wildfires, the YD cooling, megafaunal extinctions, and the disappearance of the Clovis culture. There is no evidence that there were continent-wide wildfires at the onset of the YD and it is still debated whether the megafaunal extinctions were indeed sudden or whether there was a gradual megafaunal population decline. Furthermore, wildfires were common and the climate change as well as the megafaunal extinctions can be explained without invoking an extraterrestrial impact. There is thus no evidence that the YD impact event as presented by Firestone et al. (2007) took place. However, just because these large-scale environmental changes can be explained by terrestrial mechanisms does not mean that an extraterrestrial impact event could not have taken place around the same time. It is thus important to critically examine the different type of markers found (see Table 6 for a summary).

It has been argued that material resulting from gradual processes has been interpreted as catastrophic, and terrestrial materials as extraterrestrial, while at the same time no unambiguous impact signatures were reported (Pinter et al., 2011). In addition, other groups failed to reproduce the results (e.g. Paquay et al., 2009; Surovell et al., 2009; Daulton et al., 2010). Proponents of the YDIH have reported more elaborate analyses, in response to

Table 6

Reproducibility of (peaks in) markers reported as evidence for the YDIH and their use as impact markers. See Section 2 for a discussion of the details. Note that there is a discrepancy in reported findings of shocked quartz and that lechatelierite is a very recent finding. + indicates positive – indicates negative.

Markers	Found in impact layers?	Diagnostic?	Other explanations	Reproduced?
Magnetic microspherules	+	–	++	±
Scoria-like objects	+	–	+	
Lechatelierite	+	+	±	
Iridium	+	+	–	–
Shocked quartz	+	++	–	–
Charcoal/soot	+	–	++	±
Carbon spherules/ glass-like carbon	–	–	++	±
Cubic nanodiamonds	+	–	±	+
Lonsdaleite	+	±	±	–
n-diamond	+	–	±	–

some of the criticism directed at the YDIH, which have focused on magnetic spherules and nanodiamonds (e.g. Israde-Alcántara et al., 2012). Research on the magnetic spherules now includes SEM analysis showing patterned surfaces as well as chemical analysis (Bunch et al., 2012; Israde-Alcántara et al., 2012; Wittke et al., 2013b). Some researchers even argue that only spherules with certain surface patterns and composition should be included (LeCompte et al., 2012), resulting in a discrepancy in the type of spherules counted in different studies. Based on the SEM results, YDIH proponents no longer consider the magnetic spherules as extraterrestrial but as terrestrial material that was melted into droplets by an airburst fireball and dispersed in the atmosphere following the shockwave (Bunch et al., 2012; Israde-Alcántara et al., 2012; Wittke et al., 2013b). There is however, an alternative explanation for the peak concentrations of magnetic spherules, as well as iridium, both of which tend to accumulate near the bottom of black-mat-type deposits of any age due to unknown processes (Pigati et al., 2012). In addition, other studies on magnetic spherules have shown that similar surface textures and composition are found in magnetic spherules of different origins (e.g. Franke et al., 2007; Grebennikov, 2011; Voldman et al., 2012) and are thus not unique to impact related spherules.

New evidence in the form of lechatelierite in magnetic spherules and scoria-like objects, found only at three sites, might point to an impact-related origin for the spherules at these locations only if lightning strikes are ruled out (French and Koeberl, 2010; Glass and Simonson, 2012). Nanodiamonds, one of the other important lines of evidence, have not been reported at the three sites said to contain lechatelierite, but nanodiamonds have been the focus of other studies at different locations (Kennett et al., 2009a, 2009b; Tian et al., 2011; Israde-Alcántara et al., 2012; van Hoesel et al., 2012). Although some researchers failed to find any diamonds, 3C diamonds are present at some of the sites. Whether the particles interpreted as being lonsdaleite and n-diamond are indeed diamond, is however still questioned (Daulton, 2012). Although nanodiamonds can form through impact-related processes, nanodiamonds in distal ejecta layers are not considered diagnostic evidence for an impact (French and Koeberl, 2010). However, there is not much research on nanodiamonds in the geological record and other explanations for the origin of the Allerød-YD boundary nanodiamonds are currently not much more convincing. It is therefore important to investigate other plausible nanodiamond formation mechanisms and occurrences in the geological record in order to convincingly rule out or confirm an impact-related origin.

Most critically, there is an age discrepancy of up to two centuries between sites where YD impact markers have been found (see

Figs. 3 and 4). If the original YDIH of a single event that created all the impact markers at the same instant in time is valid, the chronology of some of the sites must be erroneous. If, on the other hand the age discrepancy is real, then there are three possibilities to explain the age difference between sites:

- The age discrepancy could indicate that there is no impact origin for the markers that have been reported. Pigati et al. (2012), for example, give a plausible explanation for the occurrence of magnetic spherules and iridium anomaly, leaving only the nanodiamonds and possibly the lechatelierite unexplained.
- It is possible that the markers correspond to several smaller impacts or airbursts spaced several decades to centuries apart. However, in this case it is unlikely that the multiple impacts are the cause of the YD climate change, megafaunal extinctions or changes in human culture, as multiple smaller impacts would only have had local effects.
- Some of the markers or sites might be unrelated to an impact event of any size, whereas others are related to one or more impact events.

It is crucial that a supposed impact of any type of event can only be attributed to that event if there is a clear and causal relation between the timing of the event and the supposed impact. This has been advocated as such by the INTIMATE project group for the impact of abrupt climate changes, such as the transition from Allerød to Younger Dryas (Lowe et al., 2001, 2008). It is very important in these kind of studies to select suitable sedimentary archives that have enough time-resolution and, ideally, no hiatuses. Furthermore, these ideal archives should have the possibility of applying independent dating techniques in order to establish a reliable chronology. In many of the cases, the evidence used by for example Firestone et al. (2007) to support the YD impact hypothesis these criteria are not met.

Reproducibly analysing various well-dated annually laminated records containing the Allerød-YD transition, preferably with one or more independent marker horizons to link the records, might shed light on the apparent age discrepancy. This type of analysis would show whether the markers are found right at the Allerød-YD boundary and whether the markers at different locations point to the same point in time. In addition, analysing longer records would show whether the markers only occur at the Allerød-YD boundary or are a more common phenomenon, regardless of their origin. For example, if nanodiamonds turn out to be more common in sediments than previously thought, it would bring the use of nanodiamonds as impact indicator further in question. If, on the other hand, nanodiamonds are only found at one single point in time in several records, this would indicate that probably some sort of event took place and might provide an additional marker that can be used to link different records. Furthermore, we suggest that both the stratigraphy of the sedimentary archive and the methods used to analyse it, as well as the results are documented in detail. Sampling across the Allerød-YD boundary and the rest of the record should be continuous rather than taken at intervals, as was done in some studies, and sample thickness should be equal for all samples, preferably representing an equal amount of time. Doing so, insures that no peaks in markers at non-Allerød-YD boundary levels are missed and concentrations across the profile are comparable.

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