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2. End-Cretaceous Acid Rain as a Selective Extinction Mechanism between Birds and Dinosaurs

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Abstract

Acid would have been a consequence of catastrophic events postulated for the Cretaceous-Tertiary boundary: nitric acid from atmospheric shock by bolides and from burning of trees; sulfuric acid from volcanic aerosols and from impact vaporization of evaporites; hydrochloric acid from volcanic aerosols; and carbonic acid from carbon dioxide of volcanoes, fires, and methane-hydrate release. Pedomassays for buffering of soil acid above pH 4 are indicated by the clayey, little-leached nature of latest Cretaceous and earliest Tertiary paleosols in Montana. Chemoassay of 2.7×10^{11} to 4.6×10^{17} moles of acid has been estimated from base-cation leaching of Cretaceous-Tertiary boundary beds and paleosols in eastern Montana, and these estimates are compatible with other independent chemoassays. Marine bioassay of pH suppression to no less than 7.6, allowing survival of coccolithophores, foraminifera, and dinoflagellates, requires a total acid load of less than 5×10^{16} moles. Similar limits come from a non-marine bioassay of pH suppression to less than 5.5 but no less than pH 4, allowing survival of amphibians and fish, but strong extinctions of non-marine mollusks in Montana. Acidification also may have been responsible for heavy extinctions among evergreen angiosperms. Vegetation browning would have been difficult for herbivorous dinosaurs and their predators, but less problematic for

small insectivorous and detritivorous mammals and birds. Acid rain may have been an important agent of selective mortality and extinction across the Cretaceous-Tertiary boundary.

Introduction

Although differences between birds and dinosaurs have been blurred by recent fossil finds (Qiang et al. 1998; Benton 1999; Burnham et al. 2000) and by cladistic theory (Chiappe 1995; Padian 1998), birds are still with us, but dinosaurs have been gone for 65 million years. Why did birds survive mass extinction at the Cretaceous-Tertiary boundary, and not dinosaurs? The general question of differential extinction is critical to understanding the role of catastrophic events in evolution (Jablonski 1996; Sheehan et al. 1996). What, if anything, do mass extinctions select? Although survival could have been just a matter of luck, or due to tolerance of impact winter, disease, allergies, or a long list of other potential causes of end-Cretaceous extinctions (Bakker 1986; Archibald 1996), this chapter examines just one proposition: that differential extinctions at the end of the Cretaceous were the result of acid generated by massive asteroid impact.

Catastrophic impact of a large bolide at the Cretaceous-Tertiary boundary is now established beyond scientific doubt in many localities and by many lines of evidence (fig. 2.1): iridium anomalies (Alvarez et al. 1980; Orth et al. 1990; Claeys et al. 2002); carbon and carbon isotopic anomalies (Wolbach et al. 1988; Arthur et al. 1987; Arens and Jahren 2000); nitrogen and nitrogen isotopic anomalies (Gilmour et al. 1990); shocked quartz (Bohor 1990; Izett 1990; Claeys et al. 2002); stishovite (McHone et al. 1989); nanometer-sized diamonds (Carlisle and Braman 1991); dramatic changes in fossil plants, including transient abundance of fern spores (Wolfe and Upchurch 1987; Nichols et al. 1990; Johnson and Hickey 1990); and a large impact crater in the Yucatan (Sharpton et al. 1993, 1996; Kring 1995; Morgan et al. 1997). Also at this time, there were submarine landslides around the North Atlantic Ocean (Norris and Firth 2002), and flood basalt eruptions of the Deccan Traps in India (Duncan and Pyle 1988; Courtillot et al. 1990), perhaps stimulated by impact seismicity (Boslough et al. 1996; Chatterjee 1997), as well as widespread wildfires set by the impact fireball, and later ignition of browned vegetation (Wolbach et al. 1988; Heymann et al. 1996).

Acid is a likely consequence of all these events: nitric acid from atmospheric shock by the bolide and from burning of trees (Zahnle 1990); sulfuric acid from volcanic aerosols and impact vaporization of evaporites (Sigurdsson et al. 1992; Brett 1992; Yang et al. 1996); hydrochloric acid from volcanic aerosols (Caldeira and Rampino 1990); and carbonic acid from carbon dioxide of volcanoes, fires, and methane oxidation (Wolbach et al. 1988; Tinus and Roddy 1990; Ivany and Salawich 1993). All this acid should have left records in paleosols (pedoassay), in boundary beds (chemoassay), and in the differential extinction of acid-sensitive organisms (bioassay): These three methods of assessing environmental acidification will each be considered in turn.

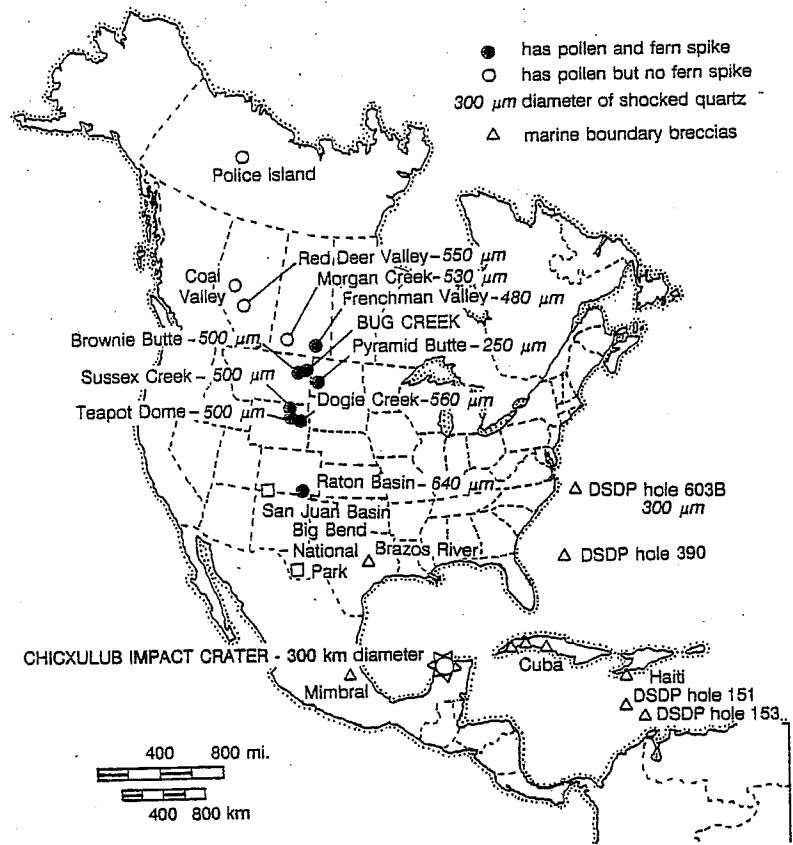


Figure 2.1. Locations of Bug Creek, Brownie Butte, and other important Cretaceous-Tertiary boundary sites in North America.

Figure 2.2. (below) The Cretaceous-Tertiary boundary paleosol sequence in Bug Creek, Montana.

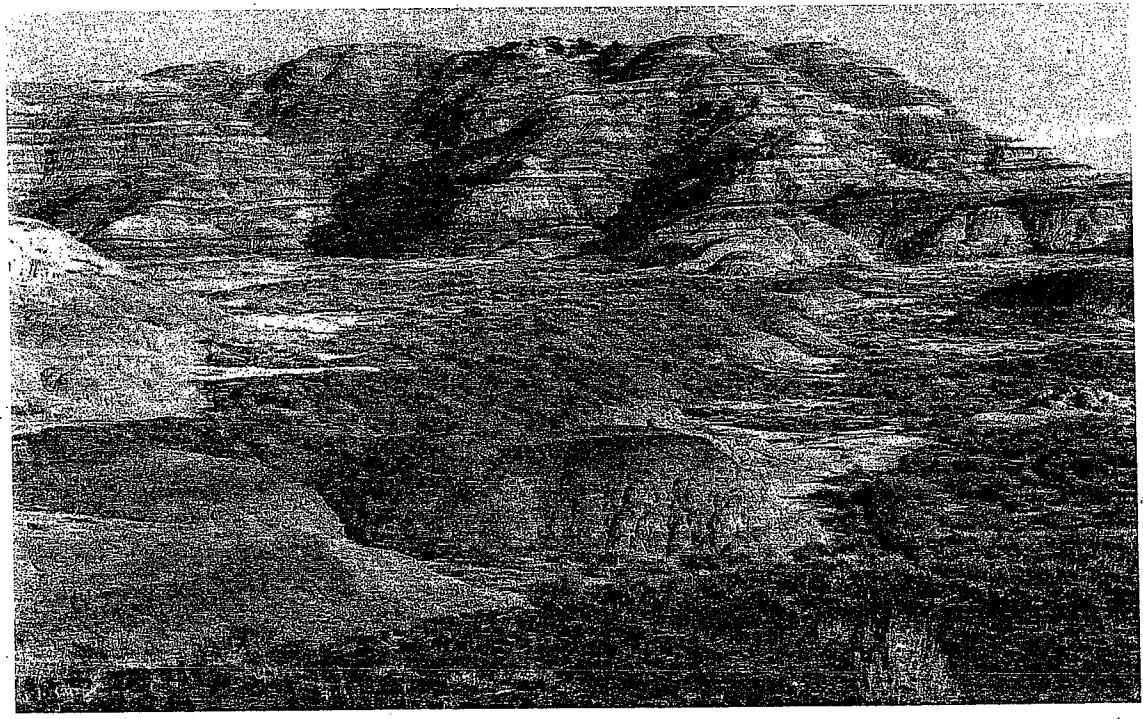
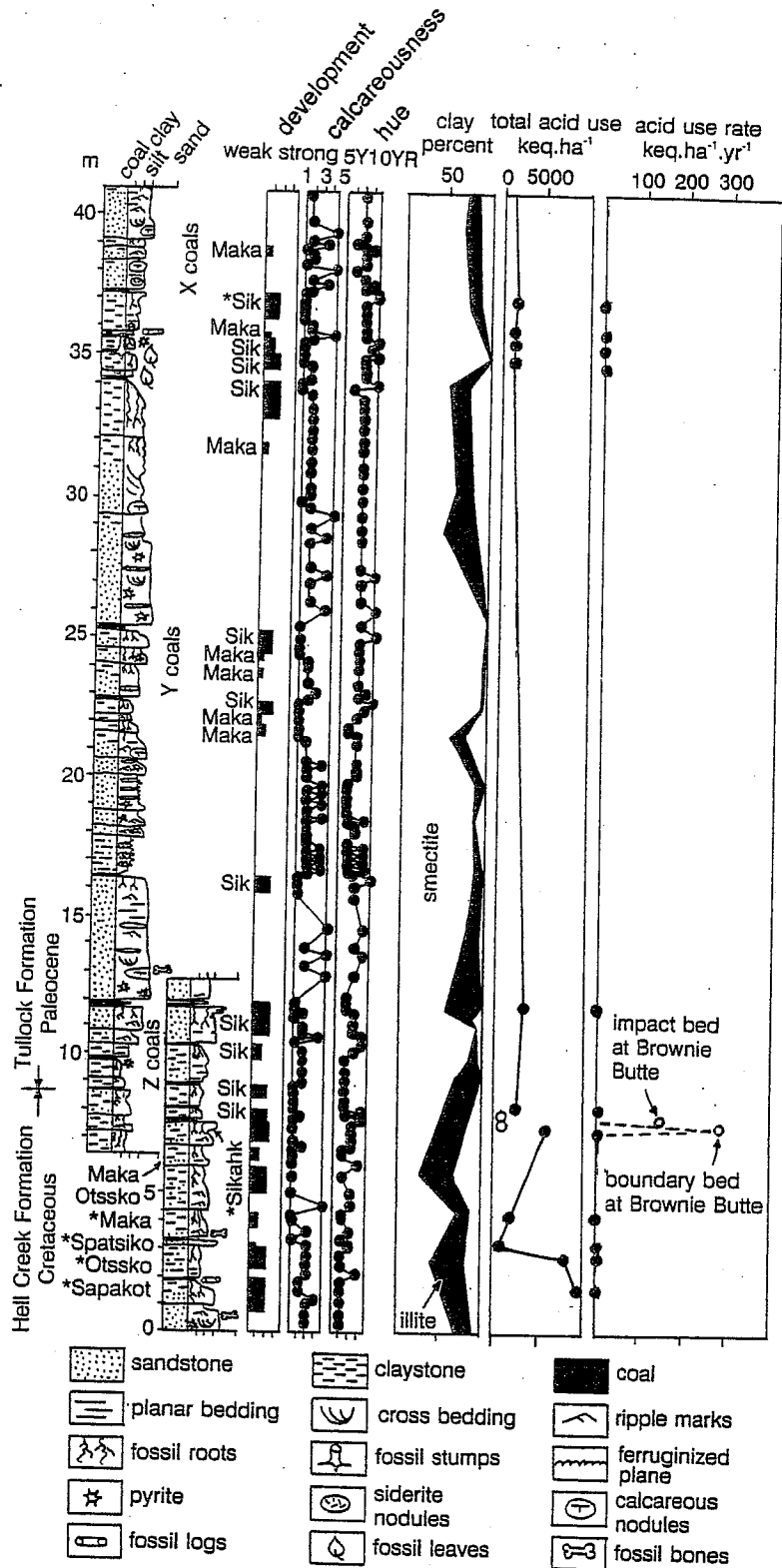


Figure 2.3. Measured section and acid use of paleosols across the Cretaceous-Tertiary boundary in Montana. Positions of individual paleosols are shown by black boxes in the development column, with width proportional to physical (not chemical) development. (Calcareousness was estimated by field application of dilute acid and hue from Munsell charts. Clay mineral proportions from Bell 1965, acid use from Retallack 1996.)



Pedoassay

Paleosols in the Bug Creek area of eastern Montana are a remarkably fossiliferous record of the Cretaceous-Tertiary boundary (figs. 2.1-2.3; Retallack et al. 1987; Retallack 1994). Only a weak iridium anomaly and no distinctive boundary beds have been found in Bug Creek (Smit et al. 1987; Rigby and Rigby 1990; Swisher et al. 1993), but the Cretaceous-Tertiary boundary can be located there by means of unusually abundant fern spores, fossil plant extinctions (Hotton 1988), and a carbon isotopic excursion (Arens and Jahren 2000). The last known dinosaur bone in place within a paleosol in this area is a poorly preserved *Triceratops* vertebral centrum 1 m below the palynologically defined extinction level, but bone is not unusually rare in paleosols 3 m below the extinction zone within the lower Z coal (Sheehan et al. 2000; contra Williams 1994). Dinosaur bone also is found in sandstone paleochannels at higher stratigraphic levels, where it was probably redeposited (Lofgren 1995; Archibald 1996). Although a case has been made for gradual extinction of dinosaurs (Sloan et al. 1986) and even for modest rather than mass extinction in this area (Archibald and Bryant 1990; Archibald 1996), comprehensive collections from nearby regions of Montana and North Dakota have shown that dinosaur extinction was abrupt at the level of the plant extinctions (Bryant 1989; Sheehan et al. 1991; Pearson et al. 1999; Sheehan et al. 2000). The dramatic plant extinctions revealed by pollen and spores (Hotton 1988; Nichols and Fleming 1990) are now supported by massive collections of fossil plants through this same region (Johnson and Hickey 1990). The "zone of death" revealed by fossil fern spores and the carbon isotopic excursion in Bug Creek (Hotton 1988; Arens and Jahren 2000) is a carbonaceous surface of a moderately developed paleosol (figs. 2.2, 2.3: Sikahk pedotype of Retallack 1994). Thin layers of impact ejecta found at many Cretaceous-Tertiary boundary sections (Bohor 1990; Izett 1990) were not found in Bug Creek, where they were presumably eroded away or mixed by the action of later roots and burrows of the Sikahk paleosol.

The gray and brown clayey paleosols and black lignitic paleosols of the upper Hell Creek and lower Tullock Formations in Bug Creek are representative of paleosols in these somber-colored formations over a wide area of the northern High Plains from Buffalo in South Dakota, to Marmarth in North Dakota, and Jordan in Montana, a distance of some 400 km (Fastovsky and McSweeney 1987; McSweeney and Fastovsky 1987). The lignitic facies of the Tullock Formation began accumulating well before the Cretaceous-Tertiary boundary in South Dakota, which was closer to the sea (Pearson et al. 1999), but only a little before the boundary in Bug Creek (Swisher et al. 1993). Thus the Cretaceous-Tertiary boundary fell at a time of local marine transgression, not the regression that has been advocated as a global explanation for end-Cretaceous events by Hallam (1987). The peaty paleosols of Montana represent swamps of water pine (*Glyptostrobus*) and dawn redwood (*Metasequoia*), which became much more widespread during

the Early Paleocene than Late Cretaceous. Even well-drained paleosols of the Hell Creek and Tullock Formations formed on terraces only a few meters above the water table in seasonally wet lowland floodplains. Mean annual rainfall in the latest Cretaceous as estimated from paleosols was 900–1,200 mm per annum, with an increase in the earliest Paleocene to more than 1,200 mm (Retallack 1994). These estimates from paleosols are compatible with paleobotanical estimates for a postapocalyptic humid greenhouse: latest Cretaceous Lance flora indicates mean annual temperature (MAT) of 16.2°C and mean annual precipitation (MAP) of 700–800 mm, earliest Paleocene Brownie Butte flora indicates MAT 27.4°C and MAP >3,500 mm, and later Paleocene Clareton flora indicates MAT 19.8°C and MAP 2,500 mm (Wolfe 1990). In these floodplain terrace soils, diverse Late Cretaceous broadleaf forests, with dicots such as "*Cissites*" *marginatus* and *Dombeyopsis trivialis*, were replaced in the earliest Paleocene with less diverse forests of dicots such as "*Populus*" *nebrascensis* and *Cercidiphyllum genatrix* (Johnson and Hickey 1990). The great diversity of dinosaurs in Late Cretaceous paleosols is completely missing from earliest Paleocene paleosols, which contain champsosaurs and other survivors of the extinction (Archibald and Bryant 1990; Archibald 1996). A striking feature of the paleosol record is the general similarity of Late Cretaceous and Early Paleocene paleosols, despite the very different species of plants and animals that they supported (Retallack 1994).

Paleosols at the Cretaceous-Tertiary boundary in Bug Creek were examined in order to quantitatively assess acidification, compared with paleosols in the same sequence above and below the boundary. These analyses aimed to determine depletion of acid-soluble bases, such as the alkaline earth (Ca, Mg) and alkali (Na, K) elements (Retallack 1996). Ordinary weathering is a process of acidification, and an acid rain signature can be detected only as an unusually severe depletion of weatherable bases. Thus acidification in the paleosol at the Cretaceous-Tertiary boundary needs to be compared with background acidification due to normal weathering of paleosols above and below the boundary. These analyses of major elements (fig. 2.4) and of rare earth trace elements (fig. 2.5) show significant acidification of the boundary paleosol compared within those stratigraphically above and below, but not so profound as would indicate strong acids. Barium/strontium and base/alumina molar ratios should be particularly sensitive to acidification, and these also fail to show profound perturbation (fig. 2.5). Nor do the metals Cu, Ni, and Zn show marked anomalies (fig. 2.4), as might be predicted from strong acidification or influx of meteoritic material (Davenport et al. 1990). The total amount of acid consumed by mineral horizons of four Cretaceous paleosols averaged 5,297 \pm 3,758 keq.ha⁻¹ acid (error of 1 Σ), but nine Paleocene paleosols used 2,069 \pm 1,481 keq.ha⁻¹ (Retallack 1996). Estimates of the rate of acid consumption also were made, using maximum values for duration of ancient soil formation estimated by comparison with studies of morphological (*not chemical*) differentiation of Quaternary soils. These calculated minimal rates of acid consumption of Late Cretaceous and Early Paleocene paleosols are not appreciably different from each other

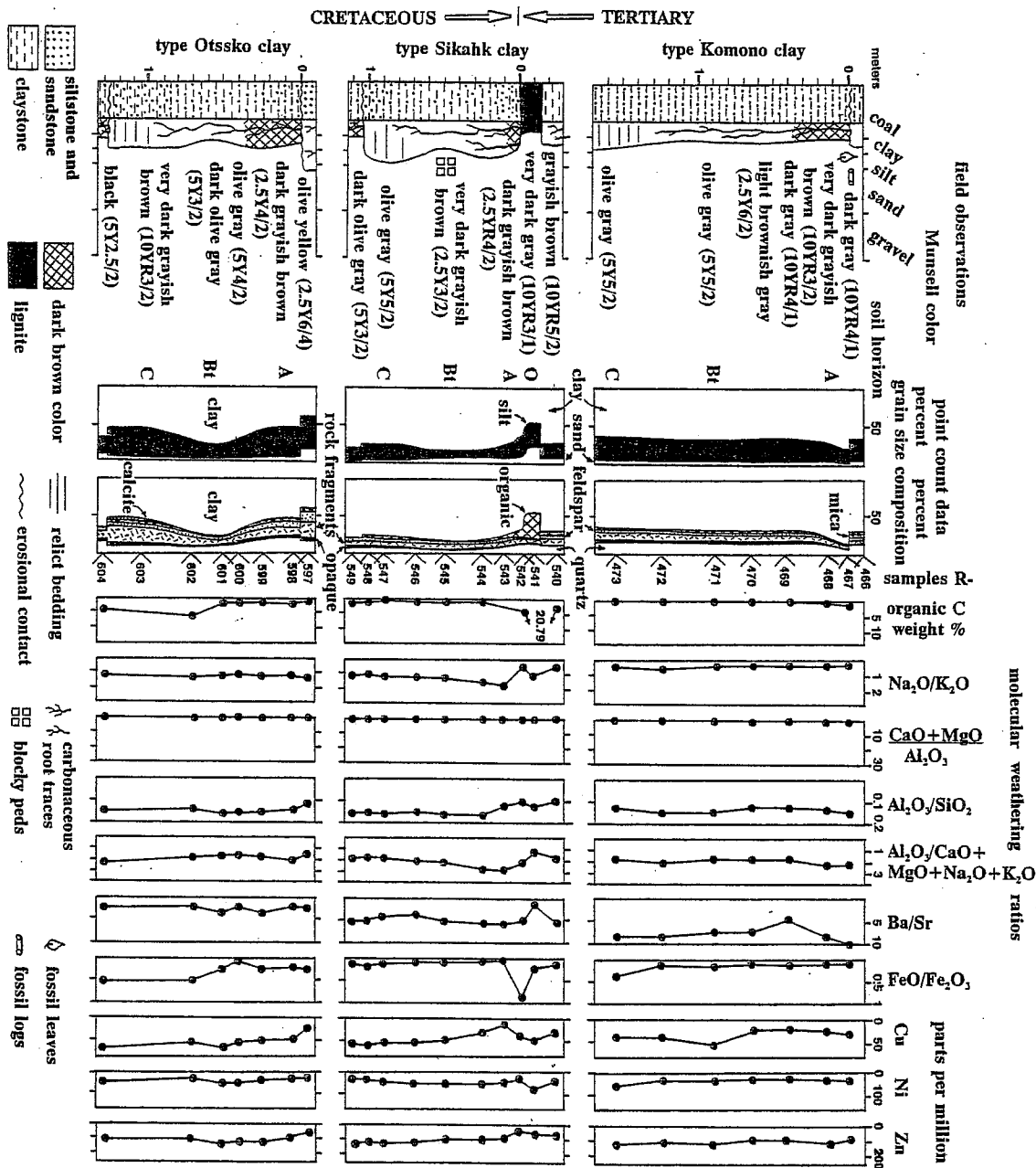


Figure 2.4. Chemical depth functions of paleosols at, above, and below the Cretaceous-Tertiary boundary in Bug Creek, Montana, showing little significant difference and no indications of podzolization at the boundary.

or from Holocene soils (Fölster 1985), which generally fall between limits of 0.2–2.3 keq.ha⁻¹.yr⁻¹. The four latest Cretaceous paleosols had an average rate of acid consumption of 2.0 +/- 1.7 keq.ha⁻¹.yr⁻¹ and 9 earliest Paleocene paleosols of 0.9 +/- 0.4 keq.ha⁻¹.yr⁻¹. Such calculations for 2 paleosols at the boundary in Bug Creek give an average consumption of 6,585 +/- 199 keq.ha⁻¹. These paleosols show profile differentiation and little remaining relict bedding compatible with some

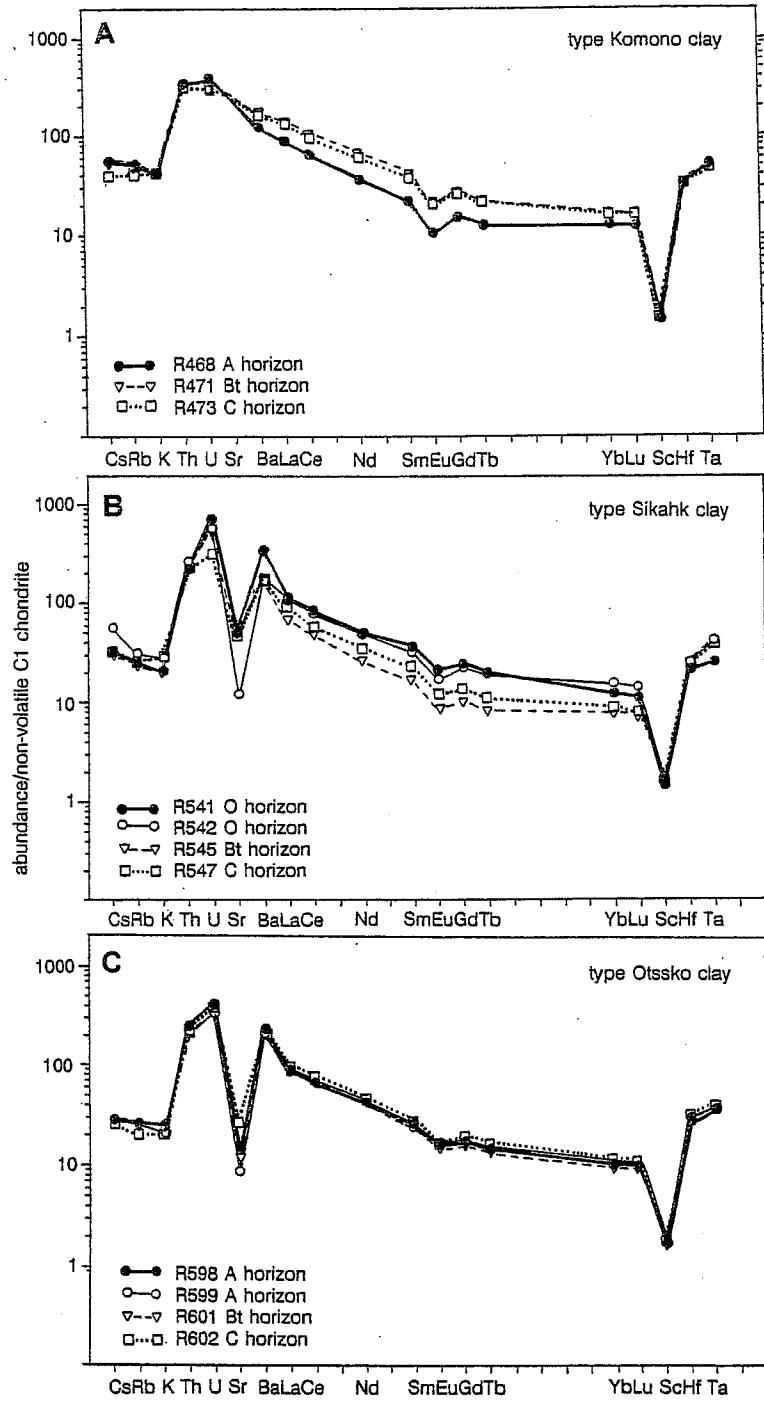


Figure 2.5. REE analyses normalized to North American shales of paleosols at, above and below the Cretaceous-Tertiary boundary in Bug Creek, Montana, showing slight, but not significant, spread of values in the boundary paleosol attributable to acid rain.

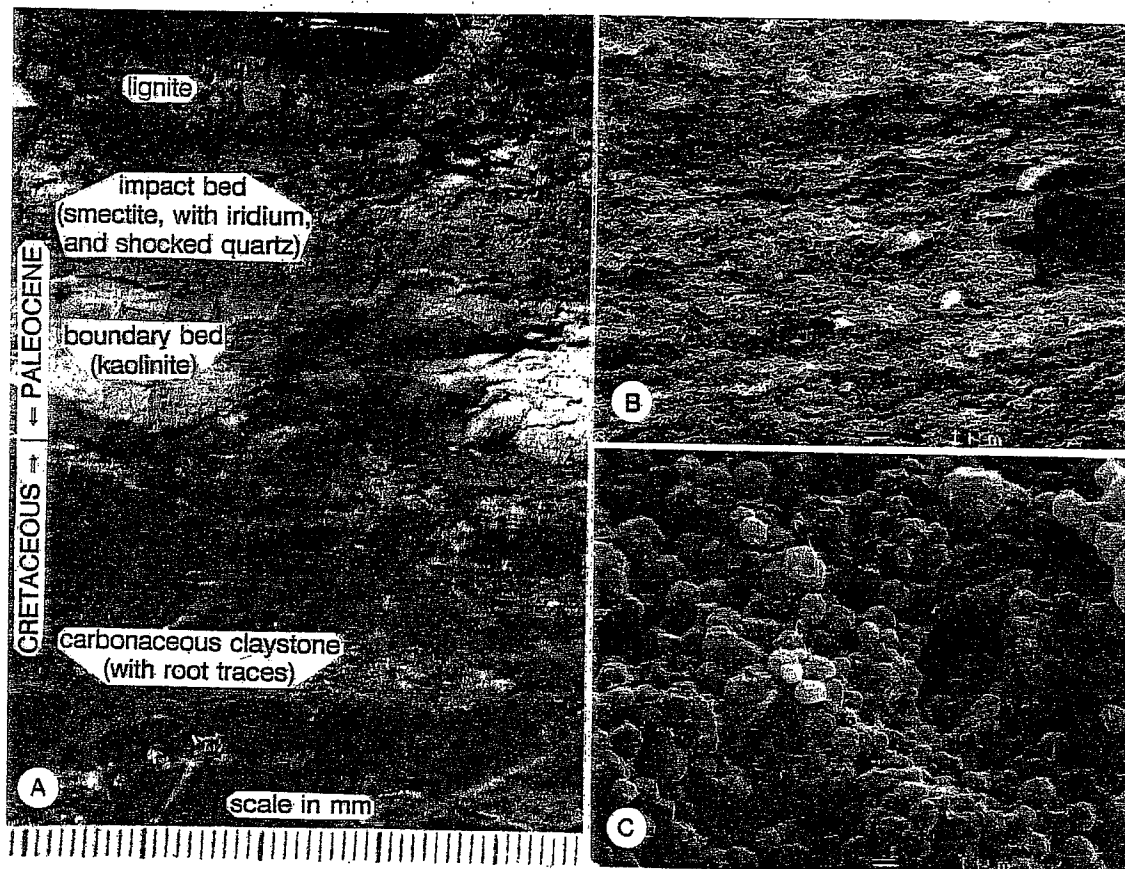


Figure 2.6. Cretaceous-Tertiary boundary beds at Brownie Butte, Montana, with their very different microstructures visible under SEM (B and C): A, field view of boundary bed and impact bed between terminal Cretaceous paleosol below and Paleocene lignite above; B, layered microstructure of impact bed under SEM; C, pelletoidal microstructure of boundary bed under SEM.

15,000 years of soil formation, which would give a rate of acid consumption of $0.2 \pm 0.006 \text{ keq} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. These estimates are permissive of either high acid load over a short time or of low acid load over a long time. They are highly dependent on time scales of observation, which are insufficiently resolved in Bug Creek. Nevertheless, these estimates do indicate acid consumption and place upper limits on amounts of acid involved.

Limits on acidification also come from the lack of petrographic or chemical evidence of podzolization in the boundary paleosols of Montana (Retallack 1994). Podzolization is a soil-forming process that creates quartz-rich soils locally cemented by iron oxides and organic matter (Spodosols), and it occurs at pH less than 4 (Lündstrom et al. 2000). Podzolization is also negated by a clay mineral study (Bell 1965) which found smectite abundant in paleosols above, below, and at the Cretaceous-Tertiary boundary (fig. 2.3). Base-rich clays such as smectite, as well as other chemical and petrographic data, are evidence that Late Cretaceous and Early Paleocene paleosols were Entisols, Inceptisols, Histosols, Ultisols, and Alfisols (Retallack 1994), not Spodosols. Podzolization involves not only destruction of clay, but also release of toxic metal cations (particularly of aluminum), which can affect organ-

TABLE 2.1
Estimates of pH in soils and waters at the Cretaceous-Tertiary boundary.

pH Constraint	Evidence	Author
2.0-4.0	theoretical impact-generated acid	Prinn and Fegley 1987
3.5-10.0	freshwater fish in Montana	Archibald 1996
4.0-10.0	amphibians in Montana	Archibald 1996
4.0-10.0	non-calcareous Alfisols in Montana (unpodzolized or salinized)	Retallack 1994
<5.5	freshwater clams and snails in Montana	Hartman 1998
5.4-8.2	marine foraminifera	d'Hondt et al. 1994
6.0-8.2	marine coccolithophorids	d'Hondt et al. 1994
7.6-8.2	marine dinoflagellates	d'Hondt et al. 1994

Note: Estimates accepted here are pH 4.0-5.5 for soil and groundwater in Montana and pH 7.6-8.2 for average ocean water.

isms more severely than acid alone (Howells 1995). The lack of evidence for podzolization is thus an important limit to acid load and other toxicity experienced by Cretaceous-Tertiary boundary paleosols in Montana. Thus some past theoretical estimates of acidification at the Cretaceous-Tertiary boundary of pH 2-4 are unreasonable (table 2.1).

Chemoassay

The key to quantitative assessment of acidification at the Cretaceous-Tertiary boundary is finding a geological setting in which the timing of acid input is well constrained, as for example between the various ejecta layers from Chicxulub Crater (Alvarez et al. 1995). At Brownie Butte, Montana (fig. 2.1), the Cretaceous-Tertiary meteoritic ejecta include an impact bed, which is 1 cm thick, gray, smectitic, and layered, with shocked quartz and an iridium anomaly (fig. 2.6). It lies directly above the boundary bed, which is 2 cm thick, pink to white, kaolinitic, microspherulitic, and vuggy. These two distinctive thin beds have been discovered at 30 sites from Alberta and Saskatchewan south to New Mexico at the radiometrically and palynologically determined Cretaceous-Tertiary boundary (Bohor 1990; Izett 1990). The boundary bed at Brownie Butte has been interpreted as a paleosol with roots (Fastovsky et al. 1989), but the carbonaceous structures in the boundary bed are plant stalks, 5 mm or more in diameter, and frayed upwards (fig. 2.4). They lack the fine rootlets and downward taper of roots. The

boundary bed has a trace element chemical composition most like glassy ejecta from an early ejecta blanket of melt, shocked rocks, and admixed seawater. Shocked quartz is rare in the boundary bed, but more common in the impact bed, which was probably deposited within hours by fallout from a warm fireball (Alvarez et al. 1995). Significantly, the thin boundary bed consumed much more acid than the overlying impact bed. Even if both beds were subsequently acidified further within the peaty paleosol, as argued for other kaolinitic coal partings (Staub and Cohen 1978; Demchuck and Nelson-Glatiotis 1993), their differential leaching gives a minimal acid titer. Vigorous early neutralization of hot acid by silicate ejecta may explain both the distinctive kaolinitic composition and the microspherulitic and vuggy texture of the boundary bed, in which most shocked quartz has been destroyed by profound chemical leaching (Retallack 1996).

Quantification of acid consumption of the boundary bed compared with the overlying impact bed relies on procedures developed for studies of modern soil acidification (Fölster 1985). The loss of basic cations can be used to calculate the moles of hydronium consumed from weight percent analytical values and bulk density compared with parent materials of Cretaceous-Tertiary boundary beds and paleosols (Retallack 1996). The boundary claystone is more acidified by at least $5.4 \text{ keq}\cdot\text{ha}^{-1}$ than the sharply overlying, well-bedded, smectitic impact layer. This is an enormous amount of acid for the mere hours to days between accumulation of boundary and impact beds envisaged (Alvarez et al. 1995). For comparison, after the experimental application of rain of pH 3.5, a modern soil from near Unadilla in upstate New York maintained a pH of 4.1 in mineral horizons and lost $7.8 \text{ keq}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ from these horizons (Cronan 1985), which is comparable to the loss estimated here for the boundary bed in Montana and about three times the loss from weak acids (Fölster 1985). Thus strong acids and acid rain are indicated at the Cretaceous-Tertiary boundary, rather than only ordinary weathering or weak acids such as carbonic acid.

Such calculations can also be done with a variety of other conceivable parent materials for the kaolinitic boundary bed: local Cretaceous and Paleocene sediments (Retallack 1994), melt rock from Chicxulub Crater, Mexico (Hildebrand et al. 1991), and impact glasses from Beloc, Haiti (Sigurdsson et al. 1991, 1992) and Mimbral, Mexico (Smit et al. 1992). These various calculations give estimates of from 2.7×10^{11} to 4.6×10^{17} moles of acid produced by the terminal Cretaceous impact within hours between settling of the boundary and impact beds (Retallack 1996).

These estimates are compatible with completely independent chemassays derived from the anomalous enrichment of $^{87}\text{Sr}/^{86}\text{Sr}$ in marine foraminifera at the Cretaceous-Tertiary boundary (MacDougall 1988; Martin and MacDougall 1991). This spike in strontium of continental origin is best explained as a product of increased acid-induced weathering of ^{87}Sr on land. Scaling up to this anomaly from modern deliveries of ^{87}Sr to the ocean gives a spike of 3.8×10^{15} moles of acid at the Cretaceous-Tertiary boundary (Vonhof and Smit 1997).

TABLE 2.2
Estimates of total acid produced by Cretaceous-Tertiary boundary impact

Acid Production	Basis of Estimate	Author
6×10^{14} to 1×10^{15} moles NO	impact shocking atmospheric N ₂	Prinn and Fegley 1987
1×10^{14} to 1×10^{15} moles HNO ₃	impact shocking atmospheric N ₂	Zahnle 1990
1×10^{16} moles SO ₂	impact vaporization of sulfate evaporites	Morgan et al. 1997
2×10^{14} to 1.3×10^{17} moles H ₂ SO ₄	impact vaporization of sulfate evaporites	Brett 1992; Sigurdsson et al. 1992
$2-20 \times 10^{16}$ equivalents acid	impact vaporization of evaporites	Yang et al. 1996
$<1 \times 10^{16}$ moles H ₂ SO ₄ or $<4 \times 10^{15}$ moles HNO ₃	preservation of marine microplankton	d'Hondt et al. 1994
3.8×10^{15} equivalents acid	⁸⁷ Sr/ ⁸⁶ Sr perturbation at boundary in marine rocks	Vonhof and Smit 1997
2.7×10^{11} to 4.6×10^{17} equivalents acid	acidification of non-marine boundary beds, Montana	Retallack 1996
$4,511 \pm 330$ ppmV CO ₂	stomatal index of fossil ginkgo leaves	Retallack 2001

Note: Estimates accepted here are less than 10^{16} equivalents of all acids combined.

These chemoassays from the boundary beds and ⁸⁷Sr/⁸⁶Sr anomaly support some, but not all, theoretical estimates of acid production by impact and its attendant effects (tables 2.1, 2.2). Theoretical estimates on the production of NO₂ by a bolide capable of creating Cretaceous-Tertiary iridium anomalies have varied from 1×10^{14} to 1.2×10^{17} moles (Lewis et al. 1982; Prinn and Fegley 1987; Zahnle 1990) or some 2–2,350 keq.ha⁻¹ of the earth's surface area. An additional source of acid on short time scales is vaporization of anhydrite evaporites under the impact crater of Chicxulub, Mexico. This may have produced 4×10^{17} to 1.3×10^{19} g SO₂ (Brett 1992; Sigurdsson et al. 1992), which is 6.2×10^{15} to 2.0×10^{17} moles, or 254–7,840 keq.ha⁻¹ globally. Wildfires would produce comparable amounts of NO and CO₂ (Zahnle 1990), perhaps focused at the boundary (Wolbach et al. 1988; Tinus and Roddy 1990). An additional estimate from hypothetical oceanic titration (d'Hondt et al. 1994) is a total acid load of no more than 5×10^{16} moles, or 980 keq.ha⁻¹ globally. The chemoassays already presented here indicate that lower estimates of acid load are reasonable, but the higher estimates are excessive. Nitrogen and nitrogen isotopic studies (Gilmour et al. 1990) and sulfur and sulfur isotopic studies (Yoder et al. 1995) of the Cretaceous-Tertiary boundary are evidence that both nitric and sulfuric acids were involved. A combination of both acids not exceeding 10^{16} moles seen from the boundary beds in Montana is further indication

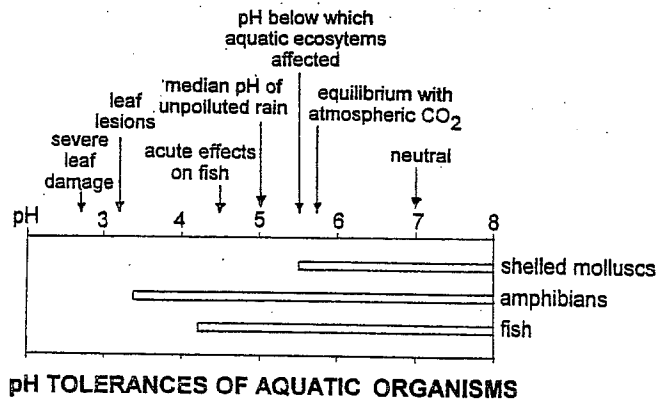


Figure 2.7. Tolerances of aquatic organisms for different pH levels. (After Howells 1995)

that estimates of the load of each acid approaching this value are also excessive, unless there was some other buffer of acidity such as scrubbing by silicate dust entrained in the ejecta cloud (Retallack 1996).

Bioassay

The pH of modern lakes fluctuates daily and seasonally, and it is convenient to assess acidification by bioassay, that is to say from the presence or absence of species of fish or invertebrates of known pH tolerance (Howells 1995). In the case of the Cretaceous-Tertiary boundary, such bioassay would be crude and done at high taxonomic levels (fig. 2.7), because pH tolerances of individual extinct species are not known. The patterns of survival of freshwater mollusks, fish, and amphibians in Montana are particularly instructive (table 2.3). Aquatic mollusks suffered severe extinctions, with termination of most lineages of shelled bivalves and gastropods (Hartman 1998). Amphibians and fish were less affected, but suffered moderate extinction (table 2.3; Archibald and Bryant 1990; Weil 1994), especially if the diverse Bug Creek Anthills assemblage is disregarded as a fauna largely of earliest Paleocene fossils, with some admixed latest Cretaceous fossils (Lofgren 1995). Shelled mollusks would have been excluded by pH less than 5.5, but greater losses of fish and amphibians would have been expected at pH less than 4 (Weil 1994; Howells 1995). This crude bioassay thus limits terminal Cretaceous freshwater acidification in Montana to between pH 4 and 5.5. This result is in agreement with the idea advanced above, that acid buffering by calcareous smectitic soils of Montana was sufficient to prevent pH depression below 4, and to keep podzolization and heavy metal toxicity from Montana during the Cretaceous-Tertiary transition.

Yet other bioassays have been attempted for the ocean by d'Hondt et al. (1994) who noted that surface dwelling ammonites and coccolithophores suffered severe extinction, but other bottom-dwelling mollusks, as well as radiolarians and acid-sensitive dinoflagellates, survived (table 2.3). From this pattern of extinction the whole ocean could

TABLE 2.3
End-Cretaceous extinctions of fossil species from the upper
Hell Creek Formation of Montana and adjacent states

Taxon	Number of Late Cretaceous Species	Percent of Species Extinct at K/T Boundary
Plant leaves (ferns, horsetails, conifers, angiosperms)	40	79
Pteridophrye spores (ferns, horsetails)	36	25
Gymnosperm pollen (seed ferns, cycadeoids, conifers)	14	36
Angiosperm pollen (flowering plants)	149	51
Bivalvia (freshwater clams)	28	100
Insecta (damage types to leaves)	51	27
Elasmobranchi (sharks and rays)	5	100
Chondrostei and Holosteii (gars and sturgeons)	7	29
Teleostei (bony fish)	8	50
Amphibia (frogs and salamanders)	8	0
Choristodera (champsosaurs)	1	0
Crocodylia (alligators)	5	40
Testudines (turtles)	17	12
Squamata (lizards, snakes)	10	70
Pterosauria (flying reptiles)	1	100
Ornithischia (ceratopsians, ankylosaurs, duckbills)	10	100
Saurischia (tyrannosaurs and other theropods)	9	100
Aves (birds)	20	55
Multituberculata (multituberculate mammals)	10	50
Eutheria (condylarths and other early mammals)	6	0
Metatheria (marsupials)	11	91

Sources: Brodkorb (1963), Estes (1964), Estes and Berberian (1970), Nichols et al. (1990),
Nicols and Fleming (1990), Johnson and Hickey (1990), Archibald and Bryant (1990),
Lofgren (1995), Archibald (1996), Hartman (1998), Labandeira et al. (2002).
Note that the concept of species varies from pollen to leaves, and from plants to animals.

not have been acidified to less than pH 7.6, though more substantial acidification could have occurred in shallow and isolated parts of the sea. Whole ocean pH depression to 7.6 could still accommodate a total acid load of 1×10^{16} moles, such is the mixing and buffering power of the ocean (d'Hondt et al. 1994).

A different kind of bioassay for carbonic acid has recently emerged from studies of *Ginkgo* leaf cuticles across the Cretaceous-Tertiary boundary (Retallack 2001). With postindustrial atmospheric pollution, the leaves of vascular plants have reduced the density of their stomates, because this allows intake of comparable amounts of carbon dioxide while curbing water transpiration in a warmer atmosphere. The observed decline since 1888 in stomatal index, which is density normalized to changing cell size, together with greenhouse experiments (Beerling et al. 1998), has been used to estimate atmospheric carbon dioxide from stomatal index of fossil *Ginkgo* leaves, with the following results: earliest Paleocene atmospheric carbon dioxide of $4,511 \pm 330$ ppmV, much higher than Late Cretaceous ($1,194 \pm 505$ ppmV) and later Paleocene ($1,350 \pm 350$ ppmV) concentrations of this greenhouse and acidic gas (Retallack 2001). This transient spike of carbon dioxide would have come from biomass decay and burning (Ivaney and Salawich 1993), but a methane-dissociation component cannot be ruled out (as for the Aptian isotopic excursion documented by Jahren et al. 2001). The greenhouse high of carbon dioxide would have lasted no longer than 50,000 years, judging from the duration of the associated carbon isotopic anomaly (Arens and Jahren 2000). Carbon dioxide would have been rained out as carbonic acid, but the effects of this on soils are difficult to appraise, because comparably high concentrations of carbonic acid are created by soil respiration even under modern conditions (Brook et al. 1983).

Acid Rain and Selective Extinction

The pedoassays, chemoassays and bioassays presented above indicate that acid rain was a consequence of the latest Cretaceous asteroid impact in Yucatan, and put quantitative limits on its magnitude (tables 2.1, 2.2). The differential extinction of plants, insects, mammals, birds, and dinosaurs in Montana and adjacent states can be reassessed from this perspective. Also of interest is how consistent patterns and circumstances of extinctions are with other kill mechanisms, such as darkness from clouds of ejecta for days to months (Zahnle 1990), impact winter for 1–2 months (Wolfe 1991), wildfires for weeks to months (Wolbach et al. 1988; Tinus and Roddy 1990), and postapocalyptic greenhouse (Wolfe 1990; Landis et al. 1996). The duration of the postapocalyptic greenhouse has been estimated as 0.5–1 million years from paleobotanical data (Wolfe 1990), but its reflection in the carbon isotopic excursion in Montana is only about 50,000 years (Arens and Jahren 2000). Direct kill by vaporization, tsunami, and burial by debris within the blast zone of the Caribbean was probably not significant in Montana, 3,330 km north of ground zero in Yucatan (Kring 1995).

Terrestrial Plants

Acidic trauma may explain the transition in Montana from eutrophic angiosperm-dominated semievergreen forests, to a fern-dominated recovery flora, and then to oligotrophic conifer-dominated swampland and woodlands of deciduous dicots (Wolfe and Upchurch 1987; Johnson and Hickey 1990). Acidic browning, then burning and decay of green plants, may partly explain the marked lightening in $\Delta^{13}\text{C}_{\text{org}}$ across the Cretaceous-Tertiary boundary (Ivany and Salawich 1993), but excursions of as much as -2.8‰ $\Delta^{13}\text{C}_{\text{org}}$ in non-marine facies of Montana (Arens and Jahren 2000) approach levels better explained by methane hydrate dissociation (Jahren et al. 2001). Extinction levels are much higher among angiosperm pollen than among conifer pollen and fern spores (Nichols and Fleming 1990). Both acid rain and the noxious nitrous and sulfurous precursor gases would have browned broad evergreen leaves, thus selecting for deciduous plants, as seen among both dicots and conifers (Wolfe 1987). Acid rain leaching into soil would have created less fertile substrates (such as the Ultisol of the Sikahk paleosol of Retallack 1994), thus selecting for oligotrophic taxa. Other extinction mechanisms are not as well supported by the fossil plant record. Although it could be argued that impact winter would have similar effects of extinguishing evergreen rather than deciduous angiosperms (Wolfe 1987), survival of palm pollen (*Arecipites* of Nichols et al. 1990) and leaves (Wolfe 1991) is evidence against fatal chilling. Furthermore, evergreen plants did not re-emerge from refugia during the Early Paleocene, as they did after full glacial chillings of the Pleistocene (Wolfe 1987), which modeling reveals was comparable to impact chilling from massive aerosol loadings (Covey et al. 1990). Damage to leaf cuticles at the Cretaceous-Tertiary boundary at Teapot Dome, Wyoming, has been claimed as evidence of transient freezing in spring, when water lily and lotus were in bloom (Wolfe 1991). However, comparable lesions on anticlinal walls of plant cells also can be created by acid pollution of living leaves (Adams et al. 1984). I have observed similar deformation with my own overenthusiastic preparation of fossil plant cuticles. Wildfire is an unlikely cause of the plant extinctions, even though charcoal is common in the paleosols (Retallack 1994), because less flammable evergreen dicots were less prone to extinction than resinous conifers (Johnson and Hickey 1990). Recolonization after fire could explain the earliest Paleocene abundance of fern spores and, in the Raton Basin, of fern leaves like those of *Stenochlaena*, a well-known volcanic recolonizer today (Wolfe and Upchurch 1987). Nor is darkening of the sky with dust apparent from the pattern of plant extinction, because this alone would etiolate evergreen dicots, rather than kill and brown their leaves. Warming during a multimillennial postapocalyptic greenhouse is indicated by ecophysiological interpretation of fossil leaves (Wolfe 1990), but not from their taxonomic composition. Compared with those of the Cretaceous, Paleocene fossil plants have decidedly more temperate climatic modern affinities, presumably as an indirect legacy of boundary events (Wolfe 1987).

Terrestrial Invertebrates

Few insects are known from the Cretaceous-Tertiary boundary beds of Montana and adjacent states, but much can be learned from insect damage of abundant fossil leaves (Labandeira et al. 2002). Serpentine leaf mines like those of gracillariid moths, slot-hole feeding like that of Curculionid beetles, and pit feeding like that of Cerambycid beetles in Late Cretaceous leaves are specific to particular kinds of leaves, but earliest Paleocene insect damage lacks specificity for particular host plants and is less diverse (table 2.3). Host-specific insects become extinct with their plant hosts, but generalist plant-feeding insects turn to dead plant material when all other sources of food become unavailable. The record of insect trace fossils thus supports the contention of Sheehan and Hansen (1986) that feeding on dead plant material (detritivory) was critical to survival across the Cretaceous-Tertiary boundary.

Earthworms (Oligochaeta) are also detritivorous and are represented by ellipsoidal fecal pellets in petrographic thin sections of both Late Cretaceous and Early Paleocene paleosols (Retallack 1994). Burrowing bugs (Cydnidae) also are partly detritivorous, and may be represented by backfilled burrows in earliest Paleocene sediments at Pyramid Butte, North Dakota (Johnson 1989). Detritivorous soil invertebrates would be least affected by impact winter, postapocalyptic greenhouse, wildfires, or acid rain, with both their food and environment buffered from surficial chemical and physical assault.

Aquatic Invertebrates

Non-marine snails and clams suffered severe extinction in North America (Hartman 1998). Extinction among mollusks was less severe in the ocean (Jablonski 1996), which was a much larger and better-buffered system than streams and lakes of Montana. Nevertheless, many calcareous shelled organisms such as ammonites were terminated, and others such as coccolithophores and foraminifera suffered heavy extinction (d'Hondt et al. 1996; Marshall and Ward 1996). Analysis of different lineages whose feeding behavior can be inferred from living relatives reveals that the keys to survival across the Cretaceous-Tertiary boundary were starvation resistance (for example by low basal metabolic rate), sessile habit, detritivory, and non-planktotrophic larvae (Jablonski 1996). Among phytoplankton, those with cysts and spores suffered less severe extinction than those without resting stages (Kitchell et al. 1986). These patterns of extinction are consistent with carbon isotopic and other evidence for a catastrophic crash in primary productivity in the ocean (Arthur et al. 1987; Rhodes and Thayer 1991; Gallagher 1991). The primary production loss in the ocean was mainly unicellular phytoplankton rather than higher plants affected on land, and it is likely that non-marine phytoplankton production was also affected.

Aquatic Vertebrates

Most aquatic animals such as turtles, frogs, salamanders, and

champsosaurs fared relatively well across the Cretaceous-Tertiary boundary (Sheehan and Fastovsky 1992). Dead and decaying plant detritus is at the base of the food chain in many aquatic ecosystems, supporting amphibians, small fish, and turtles, which in turn support crocodiles and large fish (Webster 1983). Environmental acidification would be expected to generate widespread leaf browning and fall, clogging streams and lakes with plant detritus. Survival of large aquatic ectotherms such as champsosaurs and crocodiles is evidence that chilling due to impact winter was either not severe or very limited in duration (Wolfe 1991).

Sharks and rays are rare and suffer heavy terminal-Cretaceous extinction in non-marine facies of Montana (table 2.3), in contrast to marine facies where such fossils are common and do not show profound overturn (Kordikova et al. 2001). A few sharks and rays may have colonized fresh or estuarine waters during the Late Cretaceous (Archibald 1996). Their local extinction in Montana may have been due to change toward less marine-influenced facies, and shifting marine-biogeographic connections from Tethyan to Boreal from Cretaceous to Paleocene (Archibald et al. 1993).

Non-Dinosaurian Reptiles

Most Montanan lizards and snakes were extinguished at the Cretaceous-Tertiary boundary. Many species found in the upper Hell Creek Formation, including boas and monitor lizards, were probably terrestrial insectivores and carnivores. One species was perhaps a shell crusher (Archibald 1996). A large (3-m-long) monitor lizard (*Palaeosaniwa*) was probably an ambush carnivore. With limited ties to aquatic ecosystems, poor burrowing ability, and naked skin unprotected by fur or feathers, these creatures would have fared poorly in acidified soils.

Only one pterosaur, an azhdarchid comparable to *Quetzalcoatlus*, is known from latest Cretaceous rocks of Montana and adjacent states (Estes 1964; Archibald 1996). This was probably a scavenger of large dinosaur carcasses, and became extinct with the dinosaurs (Wellnhofer 1991). Perhaps piscivorous, insectivorous, and detritivorous niches of earlier Mesozoic pterosaurs had already been usurped by birds during the Late Cretaceous.

Mammals

Extinction was heavy among mammals at the Cretaceous-Tertiary boundary, though not as severe as indicated by the figures for species-level extinction given here (table 2.3), because eutherians, marsupials, and multituberculates all survived into the Paleocene and founded a dramatic evolutionary radiation (Sloan et al. 1986). Eutherians and deltatherians all had sharp-cusped teeth and were probably insectivorous (Kielan-Jaworowska et al. 1979a,b). Late Cretaceous multituberculates and marsupials included insectivores, omnivores, shell crushers, and herbivore-frugivores, but only insectivorous and omnivorous forms survived into the Paleocene (Clemens 1979; Clemens and Kielan-Jaworowska 1979; Krause 1984; Archibald 1996). Mollusks, fresh

leaves, and fruit were probably scarce at the Cretaceous-Tertiary boundary, when simplified food chains were based on dead plant matter, with insects and other invertebrates that feed on such detritus (Sheehan and Hansen 1986). Although clear fossorial adaptations are not yet known from Cretaceous mammals (Kielan-Jaworowska et al. 1979a; Novacek 1996), all were small. They may have survived transient cold, dark, and heat within hollow logs, caves, or burrows.

Dinosaurs

Large carnivorous and herbivorous dinosaurs were terminated at the Cretaceous-Tertiary boundary instantaneously within limits of resolution (10^1 – 10^3 years) of the record (Sheehan et al. 1991, 2000; Pearson et al. 1999). Redeposition of bone in paleochannels, lack of bone preservation in non-calcareous paleosols, and statistical artifacts of range extensions all potentially compromise this conclusion (Fassett et al. 2002), but have been addressed at length (Retallack 1994; Lofgren 1995; Marshall 1998). An especially promising, and still little exploited, line of evidence is fossil footprints, which are clear evidence of living dinosaurs in place. Tracks of large duckbill dinosaurs have been found on the last sandstone bed suitable for their preservation, only 37 cm below the Cretaceous-Tertiary boundary beds in Colorado (Lockley 1991), again effectively at the boundary within temporal resolution for this fluvial sequence.

Latest Cretaceous duckbill and ceratopsian dinosaur herbivores had specialized dental batteries for processing large quantities of fresh leaves. Specializations for carnivory in latest Cretaceous theropod dinosaurs include sickle claws and fearsome arrays of sharply crested and serrated teeth, well suited for killing and slicing large quantities of fresh meat (Paul 1988a). None of these herbivorous or carnivorous specializations had any parallel among Late Cretaceous or Early Paleocene mammals or birds. Large dinosaurian herbivore extinction may have followed leaf browning and fall from acidification. Large carnivores would follow herbivores into extinction, unable to sustain themselves on small insectivorous and piscivorous mammals and birds.

Other extinction mechanisms are less appealing. Dinosaurs were no strangers to wildfires, either in the earlier Mesozoic (Harris 1957, 1981) or in the latest Cretaceous of Montana (Retallack 1994, 1997). Dinosaur bones and eggs in Indian paleosols between the first few basalts of the Deccan Traps are found only as high as the iridium anomaly (Courtilot et al. 1990; Bhandari et al. 1996; Sahni et al. 1994; Chatterjee 1997), and so support the idea of extinction related to impact rather than due to local volcanic eruption. Climatic extremes are unlikely to have extinguished dinosaurs either, because they lived at both high and low latitudes (Paul 1988b; Clemens and Nelms 1993; Vickers-Rich and Rich 1993; Hammer and Hickerson 1994). Wildfires, volcanic eruptions, impact winter, transient dust clouds, and post-apocalyptic greenhouse conditions are unlikely to have terminated such a successful, diverse, and widespread clade of ecologically dominant organisms.

Birds

Latest Cretaceous and earliest Paleocene birds remain poorly known. Eight species of birds including two loon-like divers (Gaviiformes), a flamingo-like wader (Ciconiiformes), four shorebirds (transitional Charadriiformes), and a toothed bird (Ichthyornithiformes) have been described from the Late Cretaceous Lance Formation of Wyoming (Brodkorb 1963; Estes 1964). A latest Cretaceous enantiornithiform (*Avisaurus*) is known from the upper Hell Creek Formation of Montana (Chiappe 1992; Archibald 1996), along with many undescribed species (Stidham, 2002). In North America there were at least 20 species of latest Cretaceous birds, but only seven sure and two dubious species of earliest Paleocene birds (Stidham pers. comm. 2002). The earliest Paleocene, Bug Creek Anthills assemblage includes bones of at least one species referable to the Late Cretaceous genus *Cimolopteryx* (Estes and Berberian 1970), which was an avocet-sized shorebird (transitional Charadriiformes) with some similarities to avocets (Recurvirostridae), thick-knees (Burhinidae), and pratincoles (Glareolidae; Brodkorb 1963). Both molecular biological (Cooper and Penny 1997) and paleontological evidence (Chiappe 1995) indicate that crown-group birds (Neornithes) survived, whereas archaic hesperornithiformes and enantiornithines went extinct (Stidham 2002). The small-bodied shorebirds that are known to have survived were probably piscivores or scavengers of aquatic ecosystems, and may have been sustained through the crisis by food chains based on plant detritus (Sheehan and Hansen 1986).

Stratigraphic and taxonomic considerations compromise other potential evidence of terminal Cretaceous bird survival. Late Cretaceous loons (Gaviiformes) are known from Chile and Antarctica (Chatterjee 1997), and flightless ground birds (*Patagopteryx*) from Patagonia (Chiappe 1996), but exactly when they went extinct is unknown. Similarly, a Late Cretaceous giant ground bird (*Gargantuavis*) from southern France is unrelated to Paleogene giant ground birds, and thus is unknown from the Tertiary (Buffetaut 2002). The late Paleocene shorebird *Dakotornis* from nearby North Dakota (Erickson 1975), and the adaptive radiation of birds documented from Eocene lacustrine deposits (Chatterjee 1997) are too geologically young to be relevant to Cretaceous-Tertiary survival. Some Late Cretaceous records, such as parrots (Stidham 1998), have been questioned (Dyke et al. 1999). Well-preserved shorebirds from New Jersey (Olson & Parris 1987; Gallagher 2002) may be Paleocene rather than Cretaceous (Benton 1999), although this is also debated (Dyke et al. 1999).

Acid Rain and Quality of Fossil Record

Much of what we know about Cretaceous-Tertiary extinctions on land comes from long-term studies of the badlands of eastern Montana, where the total extinction of dinosaurs and massive extinctions within many other groups of organisms offer a grim picture (fig. 2.8). Ironically, the calcareous and smectitic floodplains of Montana offered

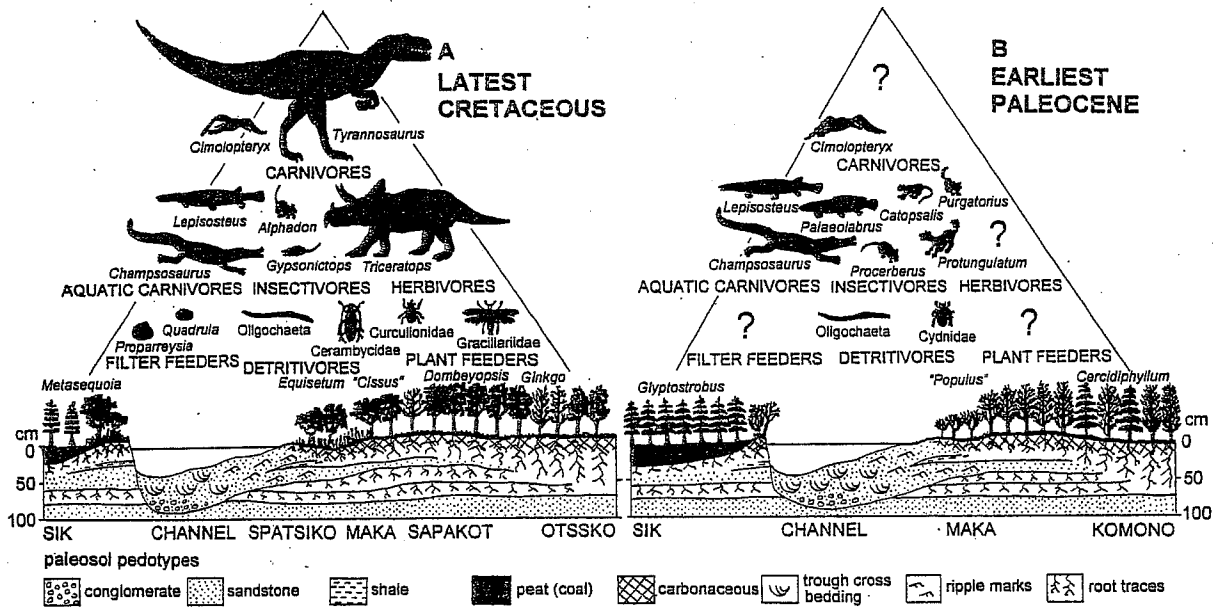


Figure 2.8. Changes in trophic structure across the Cretaceous-Tertiary boundary in non-marine communities of Montana, U.S. (Data from Brodkorb 1963; Estes and Berberian 1970; Lofgren 1995; Hartman 1998; and Labandeira et al. 2002)

considerable buffering of acid rain, and may have been one of the best places to weather the acid storm. In addition, this sequence of little-oxidized paleosols and paleochannels with calcareous cements and smectite clays was also one of few sequences favorable to preserving a record of both bones and plant debris (Retallack 1998). Acid rain may have compromised our fossil record of bones from the last meter or so in Bug Creek, but geochemical variability indicates little influence deeper than that (Retallack 1994). Paleosol sequences of Montana and adjacent states were thus uncommon preservational environments both for creatures weathering an acid crisis and for their fossils.

Other promising Cretaceous-Tertiary fossiliferous successions of calcareous paleosols have been discovered in southeastern China (Stets et al. 1996), peninsular India (Sahni et al. 1994; Bhandari et al. 1996), and southern France (Cousin et al. 1994). However, these red, highly oxidized paleosols are unlikely to yield a good record of fossil plants (Retallack 1998). These areas also may have been important refugia and preservational environments for animals with shells, bone, teeth, and shelled eggs, because their soils supplied abundant calcium and phosphorus for calcite and apatite, and also buffered these mineralized skeletal parts from acid rain. In contrast, areas of granitic and siliceous soils, like currently acidified regions of Scandinavia and northeastern North America (Howells 1995), would have lost more lives and fossils to acidification at the Cretaceous-Tertiary boundary. Acid rain may explain why end-Cretaceous fossil bones and shells were not preserved in many sequences.

Acid rain offers selectivity of mortality and extinction that may account for the complex pattern of extinctions in Montana and adjacent states, where the biota of the Cretaceous-Tertiary boundary is best

understood. Even in this area there remains much to be learned about patterns and mechanisms of extinction from insect-damaged leaves, fossil footprints, and the isotopic chemostratigraphy of carbon, sulfur, and nitrogen. There is also promise for extending such studies to other parts of the world. Although the hypothesis of impact-induced acid rain as a proximate cause of dinosaur demise and bird success remains unfalsified by existing data, it is clearly a hypothesis deserving and capable of further testing. Simply put, the standing hypothesis is that the fatal component of end-Cretaceous events for dinosaurs and other creatures was browning of leaves and other transient destruction of primary productivity by impact-induced acid rain.

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