Earth and Planetary Science Letters 310 (2011) 401–408

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

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

U–Pb ages of shocked zircon grains link distal K–Pg boundary sites in Spain and Italy with the Chicxulub impact

Sandra L. Kamo [a,*], Cristiano Lana [b], Joanna V. Morgan [c]

[a] Jack Satterly Geochronology Laboratory, Department of Geology, University of Toronto, 22 Russell St., Toronto, Ontario, Canada M5S 3B1
[b] Departamento de Geologia, Universidade Federal de Ouro Preto, Ouro Preto, Minas Gerais, 35400000, Brazil
[c] Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

ARTICLE INFO

Article history:
Received 7 June 2011
Received in revised form 8 August 2011
Accepted 23 August 2011
Available online 29 September 2011

Editor: R.W. Carlson

Keywords:
shocked zircon
U–Pb ID-TIMS geochronology
K–Pg boundary
Chicxulub impact

ABSTRACT

The U–Pb ages of shocked zircon crystals from the Chicxulub impact crater and Cretaceous-Paleogene (K-Pg) boundary sites in Haiti, the USA, and Canada, and the pattern of decreasing particle size with paleodistance from the crater, have been used as evidence of a genetic link between Chicxulub and the K–Pg boundary. Despite this, the inference that the K–Pg boundary layer formed as a direct consequence of the Chicxulub impact has been repeatedly questioned. Here we present U–Pb (ID-TIMS) ages and textural evidence of shock metamorphosed zircon grains from the K–Pg boundary at Caravaca, Spain, and Petriccio, Italy, that establish a causal connection between the impact and formation of the K–Pg boundary layer. The shocked zircon grains give data that produce a characteristic age pattern, which indicates a primary source age of 549.5 ± 5.7 Ma and a secondary event at the approximate time of impact at 66 Ma. The intensity of the shock features is proportional to the degree of isotopic resetting, and all textural features and ages are analytically identical to those of previously analyzed zircon from Chicxulub and K–Pg boundary sites in North America. Caravaca and Petriccio were >8000 km from Chicxulub at the time of impact, and are therefore the farthest K–Pg sites identified that can be linked to Chicxulub through the dating of individual shocked zircon grains. We conclude that the combined age data and textural observations provide unambiguous evidence that ejecta from the Chicxulub impact formed the global K–Pg boundary layer. These data cannot be explained by the alternative scenario that the Chicxulub impact occurred ~300 ka prior to the K–Pg boundary.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

It is widely accepted that the Cretaceous-Paleogene (K-Pg) boundary clay layer was formed by an asteroid impact because it contains anomalous concentrations of iridium (Alvarez et al., 1980) and other platinum group elements in chondritic proportions (Kyte et al., 1985; Shukolyukov and Lugmair, 1998) that cannot have been produced by any terrestrial process. The K–Pg layer also contains terrestrial minerals (quartz, feldspar and zircon) that acquired diagnostic shock features (e.g., planar deformation lamellae) when subjected to high pressures (>15 GPa; e.g., Bohor et al., 1984). Such characteristic shock features in minerals are observed at impact craters and nuclear test sites (e.g., Cordier and Gratz, 1995), but are not associated with explosive volcanic eruptions where maximum pressures are much lower (≤5 GPa). Hence, the only plausible explanation for the K–Pg layer is that it was formed by a large asteroid impact, causing the ejection of both meteoritic material and shocked fragments of target rock around the globe.

The Chicxulub impact as the source of the K–Pg boundary clay is supported by a similarity in crystallization age and chemical composition between impact melt rock in the crater and tektites (i.e., glassy spherules) in the clay layer (e.g., Sigurdsson et al., 1991; Sharpton et al., 1992; Swisher et al., 1992; Blum et al., 1993). However, two additional lines of evidence provide the strongest support of a genetic link: the decrease in size of the ejected particles with paleodistance from Chicxulub (e.g., Hildebrand et al., 1991; Claeys et al., 2002; Croskell et al., 2002; Morgan et al., 2006), and identical U–Pb ages and systematics of ejected shocked zircon grains from several K–Pg sites in North America and Chicxulub impact breccia (Krogh et al., 1993a,b; Kamo and Krogh, 1995).

However, even with such apparently incontrovertible evidence for a causal connection of the Chicxulub impact event and the formation of the globally-observed K–Pg boundary clay layer, some authors have suggested that the Chicxulub impact occurred ~300 ka before the K–Pg boundary (Keller et al., 2004, 2007, 2009). There is agreement on a genetic link between Chicxulub and beds containing ejecta spherules close to Chicxulub, but Keller et al. (2004, 2007, 2009) suggested that the clastic deposits between the spherules and earliest Paleogene sediments represent a few hundred thousand years of sedimentation.

* Corresponding author at: Tel.: +1 416 946 0364; fax: +1 416 978 3839.
E-mail address: skamo@geology.utoronto.ca (S.L. Kamo).

0012-821X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2011.08.031

To help resolve this issue we have undertaken a test to evaluate the ages, textural characteristics, and U–Pb (ID-TIMS) systematics of shocked zircon grains at distal sites (>8000 km) from the Chicxulub impact structure at K–Pg localities at Caravaca, Spain, and Petriccio, Italy. The results are compared to previously determined U–Pb ages of shocked zircon from the suevitic breccia at Chicxulub, and the upper layer at other K–Pg boundary locations in Colorado, Saskatchewan and Haiti (Krogh et al., 1993ab; Kamo and Krogh, 1995). These data provide a rigorous test of whether a global correlation between Chicxulub and the K–Pg boundary is valid.

2. Shock metamorphic features and U–Pb dating of zircon

Zircon is a remarkably useful mineral for verifying impact events because it acquires diagnostic shock metamorphic features under the brief, high-pressure and -temperature conditions produced by hypervelocity impact. With increasing pressures and temperatures zircon develops microdeformation features such as planar fractures (PFs; see French, 1998) and planar deformation features (PDFs; Bohor et al., 1993), is transformed to reidite (Glass et al., 2002), develops granular textures (Bohor et al., 1993) and finally dissociates to baddeleyite (ZrO_2) and silica at ~1770 °C (e.g., Chao, 1968). This progressive development of impact-induced microstructures has been reproduced experimentally (Mashimo et al., 1983; Kusaba et al., 1985; Leroux et al., 1999). Wittmann et al. (2006) identified four stages: Stage I (10–30 GPa; 100–400 °C) produced planar deformation features, Stage II (30–45 GPa; 400–900 °C) showed further development of planar microstructures and transformation to reidite (i.e., high pressure polymorph of zircon), Stage III (45–60 GPa; 900–1500 °C) was marked by the development of granular textures, decorated microstructures and the complete transition of zircon to reidite, and Stage IV (>60 GPa; >1500 °C) was characterized by granular textures and amorphization of zircon and decomposition to baddeleyite and SiO_2.

In addition to recording pressure and temperature conditions during the impact event, shocked zircon crystals are extremely useful U–Pb geochronometers. Their paired parent–daughter isotopic systems (i.e., ^{235}U decays to ^{207}Pb and ^{238}U decays to ^{206}Pb) uniquely allow the determination of both the time of initial crystallization of the grains and the time of impact-induced isotopic disturbance. Measured parent–daughter ratios that plot on the Concordia curve originate from a closed isotopic system, whereas data points that plot below the curve may define a linear array (mixing line) that intersects the Concordia curve at the primary age of the zircon (upper intercept) and the time of disturbance (lower intercept). Grains with minimal impact-induced structural change (PFs) best define the igneous crystallization age, or upper part of the line, and those that are granular plot closest to the time of the isotopic disturbance at the lower end of the line.

The refractory nature and high melting temperature (1676 °C) of zircon ensure that shock features are preserved, even in ancient metamorphosed and tectonically modified impact structures such as at the 2.023 Ga Vredefort impact structure (Kamo et al., 1996; Gibson et al., 1997). Due to such thermal and chemical resilience, its shock-induced isotopic characteristics can be retained even after impact-related thermal overprinting and subsequent hydrothermal activity or exposure to prolonged weathering after deposition (c.f., Moser et al., 2009; Cavosie et al., 2010). Together, the textural and isotopic features provide a unique combination that offers a powerful diagnostic tool for investigations of impact events. Despite the utility of this dating application, few such studies exist, perhaps due to the relative scarcity of shocked zircon at impact-related sites compared to the more commonly observed shocked quartz and feldspar. For example, the distal K–Pg boundary layer is dominantly comprised of clay, with <1% clastic material (e.g. Pope, 2002), of which only a small proportion is zircon.

The first published U–Pb dating study of zircon from the K–Pg fireball (upper) layer in Colorado (Krogh et al., 1993a) showed that grains exhibiting the least shock (i.e., multiple sets of PFs) were slightly discordant from a 544 ± 5 Ma primary age, whereas highly shocked grains (i.e., granular) were strongly displaced to the time of impact at 65 ± 3 Ma. A subsequent U–Pb dating study showed that shocked zircon grains from the Chicxulub impact breccia from within the crater, as well as from the K–Pg boundary in Haiti, were identical in age, texture and correlated Pb loss pattern to those from Colorado (Krogh et al., 1993b). This study also revealed a subset of 418 Ma shocked grains from Chicxulub and Haiti. Finally, shocked zircon grains from the K–Pg fireball layer in Saskatchewan, Canada were also found to be indistinguishable in age from those at Chicxulub, Colorado and Haiti (Kamo and Krogh, 1995). It was concluded from these studies that zircon grains ejected from the excavated target rocks at Chicxulub were distributed to distal sites by a large meteorite impact as proposed by Alvarez et al. (1980) and that the Chicxulub impact was the sole source.

3. Sampling

The samples are from two well-studied K–Pg boundary sites in Spain (Caravaca) and Italy (Petriccio), which were located ~8200 km and ~9200 km, respectively, from Chicxulub at the time of impact (Morgan et al., 2006). The Caravaca section at the Barranco del Gredero site (Fig. 2a) is considered by many to be one of the five most complete K–Pg boundary sections in the world due to its expanded, undisturbed stratigraphy (e.g. Smit, 2004). The impact horizon is about 3 mm thick and contains anomalous concentrations of Ir, Ni, Cr, As, Sb, Zn (Smit, 1999), plus platinum group elements that are present in chondritic abundances (Kyte et al., 1985), and $^{53}Cr/^{52}Cr$ isotopic ratios that indicate a carbonaceous chondrite source (i.e., a strong negative epsilon ^{53}Cr; Shukolyukov and Lugmair, 1998). The K–Pg boundary clay is hosted in hemi-pelagic deep-water facies marl and limestone. Further details on the stratigraphy and the nature of the ejecta horizon at this location can be found in Díaz et al. (2002), Martínez-Ruíz et al. (1997), and Smit (1999, 2004). Because a higher concentration of shocked quartz was previously observed in the lower part of this layer (e.g., Morgan et al., 2006), we have preferentially sampled the lower ~10–20 mm of the K–Pg layer. Approximately 15 kg of green clay was collected from this site.

The Petriccio site is one of five exposures of the K–Pg boundary so far described in Italy (Montanari, 1991; Montanari and Koeberl, 2000). The stratigraphy and magnetostratigraphy (Arthur and Fischer, 1977; Lourie and Alvarez, 1977) and impact-related material observed

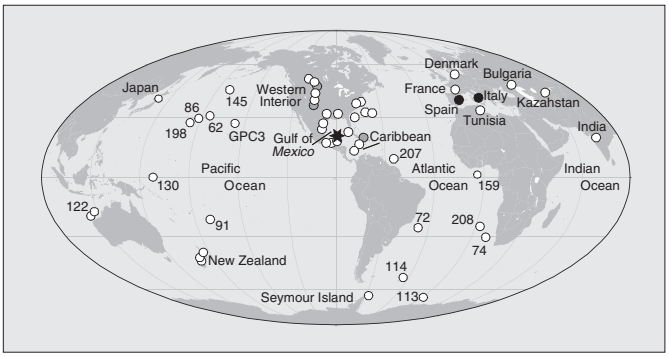

Fig. 1. Map of K–Pg sites around the globe with K–Pg boundary locations indicated by circles (numbers refer to Deep Sea Drilling Project (DSDP) or Ocean Drilling Program (ODP) drill sites). Filled black circles represent K–Pg sample locations in Spain (near Caravaca) and Italy (Petriccio site) of the present study. The location of the Chicxulub crater is indicated by the filled black star. The filled gray circles represent the K–Pg boundary locations of previous U–Pb dating studies on shocked zircon in Haiti, Colorado, USA, and Saskatchewan, Canada (data for these sites are plotted in Fig. 4b).
Map redrawn from Claeys et al. (2002), courtesy of P. Schulte.

Fig. 2. (a). Field photograph of the K–Pg boundary exposure and sample collection site, Barranco del Gredero section, Caravaca, Spain. The dark layer is the K–Pg boundary clay (white arrows), which varies in thickness from 3 to 4 cm, and is hosted within a sequence of marl and limestone. Photo courtesy of E. Díaz Martínez. (b). Field photograph of the K–Pg boundary exposure and sample collection site near Petriccio, Italy. The K–Pg boundary clay is a thin, 3 to 5 cm thick, reddish layer (black arrows) that is hosted within a sequence of marl and limestone. Photo courtesy of S. Montanari.

at these sites have been described previously (Montanari, 1991). The relatively undisturbed and expanded, 20–30 mm thick, K–Pg boundary clay contains shocked quartz and impact-related microspherules and has a high Ir concentration of 8.3 ppb, one of the highest among the Italian sites (Montanari and Koeberl, 2000). The boundary clay is hosted within deep water marine limestone. Shocked quartz grains are concentrated in the 5 mm thick, green basal layer of the boundary clay (Montanari and Koeberl, 2000). Approximately 13 kg of the basal material was collected from the Petriccio site. A field photograph of the sampling site is shown in Fig. 2b and in Montanari and Koeberl (2000; p. 229). Further details regarding impact-related materials in this sample are reported in Morgan et al. (2006).

Samples from both sites were disaggregated in the geochemistry laboratory at the Department of Earth Science and Engineering, Imperial College London, London. Clay minerals were dissolved in acid leaving a residue of oxide minerals, and a small proportion of silicate minerals. The zircon grains were hand-picked using either a binocular microscope or, if the grains were too small, an optical microscope. Approximately 30 grains were recovered from the sample from the Caravaca site. A similar number of zircon grains was obtained from the Petriccio sample, but a significantly reduced number of grains (less than 10) were considered large enough for single grain U–Pb dating. Secondary electron images of all zircon grains were obtained using a scanning electron microscope (SEM), and only a small fraction of these showed discernible shock features.

3.1. U–Pb methods

U–Pb analysis was done by isotope dilution thermal ionization mass spectrometry methods (ID-TIMS) at the Jack Satterly Geochronology Laboratory of the University of Toronto. Prior to dissolution, the zircon grains were imaged using a JEOL 840 scanning electron microscope followed by cleaning in aqua regia to remove the gold coating. In previous studies the grains were etched briefly in sodium hydroxide prior to imaging to enhance the shock features (Kamo et al., 1996; Krogh et al., 1993a). However, the grains in this study are significantly smaller (~60–80 μm) and in light of their scarcity, and the observation that some features were visible without etching, this step was avoided.

Zircon grains were dissolved using ~0.10 ml of concentrated HF and ~0.02 ml of 7 N HNO_3 in the presence of a ^{205}Pb–^{235}U spike solution, at 195 °C for 5 days. The solutions were dried to a precipitate, re-dissolved in ~0.15 ml of 3 N HCl, and Pb and U were isolated using anion exchange chromatography (Krogh, 1973). Pb and U were deposited onto outgassed rhenium filaments with silica gel (Gerstenberger and Haase, 1997), and analyzed with a VG M354 mass spectrometer using a Daly detector in pulse counting mode. Dead time of the measuring system for Pb was 22 ns and 20.8 ns for U. The correction for the Daly detector bias is constant at 0.05% per atomic mass unit. Amplifier gains and Daly characteristics were monitored using the SRM982 Pb standard. A thermal mass fractionation correction of 0.10% per atomic mass unit was used, with errors of 0.06% and 0.04% (2σ) for Pb and U, respectively. Corrections to the ^{206}Pb–^{238}U and $^{207}Pb/^{206}Pb$ ages for initial ^{230}Th disequilibrium in the zircon have been made assuming a Th/U ratio in the magma of 4.2. The total amount of common Pb in each analysis ranged from 0.2 to 0.6 pg, which was assigned to procedural Pb blank. U blank was estimated at 0.01 pg. The spike calibration error on the U/Pb ratio is estimated at ~0.1% (2σ). Decay constants are those of Jaffey et al. (1971). All age errors quoted in the text and table, and error ellipses in the Concordia diagrams are given at the 95% confidence interval. Plotting and age calculations were done with Isoplot 3.00 (Ludwig, 2003).

4. Results

The studied zircon grains record a range of shock features from PFs, PFs with granular texture, to extensively recrystallized to granular grains (i.e., comprising ~1–2 micron granules). Representative examples of SEM images of grains with shock features are shown in Fig. 3a–f. Only grains that appeared shocked were selected for U–Pb analysis in order to confirm that they were associated with an impact. The grains were relatively small, weighing 0.2–0.9 μg, and requiring sub-picogram Pb contamination levels in each U–Pb analysis.

Under a binocular microscope the grains range from slightly hazy to milky and opaque. Such characteristics are usually attributed to zones of high uranium that have undergone alteration, but Krogh et al. (1984) showed that the opacity can result from reflections of multiple displaced crystal planes in unaltered grains. Bohor et al. (1993) noted that grains with well-developed granular texture also had rounded grain outlines. Here too, a correlation can be observed between the degree of rounding of the grains with increased shock pressure, i.e., euhedral grain with PFs (Fig. 3a–b), a grain with PFs combined with partial development of granules is euhedral but with rounded tips (Fig. 3c–d), and a grain that exhibits the most

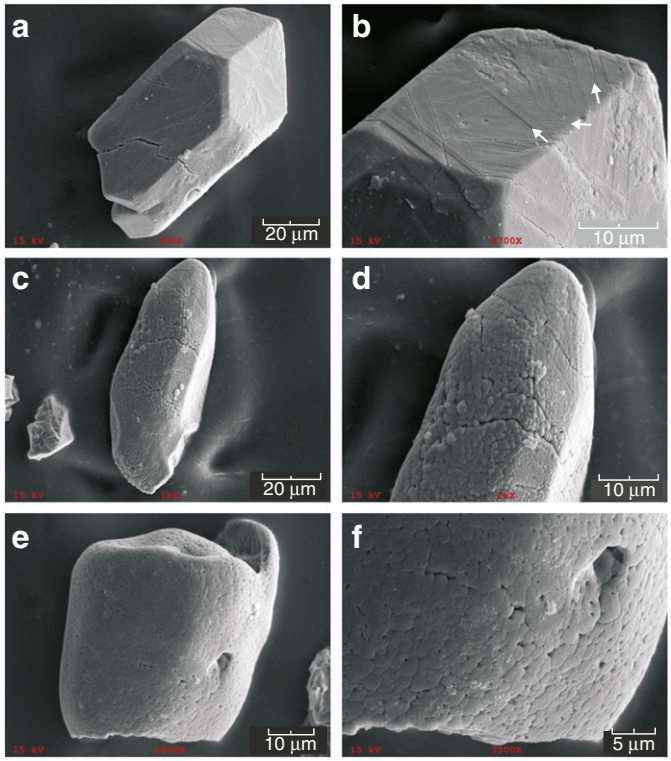

Fig. 3. SEM images of three of the zircon grains analyzed for U and Pb. The grain in (a–b) is euhedral and has planar features (PFs; grain 2 in Table 1), (c–d) contains both PFs and partial development of granules, and is rounded at its edges but still preserves its faces (grain 5 in Table 1), and (e–f) exhibits recrystallization and has well rounded surfaces (grain 7 in Table 1). U–Pb data for these grains are plotted in Fig. 4.

extensively developed granules has well-rounded surfaces (Fig. 3e–f). In fact, this crystal is dimpled in places and has a large concavity at one end, perhaps where it has collapsed due to localized internal melting. Deutsch and Schärer (1990) showed TEM diffraction patterns of grains shocked under experimental conditions to 59 GPa, which revealed multiple intra-granular c-axes consistent with transition to polycrystalline aggregates. The smooth surface may be the result of individual granules coalescing as a result of high temperatures following extreme shock pressure.

A high proportion of the zircon grains recovered from the site in Spain exhibited shock metamorphic effects whereas fewer of the grains from Italy appeared to have shock textures. U–Pb ID-TIMS analyses of six shocked grains from Spain and one from Italy are collinear (Table 1 and Fig. 4a). The most striking aspect of the array is the relationship between degree of discordance and structural damage of the grains, which was also observed in previous such studies. Discordance of the data (as distance from the upper intercept age along a line constrained at 66 Ma, see below) is 11% to 25% for grains that exhibit only planar microdeformation features (PFs; grains 1–4), whereas those that show variable degrees of recrystallization into microgranules (granular texture; grains 5–7) are 33%, 61% and 99% discordant, respectively. The latter most discordant data point (#7) has a $^{206}Pb/^{238}U$ age of 69.1 ± 0.6 Ma, and therefore indicates near complete isotopic resetting due to recrystallization. Such granular grains have been reported previously in pseudotachylitic breccia and granophyre of the Vredefort, Sudbury and Chicxulub structures (Kamo et al., 1996; Krogh et al., 1993a, 1996; Moser, 1997) and ejecta in the K–Pg layer and in Muong Nong tektites (Bohor et al., 1993), but never in unshocked materials of terrestrial origin, and they therefore provide a useful diagnostic indicator of materials shocked by extraterrestrial impact.

A line calculated through the data for grains 1 to 7 has intercept ages of 545.4 ± 7.6 Ma and 42 ± 32 Ma (MSWD for mean square of the weighted deviates is 0.6). The imprecise lower intercept age is an artifact of the uncertainties of the $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$ ages, which is due to the small amounts of ^{207}Pb (see Table 1) of the more discordant, highly shocked grains. Small amounts of recent, post-impact Pb loss will produce younger Pb/U ages and this effect can be expected to be greater in grains with higher surface/volume ratios such as in the smaller recrystallized zircon grains found at the European sites (Table 1). This will produce a lower intercept age that is too young, and in such cases, where the goal is to determine the primary age, it is best to anchor the mixing line at the independently determined age of the K–Pg horizon of 66 Ma, which is based on ages of multiple ash beds that bracket the boundary (U–Pb ID-TIMS dating of chemically-abraded zircon, S.A. Bowring, personal communication; also Kuiper et al., 2008, based on orbital chronology of K–Pg boundary spherules). This gives an upper intercept of 549.5 ± 5.7 Ma (95% confidence, excluding decay constant errors; MSWD = 0.8), which is interpreted as the best estimate of the primary crystallization age.

Analyses 8 and 9 were not included in the line calculation. Grain 8 exhibited multiple directions of PFs and the data are concordant and plot slightly above the mixing line with $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages of 496.3 ± 1.6 Ma and 502 ± 36 Ma, respectively. The data point for grain 9 plots below the line and could indicate a source age as old as 823 ± 20 Ma if anchored at the time of impact. But this requires a long projection given that the $^{206}Pb/^{238}U$ age is 422.8 ± 1.2 Ma, and it is therefore more likely that the grain experienced multiple episodes of Pb loss.

Shock alone (PFs) was shown experimentally to produce, at most, only minor amounts of Pb loss in zircon (Deutsch and Schärer, 1990) but Krogh et al. (1996) noted that it may be the extent of structural damage that controls the amount of Pb loss, which is induced by the impact-related thermal pulse. Recrystallization of the zircon into micro-granules resets the U–Pb systems to the greatest extent by excluding in-grown radiogenic Pb, which is likely volatilized during the high-temperature recrystallization process. Partial recrystallization will result in incomplete resetting of the U–Pb systems. This is demonstrated in grain 7 (Fig. 3c) which has a $^{206}Pb/^{238}U$ age of ~69 Ma, indicating near complete recrystallization. The results of the present study therefore support earlier observations of correlated discordance with shock-induced crystallographic structural changes. Crystal-plastic deformation as a mechanism for Pb loss (Reddy et al., 2006) has been suggested to have produced significant Pb loss in zircon near the time of impact in basement rocks of the Vredefort structure by Moser et al. (2009). It is unknown whether such a Pb loss mechanism affected zircon in Chicxulub breccia or ejecta, or if shock features such as microtwinning may be present (Moser et al., 2011), but further investigation in zircon from such rocks at Chicxulub may reveal examples of these occurrences.

5. Discussion

Impact breccias are formed mainly from melted, shocked and unshocked target rocks (e.g., Hörz et al., 1983), and may contain a small fraction of meteoritic material. At the time of impact, ~3 km of carbonate and evaporite sediments covered the basement at Chicxulub (Hildebrand et al., 1991). According to scaling laws (Melosh, 1989) and using an estimated transient cavity of ~100 km (Morgan et al., 1997; Hildebrand et al., 1998), the maximum depth of excavation is 10–12 km, thus the shocked minerals in the local impact breccias would have originated from the basement rocks at Chicxulub. Shocked minerals that were ejected to distal localities by the impact process should therefore have the same ages as the excavated basement rocks in the breccias.

Previous U–Pb dating studies on zircon from North America have tested and supported this idea. Basement ages determined on single, shocked grains extracted from fragments of granitic gneiss and quartz mica schist in the Chicxulub impact breccia from the Y6 drill hole

Table 1
U–Pb ID-TIMS data for single shocked zircon grains from the K–Pg boundary at Caravaca, Spain, and Petriccio, Italy.

No.	Zircon description	Wt. (μg)	U (ppm)	Pbtot (pg)	Th/U	PbC (pg)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{238}U$	2σ	$^{207}Pb/^{235}U$	2σ	Error Corr	$^{206}Pb/^{238}U$ (Ma) age	2σ	$^{207}Pb/^{235}U$ (Ma) age	2σ	$^{207}Pb/^{206}Pb$ (Ma) age	2σ
1	PFs, euhedral (~90×50×40 μm)	0.8	110	7.6	0.67	0.3	1353	93.6	0.07887	0.00034	0.6354	0.0060	0.505	489.4	2.0	499.4	3.8	546	18
2	PFs, euhedral (~90×45×40 μm)	0.8	432	28.3	0.61	0.4	3858	239.3	0.07614	0.00025	0.6113	0.0028	0.759	473.1	1.5	484.4	1.7	539	6
3	possible PFs, euhedral (~85×30×30 μm)	0.4	356	11.8	0.75	0.3	2112	137.9	0.07464	0.00026	0.6008	0.0040	0.558	464.0	1.5	477.8	2.5	544	12
4	possible PFs, euhedral (~120×40×40 μm)	0.9	230	15.5	0.76	0.6	1557	104.8	0.06853	0.00011	0.5475	0.0050	0.545	427.3	0.7	443.4	3.2	528	18
5	PFs and granular, rounded tips (~80×25×25 μm)	0.2	86	0.9	n/a	0.2	301	32.3	0.06169	0.00045	0.5025	0.0198	0.522	385.9	2.7	413.4	13.4	570	80
6	granular, one tip rounded, one tip euhedral (~85×25×25 μm)	0.2	460	4.0	0.62	0.5	510	43.8	0.04037	0.00016	0.3190	0.0082	0.540	255.1	1.0	281.1	6.3	504	52
7	granular, well rounded (~40×30×30 μm)	0.2	188	0.3	n/a	0.2	124	21.1	0.01077	0.00010	0.0771	0.0103	0.903	69.1	0.6	75.4	9.7	282	292
8	PFs, euhedral (~90×45×40 μm)	0.8	33	2.3	0.81	0.2	666	52.7	0.08003	0.00027	0.6320	0.0114	0.514	496.3	1.6	497.4	7.1	502	36
9	possible developing granules, euhedral (~85×45×30 μm)	0.5	261	9.7	0.66	0.5	1132	88.0	0.06812	0.00020	0.6102	0.0058	0.506	424.8	1.2	483.7	3.7	773	18

Notes: Analysis no. keyed to concordia figure; ** denotes grain from Italy, all others from Spain; PF for planar fracture; in brackets estimated dimensions of grains in microns.
Th/U calculated from radiogenic $^{208}Pb/^{206}Pb$ ratio and $^{207}Pb/^{206}Pb$ age assuming concordance; Pbtot is total amount of Pb excluding blank; PbC is total common Pb assuming the isotopic composition of laboratory blank: $^{206}Pb/^{204}Pb$=18.221; $^{207}Pb/^{204}Pb$=15.612; $^{208}Pb/^{204}Pb$=39.360 (2σ errors of 2%); $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ measured ratios corrected for fractionation and common Pb in the spike, Pb/U ratios also corrected for blank. Error Corr is correlation coefficients of X–Y errors on the concordia plot. Correction for ^{230}Th disequilibrium in $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ assuming Th/U of 4.2 in the magma.

(Krogh et al., 1993a) give the same igneous crystallization ages as those found in the K–Pg boundary clay in Colorado (Krogh et al., 1993b), Saskatchewan (Kamo and Krogh, 1995) and Haiti (Krogh et al., 1993a). U–Pb data at the four localities are dominated by zircon with igneous crystallization ages within error of 544.5 ± 5 Ma. Each grain that plots on the linear array records this primary age and the time of partial recrystallization near ~66 Ma. The dated grains are best explained as residual, coherent remnants of the Chicxulub target rock. A minor 418 Ma component provides an additional link between Chicxulub and Haiti. In each of the studies, it was noted that there is a strong correlation between the extent of the shock-induced crystallographic changes and the amount of U–Pb discordance along the mixing line between the primary igneous crystallization age and the time of isotopic resetting. There is no known terrestrial mechanism that will produce this distinctive combination of isotopic correlation with structural features. This correlated discordance pattern and the 545–550 Ma ages provide a 'fingerprint' of the basement target source.

In the present study, individual shocked zircon from the K–Pg clay layer in Spain and Italy again indicates a dominant Pan-African source age of 549.5 Ma, indistinguishable from the ages determined in those previous studies in North America. The presence of shock features in the dated grains confirmed their derivation from an impact site. The lower intercept age approximates the time of impact, but does not precisely determine it due to minor post-impact Pb loss. A compilation of data from this and previous such studies (Fig. 4b) shows that data for 36 grains plot on or very near a single chord indicating a common igneous crystallization age. The conformity of the collective data is remarkable given the widely-spaced localities of the ejecta sampling sites and the potential for lithological diversity in a large 100-km-diameter excavation cavity. It is noted that the full spectrum of shocked crystals, i.e. those with PFs to granular grains, is represented at all localities, which indicates that impact ejecta underwent thorough mixing prior to or during dispersal around the globe.

Despite the predominance of 545–550 Ma zircon ages at Chicxulub and in K–Pg ejecta, there is evidence of lithological heterogeneity in the target basement. Clasts in impact breccia from PEMEX drill holes C-1 and Y-6 and in the more recent Yaxcopoil-1 drill hole include granitic gneiss, quartzite, amphibolite, and quartz-mica schist as well as abundant glass and deformed melt clasts (e.g., ICDP, 2002; Sharpton et al., 1992; Shuraytz et al., 1994). Further evidence for a heterogeneous basement is given by the range in chemical composition and Sr and Nd isotopic data in clasts of impact melt lithologies (Kettrup et al., 2000; Kettrup and Deutsch, 2003). Lithological diversity in the basement target lithology is also supported by distinct single zircon ages in K–Pg ejecta and Chicxulub breccia. Premo and Izett (1993) reported an older Pan-African age of 575 ± 5.5 Ma for shocked zircon from the Raton Basin, Colorado. A single crystal with PFs from Spain in the present study is 496 ± 2 Ma. A 418 Ma age for grains was found in Haiti and Chicxulub (Krogh et al., 1993a), similar to that reported by Steiner and Walker (1996) for plutonic rocks of the Maja Mountains, Yucatán basement. A younger zircon grain of ~360 ± 26 Ma from Saskatchewan is within error of two shocked grains from Colorado, one at 320 ± 31 Ma (Kamo and Krogh, 1995) and the other at ~330 Ma (Premo and Izett, 1993). The predominance of the 545–550 ages is likely due to the dominance of granitic gneiss in the target (Sharpton et al., 1992) as indicated by the estimated high percentage of granitic clasts (~67%) found in impact breccias from Yaxcopoil-1 (ICDP, 2002). Mafic lithologies that generally do not contain zircon, may have comprised a significant proportion of the Yucatán basement target (Pilkington et al., 2004) and influenced the chemical and isotopic compositions observed in melt clasts (Kring and Boynton, 1992; Kettrup et al., 2000; Kettrup and Deutsch, 2003).

Globally, crustal basement of Pan-African age is relatively uncommon (e.g., Sclater et al., 1981) and has been reported close to Chicxulub in the Maya terrane in the Yucatán (Keppie and Ortega-Gutierrez,

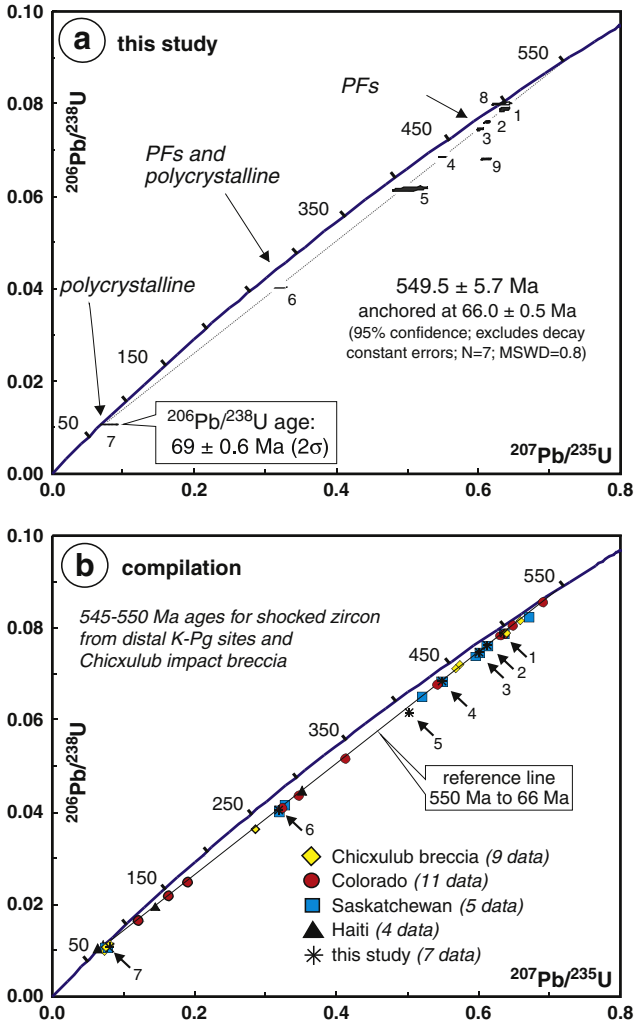

Fig. 4. a) Concordia diagram for U–Pb data for shocked zircon from Caravaca, Spain and Petriccio, Italy. Results from previously analyzed zircons from Chicxulub, Haiti, Colorado, USA and Saskatchewan, Canada, are shown in Fig. 3b. Note that the least shocked zircons plot near the top of the mixing line, while those that preserve the highest degrees of shock (granular grains) plot furthest down the mixing line. b) Compilation of 36 U–Pb data for shocked zircon from the Chicxulub impact breccia and K–Pg boundary sites in North America and Europe (data points noted by arrows and numbered 1–7) indicate a dominant 545–550 Ma age.

1995) and Florida (Mueller et al., 1994), which were likely contiguous prior to the opening of the Gulf of Mexico (e.g., Dickinson and Lawton, 2001). Pan African basement is found in some terranes on the east coast of North America, such as the Avalon terrane (e.g., Bevier et al., 1990), whereas no basement of this age has been reported in Italy. Local derivation of the zircon grains at the K–Pg sites is highly improbable, as each of the widely distributed sampling localities would require a source of impact-derived 545–550 Ma zircon grains, showing correlated partial recrystallization with discordance towards ~66 Ma. Given the rare occurrence of shocked zircon grains, and that of ~66 Ma impact structures in Pan-African basement, and given that the K–Pg layer is hosted in deep-water limestones and/or marls (Haitian and European sites), the possibility of introducing the grains into the boundary clay by sedimentary processes is extremely unlikely. In addition, sedimentary transport of zircon grains usually results in surface abrasion, rounding, and a frosted exterior, which were not observed in the dated grains of this or in those from previous such studies. The presence of shocked zircon with identical primary ages at Chicxulub and K–Pg sites in North America, up to 3500 km from the Chicxulub crater, and Europe, at paleodistances of >9000 km (Fig. 1), provides robust evidence that the K–Pg layer was globally-distributed by an impact at the Chicxulub site on the Yucatán peninsula in southern Mexico.

The suggestion that the Chicxulub impact occurred prior to the K–Pg boundary is based on observations within the crater itself (Yaxcopoil-1 drill hole) and at sites close to Chicxulub (in Mexico and Texas), where the K–Pg transitional sequence contains one or more laterally discontinuous spherule layers (Schulte et al., 2003), and where there are clastic deposits between the spherule layer(s) and the overlying Paleocene deposits (e.g., Keller et al., 2004, 2009). The clastic sequence is reported to contain late Maastrichtian planktonic foraminiferal assemblages, and is interpreted by Keller et al. (2004, 2007, 2009) as having accumulated over several hundred thousand years. These observations were interpreted by Keller et al. (2004, 2007) as indicating that there were two separate large impacts, (i) the Chicxulub impact, and (ii) an impact at the K–Pg boundary, that were separated by ~300 ka. In a subsequent interpretation of events, however, Keller et al. (2009) suggested that there was only one large impact, Chicxulub, and explained the presence of Chicxulub ejecta at the K–Pg boundary at many deep sea sites (e.g., Demerara Rise, Blake Nose) as due to erosion and low sedimentation rates (but see Macleod et al., 2007; Norris et al., 1999; Schulte et al., 2009; Berndt et al., 2011).

Theoretical calculations, scaling relationships, and numerical models all show that an impact of this size would eject material at high velocity around the world (Alvarez et al., 1995; Kring and Durda, 2002; Artemieva and Morgan, 2009). During the impact the crust was compressed to form a transient cavity that was ~100 km wide and ~30 km deep, surrounded by a transient wall structure the height of the Himalayas, a few 10s of seconds after impact (Collins et al., 2002; Ivanov, 2005). The impact site was a shallow marine continental shelf, and it is plausible that it led to significant collapse of the Yucatán shelf (Bralower et al., 1998; Grajales-Nishimura et al., 2000), landslides, gravity flows (Bralower et al., 1998), mass wasting (Klaus et al., 2000), multiple tsunamis (Bourgeois et al., 1988; Smit, 1999; Schulte et al., in press), earthquakes and aftershocks, to produce a relatively thick and complex sequence of deposits around Chicxulub. In contrast, the interpretation by Keller et al. (2009), that the Chicxulub impact produced only layers of ejected spherules in the local sedimentary record, is unlikely.

The separation of spherule layers from the first Paleocene deposits and a small iridium anomaly at proximal sites is expected given the different origin of these two ejecta components. The mm-sized spherules at sites around Chicxulub and in the lower layer in North America are formed mostly from melted target rocks (e.g., Sigurdsson et al., 1991) and are ejected ballistically at relatively low velocities (Artemieva and Morgan, 2009). The finer-grained, iridium-rich layer that comprises the upper layer in North American sites as well as the distal K–Pg layer is formed mainly from vaporized projectile and target rocks, ejected at high velocity within an expanding vapor plume (Alvarez et al., 1980; Melosh and Vickery, 1991; Toon et al., 1997; Smit, 1999; Berndt et al., 2011). Artemieva and Morgan (2009) showed that material ejected at sufficiently high velocities to travel around the globe is enriched in meteoritic matter, and that ejected fragments of shocked basement (including zircon) probably reached their final destination by skidding around the Earth through re-distribution from a hot, expanding atmosphere. The suspension of the smaller ejected particles in a hot atmosphere (Goldin, 2008) means that the iridium-rich layer with shocked zircon and other minerals is emplaced over an extended period of time.

6. Conclusions

Zircon crystals recovered from the K–Pg boundary layer at Caravaca, Spain, and Petriccio, Italy, exhibit shock metamorphic features that are uniquely associated with the impact process. Multiple

U–Pb ID-TIMS zircon analyses are collinear and indicate a primary source crystallization age of 549.5 ± 5.7 Ma. The new age data are in agreement with previously reported ages of ca. 545–550 Ma from similar grains obtained from impact breccia at Chicxulub and other K–Pg boundary sites in Haiti, the USA and Canada. At each locality, the linear distribution of the data shows a correlation with the shock intensity of the zircon, and the data are collinear when anchored at the independently determined age of the K–Pg boundary. The data provide additional evidence that basement rocks of Pan-African age ejected by the Chicxulub impact from the Yucatán peninsula in Mexico are the source of the globally-distributed K–Pg boundary layer, and extend the geographic distance of directly traceable ejecta to >9000 km from the impact site. The U–Pb zircon data cannot be explained by a scenario in which Chicxulub pre-dates the K–Pg boundary by ~300 ka.

The observed shock textures and correlated U–Pb isotope systematics provide a powerful diagnostic tool for investigations of impacts.

Acknowledgements

This work is dedicated to the memory of Tom Krogh whose pioneering work on modern ID-TIMS zircon geochronology led to our ability to precisely date such vanishingly small quantities of zircon. We wish to acknowledge field support from S. Montanari and E. Diaz Martinez, and funding from the Leverhulme Trust for sample collecting. The Jack Satterly Geochronology Laboratory provided financial support for this research. We are grateful to F. Corfu and L. Heaman who provided comments on an early version of this manuscript, and to P. Schulte and an anonymous reviewer who made many helpful suggestions.

References

Alvarez, L.W., Alvarez, W., Asaro, F., Michel, H.V., 1980. Extraterrestrial cause of the Cretaceous–Tertiary extinction. Science 208, 1095–1108.

Alvarez, W., Claeys, P., Kieffer, S., 1995. Emplacement of Cretaceous–Tertiary boundary shocked quartz from Chicxulub crater. Science 269, 930–935.

Artemieva, N., Morgan, J.V., 2009. Modeling the formation of the K–Pg boundary layer. Icarus 201, 768–780. doi:10.1016/j.icarus.2009.01.021.

Arthur, M., Fischer, A., 1977. Upper Cretaceous–Paleocene magnetic stratigraphy at Gubbio, Italy I. Lithostratigraphy and sedimentology. Geol. Soc. Am. Bull. 88, 367–371.

Berndt, J., Deutsch, A., Schulte, P., Mezger, K., 2011. The Chicxulub ejecta deposit at Demerara Rise (western Atlantic): dissecting the geochemical anomaly using laser ablation-mass spectrometry. Geology 39, 279–282. doi:10.1130/G31599.1.

Bevier, M.L., White, C.E., Barr, S., 1990. Late Precambrian U–Pb ages for the Brookville gneiss, southern New Brunswick. J. Geol. 98, 955–965.

Blum, J.D., Chamberlain, C.P., Hingston, M.P., Koeberl, C., Marín, L., Shuraytz, B.C., Sharpton, V.L., 1993. Isotopic comparison of K/T boundary impact glass with melt rock from the Chicxulub and Manson impact structures. Nature 364, 325–327. doi:10.1038/364325a0.

Bohor, B.F., Foord, E.E., Modreski, P.J., Triplehorn, D.M., 1984. Mineralogic evidence for an impact event at the Cretaceous–Tertiary boundary. Science 224, 867–869.

Bohor, B.F., Betterton, W.J., Krogh, T.E., 1993. Impact-shocked zircons: discovery of shock-induced textures reflecting increasing degrees of shock metamorphism. Earth Planet. Sci. Lett. 119, 419–424.

Bourgeois, J., Hansen, T.A., Wiberg, P.L., Kauffman, E.G., 1988. A tsunami deposit at the Cretaceous–Tertiary Boundary in Texas. Science 241, 567–570.

Bralower, T., Paull, C.K., Leckie, R.M., 1998. The Cretaceous–Tertiary boundary cocktail: Chicxulub impact triggers margin collapse and extensive gravity flows. Geology 26, 331–334.

Cavosie, A.J., Quintero, R.R., Radovan, H.A., Moser, D.E., 2010. A record of ancient cataclysm in modern sand: Shock microstructures in detrital minerals from the Vaal River, Vredefort Dome, South Africa. Geol. Soc. Am. Bull. 122, 1968–1980.

Chao, C.T., 1968. Pressure and temperature histories of impact metamorphosed rocks—based on petrographic observations. In: French, B.M., Short, N.M. (Eds.), Shock Metamorphism of Natural Materials. Mono Book, Baltimore, pp. 135–158.

Claeys, P., Kiessling, W., Alvarez, W., 2002. Distribution of Chicxulub ejecta at the Cretaceous–Tertiary boundary. In: Koeberl, C., MacLeod, K.G. (Eds.), Catastrophic Events and Mass Extinctions; Impacts and Beyond: Geological Society of America Special Paper, 356, pp. 55–68.

Collins, G.S., Melosh, H.J., Morgan, J.V., Warner, M.R., 2002. Hydrocode simulations of Chicxulub crater collapse and peak-ring formation. Icarus 157, 24–33.

Cordier, P., Gratz, A.J., 1995. TEM study of shock metamorphism in quartz from the Sedan nuclear test site. Earth Planet. Sci. Lett. 129, 163–170.

Croskell, M., Warner, M., Morgan, J., 2002. Annealing of shocked quartz during atmospheric reentry. Geophys. Res. Lett. 29, 1940–1944.

Deutsch, A., Schärer, U., 1990. Isotope systematics and shock-wave metamorphism: I. U–Pb in zircon, titanite, and monazite, shocked experimentally up to 59 GPa. Geochim. Cosmochim. Acta 54, 3427–3434.

Díaz, M.E., Sanz, R.E., Martínez, F.J., 2002. Sedimentary record of impact events in Spain. In: Koeberl, C., MacLeod, K. (Eds.), Catastrophic Events and Mass Extinctions; Impacts and Beyond. Special Paper, 356. Geological Society of America, pp. 551–562.

Dickinson, W.R., Lawton, T.F., 2001. Carboniferous to Cretaceous assembly and fragmentation of Mexico. Geol. Soc. Am. Bull. 113, 1142–1160.

French, B.M., 1998. Traces of Catastrophe: A Handbook of Shock-metamorphic Effects in Terrestrial Meteorite Impact Structures. LPI Contribution No. 954 Lunar and Planetary Institute, Houston. 120 pp.

Gerstenberger, H., Haase, G., 1997. A highly effective emitter substance for mass spectrometric Pb isotope ratio determinations. Chem. Geol. 136, 309–312.

Gibson, R.L., Armstrong, R.A., Reimold, W.U., 1997. The age and thermal evolution of the Vredefort impact structure: a single-grain U–Pb zircon study. Geochim. Cosmochim. Acta 61, 1531–1540.

Glass, B.P., Liu, S., Leavens, P.B., 2002. An impact-produced high-pressure polymorph of zircon found in marine sediments. Am. Mineral. 87, 562–565.

Goldin, T.J., 2008. Atmospheric interactions during global distribution of Chicxulub impact ejecta. PhD thesis, University of Arizona, 266 pp.

Grajales-Nishimura, J.M., Cedillo-Pardo, E., Rosales-Domínguez, C., Morán-Zenteno, D.J., Alvarez, W., Claeys, P., Ruíz-Morales, J., García-Hernández, J., Padilla-Avila, P., Antonieta Sánchez-Ríos, A., 2000. Chicxulub impact: the origin of reservoir and seal facies in the southeastern Mexico oil fields. Geology 28, 307–310.

Hildebrand, A.R., Penfield, G.T., Kring, D.A., Pilkington, M., Camargo, A.Z., Jacobsen, S.B., Boynton, W.V., 1991. Chicxulub Crater: a possible Cretaceous/Tertiary boundary impact crater on the Yucatán Peninsula, Mexico. Geology 19, 867–871.

Hildebrand, A.R., Pilkington, M., Ortiz-Aleman, C., Chavez, R.E., Urrutia-Fucugauchi, J., 1998. Mapping Chicxulub crater structure with gravity and seismic reflection data. In: Grady, M.M., Hutchison, R., McCall, G.J.H., Rothery, D.A. (Eds.), Meteorites: Flux with Time and Impact Events: Special Publications, Geological Society of London, 140, pp. 155–176.

Hörz, F., Ostertag, R., Rainey, D.A., 1983. Bunte Breccia of the Ries, continuous deposits of large impact craters. Rev. Geophys. Space Phys. 21, 1667–1725.

International Continental Drilling program (ICDP), 2002. Log of Yax-1 core. http://www.icdp-online.de2002.

Ivanov, B.A., 2005. Numerical modeling of the largest terrestrial meteorite craters. Sol. Syst. Res. 39, 381–409.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., Essling, A.M., 1971. Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U. Phys. Rev. 4, 1889–1906.

Kamo, S.L., Krogh, T.E., 1995. Chicxulub crater source for shocked zircon crystals from the Cretaceous–Tertiary boundary layer, Saskatchewan: evidence from new U–Pb data. Geology 23, 281–284.

Kamo, S.L., Reimold, W.U., Krogh, T.E., Colliston, W.P., 1996. A 2.023 Ga age for the Vredefort impact event and a first report of shock metamorphosed zircons in pseudotachyltic breccias and granophyres. Earth Planet. Sci. Lett. 144, 369–387.

Keller, G., Adatte, T., Stinnesbeck, W., Rebolledo-Vieyra, M., Urrutia-Fucugauchi, J., Kramar, U., Stüben, D., 2004. Chicxulub impact predates the K–T boundary mass extinction. Proc. Natl. Acad. Sci. 101, 3753–3758.

Keller, G., Adatte, T., Berner, Z., Harting, M., Baum, G., Prauss, M., Tantawy, A., Stueben, D., 2007. Chicxulub impact predates K–T boundary: new evidence from Brazos, Texas. Earth Planet. Sci. Lett. 255, 339–356.

Keller, G., Adatte, T., Pardo, A.J., Lopez-Olivia, J.G., 2009. New evidence concerning the age and biotic effects of the Chicxulub impact in NE Mexico. J. Geol. Soc. Lond. 166, 393–411.

Keppie, J.D., Ortega-Gutierrez, E., 1995. Provenance of Mexican Terranes: isotopic constraints. Int. Geol. Rev. 37, 813–824.

Kettrup, B., Deutsch, A., 2003. Geochemical variability of the Yucatán basement: constraints from crystalline clasts in Chicxulub impactites. Meteor. Planet. Sci. 38, 1079–1092.

Kettrup, B., Deutsch, A., Ostermann, M., Agrinier, P., 2000. Chicxulub impactites: geochemical clues to the precursor rocks. Meteor. Planet. Sci. 35, 1229–1238.

Klaus, A., Norris, R.D., Kroon, D., Smit, J., 2000. Impact-induced mass wasting at the K–T boundary: Blake Nose, western North Atlantic. Geology 28, 319–322.

Kring, D.A., Boynton, W.V., 1992. Petrogenesis of an augite-bearing melt rock in the Chicxulub structure and its relationship to K/T impact spherulesin Haiti. Nature 358, 141–144.

Kring, D.A., Durda, D.D., 2002. Trajectories and distribution of material ejected from the Chicxulub impact crater: implications for post-impact wildfires. J. Geophys. Res. 107 (E6), 5062. doi:10.1029/2001JE001532.

Krogh, T.E., 1973. A low contamination method for hydrothermal decomposition of zircon and extraction of U and Pb for isotopic age determinations. Geochim. Cosmochim. Acta 37, 485–494.

Krogh, T.E., Davis, D.W., Corfu, F., 1984. Precise U–Pb zircon and baddeleyite ages for the Sudbury area. In: Pye, E.G., Naldrett, A.J., Giblin, P.E. (Eds.), The Geology and Ore Deposits of the Sudbury Structure: Ontario Geological Survey Special, Volume 1, pp. 431–446.

Krogh, T.E., Kamo, S.L., Bohor, B.F., 1993a. U–Pb ages of single shocked zircons linking distal K–T ejecta to the Chicxulub crater. Nature 366, 731–734.

Krogh, T.E., Kamo, S.L., Bohor, B.F., 1993b. Fingerprinting the K/T impact site and determining the time of impact by U–Pb dating of single shocked zircons from distal ejecta. Earth Planet. Sci. Lett. 119, 425–429.

Krogh, T.E., Kamo, S.L., Bohor, B.F., 1996. Shock metamorphosed zircons with correlated U–Pb discordance and melt rocks with concordant protolith ages indicate an impact origin for the Sudbury Structure. Geophys. Monogr. 95, 343–353.

Kuiper, K.F., Deino, A., Hilgen, F.J., Krijgsman, W., Renne, P.R., Wijbrans, J.R., 2008. Synchronizing rock clocks of earth history. Science 320, 500–504.
Kusaba, K., Syono, Y., Kikuchi, M., Fukuoka, K., 1985. Shock behavior of zircon: phase transition to scheelite structure and decomposition. Earth Planet. Sci. Lett. 72, 433–439.
Kyte, F.T., Smit, J., Wasson, J.T., 1985. Siderophile inter-element variation in the Cretaceous–Tertiary boundary sediments from Caravaca, Spain. Earth Planet. Sci. Lett. 73, 183–195.
Leroux, H., Reimold, W.U., Koeberl, C., Hornemann, U., Doukhan, J.-C., 1999. Experimental shock deformation in zircon: a transmission electron microscopic study. Earth Planet. Sci. Lett. 169, 291–301.
Lourie, W., Alvarez, W., 1977. Upper Cretaceous–Paleocene magnetic stratigraphy at Gubbio, Italy III. Upper Cretaceous magnetic stratigraphy. Geol. Soc. Am. Bull. 88, 374–377.
Ludwig, K.R., 2003. User's Manual for Isoplot 3.00: A Geochronological Toolkit for Microsoft Excel. Special Publication, 4. Berkeley Geochronology Center. 71 pp.
MacLeod, K.G., Whitney, D.L., Huber, B.T., Koeberl, C., 2007. Impact and extinction in remarkably complete K/T boundary sections from Demerara Rise, tropical western North Atlantic. Geol. Soc. Am. Bull. 119, 101–115. doi:10.1130/B25955.1.
Martínez-Ruíz, F., Ortega-Huartas, H.M., Palomo, I., Acquafredda, P., 1997. Quench textures in altered spherules from the Cretaceous–Tertiary boundary layer at Agost and Caravaca, SE Spain. Sediment. Geol. 113, 137–147.
Mashimo, T., Nagayama, K., Sawaoka, A., 1983. Shock compression of zirconia ZrO_2 and zircon $ZrSiO_4$ in the pressure range up to 150 GPa. Phys. Chem. Miner. 9, 237–247.
Melosh, H.J., 1989. Impact Cratering: A Geologic Process. Oxford University Press, New York. 245 pp.
Melosh, H.J., Vickery, A.M., 1991. Melt droplet formation in energetic impact events. Nature 350, 494–497.
Montanari, A., 1991. Authigenesis of impact spheroids in the K/T boundary clay from Italy; new constraints for high-resolution stratigraphy of terminal Cretaceous events. J. Sediment. Res. 61, 315–339.
Montanari, A., Koeberl, C., 2000. Impact Stratigraphy: The Italian Record. Lecture and Notes in Earth Sciences. Springer-Verlag, Berlin. 364 pp.
Morgan, J., Warner, M., Brittan, J., Buffler, R., Camargo, A., Christeson, G., Denton, P., Hildebrand, A., Hobbs, R., MacIntyre, H., Mackenzie, G., Maguire, P., Marin, L., Nakamura, Y., Pilkington, M., Sharpton, V., Snyder, D., Suarez, G., Trejo, A., 1997. Nature 390, 472–476.
Morgan, J., Lana, C., Kearsley, A., Coles, B., Belcher, C., Montanari, S., Diaz-Martinez, E., Barbosa, A., Neumann, V., 2006. Analyses of shocked quartz at the global K–Pg boundary indicate an origin from a single, high-angle, oblique impact at Chicxulub. Earth Planet. Sci. Lett. 251, 264–279.
Moser, D., 1997. Dating the shock wave and thermal imprint of the giant Vredefort impact, South Africa. Geology 25 (1), 7–10.
Moser, D., Davis, W.J., Reddy, S.M., Flemming, R.L., Hart, R.J., 2009. Zircon U–Pb strain chronometry reveals deep impact–triggered flow. Earth Planet. Sci. Lett. 277, 73–79. doi:10.1016/j.epsl.2008.09.036.
Moser, D.E., Cupelli, C.L., Barker, I.R., Flowers, R.M., Bowman, J.R., Wooden, J., Hart, J.R., 2011. New zircon shock phenomena and their use for dating and reconstruction of large impact structures revealed by electron nanobeam (EBSD, CL, EDS) and isotopic U–Pb and (U-Th)/He analysis of the Vredefort dome. Can. J. Earth Sci. 48, 117–139. doi:10.1139/E11-011.
Mueller, P.A., Heatherington, A.L., Wooden, J.L., Schuster, R.D., Nutman, A.P., Williams, I.S., 1994. Precambrian zircons from Florida basement: a Gondwana connection. Geology 22, 119–122.
Norris, R.D., Huber, B.T., Self-Trail, J., 1999. Synchroneity of the K–T oceanic mass extinction and meteorite impact: Blake Nose, western North Atlantic. Geology 27, 419–422.
Pilkington, M., Ames, D.E., Hildebrand, A.R., 2004. Magnetic mineralogy of the Yaxcopoil-1 core, Chicxulub. Meteor. Planet. Sci. 39, 831–841.
Pope, K., 2002. Impact dust not the cause of the Cretaceous–Tertiary mass extinction. Geology 30, 99–102.
Premo, W.R., Izett, G.A., 1993. U–Pb provenance ages of shocked zircons from the K–T boundary, Raton basin, Colorado. Abstract, 24th Lunar and Planetary Science Conference, pp. 1171–1172.
Reddy, S.M., Timms, N.E., Trimby, P., Kinney, P.D., Buchan, C., Blake, K., 2006. Crystal-plastic deformation of zircon: a defect in the assumption of chemical robustness. Geology 34, 257–260. doi:10.1130/G22110.1.
Schulte, P., Stinnesbeck, W., Steuben, D., Kramar, U., Berner, Z., Keller, G., Adatte, T., 2003. Fe-rich and K-rich mafic spherules from slumped and channelized Chicxulub ejecta deposits at the northern La Sierrita area, NE Mexico. Int. J. Earth Sci. 92, 114–142.
Schulte, P., Deutsch, A., Salge, T., Berndt, J., Kontny, A., MacLeod, K.G., Neuser, R.D., Krumm, S., 2009. A dual-layer Chicxulub ejecta sequence with shocked carbonates from the Cretaceous–Paleogene (K–Pg) boundary, ODP Leg 207, Demerara Rise, western Atlantic. Geochim. Cosmochim. Acta 73, 1180–1204. doi:10.1016/j.gca.2008.11.011.
Schulte, P., Smit, J., Deutsch, A., Salge, T., Friese, A., Beichel, K., in press. Tsunami backwash deposits with Chicxulub impact ejecta and dinosaur remains from the Cretaceous–Palaeogene boundary in the La Popa basin, Mexico. Sedimentology. doi:10.1111/j.1365-3091.2011.01274.x.
Sclater, J.G., Parsons, B., Jaupart, C., 1981. Oceans and continents: similarities and differences in the mechanism of heat loss. J. Geophys. Res. 86, 11535–11552.
Sharpton, V.L., Dalrymple, G.B., Marin, L.E., Ryder, G., Schuraytz, B.C., Urrutia-Fucugauchi, J., 1992. New links between the Chicxulub impact structure and the Cretaceous/Tertiary boundary. Nature 359, 819–821.
Shukolyukov, A., Lugmair, G.W., 1998. Isotopic evidence for the Cretaceous/Tertiary impactor and its type. Science 282, 927–929.
Shuraytz, B.C., Sharpton, V.L., Marín, L.E., 1994. Petrology of impact-melt rocks at the Chicxulub multiring basin, Yucatán, Mexico. Geology 22, 868–872.
Sigurdsson, H., D'Hondt, S., Arthur, M.A., Bralower, T.J., Zachos, J.C., van Fossen, M., Channel, J.E.T., 1991. Glass from the Cretaceous/Tertiary boundary in Haiti. Nature 349, 482–487.
Smit, J., 1999. The global stratigraphy of the Cretaceous–Tertiary boundary impact ejecta. Annu. Rev. Earth Planet. Sci. 27, 75–91.
Smit, J., 2004. The section of the Barranco del Gredero (Caravaca, SE Spain): a crucial section for the Cretaceous/Tertiary boundary impact-extinction hypothesis. J. Iber. Geol. 31, 181–193.
Steiner, M.B., Walker, J.D., 1996. Late Silurian plutons in Yucatán. J. Geophys. Res. 101, 17727–17735.
Swisher III, C.C., Grajales-Nishimura, J.M., Montanari, A., Margolis, S.V., Claeys, P., Alvarez, W., Renne, P., Cedillo-Pardo, E., Mauresse, F.J.-M.R., Curtis, G.H., Smit, J., McWilliams, M.O., 1992. Coeval $^{40}Ar/^{39}Ar$ ages of 65.0 million years ago from Chicxulub Crater melt rock and Cretaceous–Tertiary boundary tektites. Science 257, 954–958.
Toon, O.B., Zahnle, K., Morrison, D., Turco, R.P., Covey, C., 1997. Environmental perturbations caused by the impacts of asteroids and comets. Rev. Geophys. 35, 41–78.
Wittmann, A., Kenkmann, T., Schmitt, R.T., Stöffler, D., 2006. Shock-metamorphosed zircon in terrestrial impact craters. Meteor. Planet. Sci. 41, 433–454. doi:10.1111/j.1945-5100.2006.tb00472.x.