

1983)]. However, some of that sulfate is formed in the dry gas-phase prior to cloud formation.

8. We thank the project officers, R. L. Kerch of Consolidation Coal Company and J. Wootten of Peabody Coal Company, for their continuous support and interest in this work. We also thank V. A. Mohren for giving helpful advice on the model input data and for providing the measure-

ments obtained by the research group at Whiteface Mountain. We acknowledge the meticulous technical editing provided by J. Rodich and C. Lawson. This study was sponsored by the Consolidation Coal Company and the Peabody Coal Company.

17 January 1984; accepted 3 May 1984

Disruption of the Terrestrial Plant Ecosystem at the Cretaceous-Tertiary Boundary, Western Interior

Abstract. *The palynologically defined Cretaceous-Tertiary boundary in the western interior of North America occurs at the top of an iridium-rich clay layer. The boundary is characterized by the abrupt disappearance of certain pollen species, immediately followed by a pronounced, geologically brief change in the ratio of fern spores to angiosperm pollen. The occurrence of these changes at two widely separated sites implies continentwide disruption of the terrestrial ecosystem, probably caused by a major catastrophic event at the end of the period.*

Since the discovery of an anomalously high concentration of iridium and other platinum-group elements in rocks at the Cretaceous-Tertiary (K/T) boundary at Gubbio, Italy (1), over 50 more localities worldwide with anomalously high Ir concentrations have been found in marine rocks at the K/T boundary, as defined by pronounced changes in the marine fossil biota (2, 3). We report high Ir anomalies in continental rocks deposited in fluvial environments at the palynologically defined K/T boundary from 12 localities in the Raton Basin in Colorado and New Mexico and two more in the Hell Creek, Montana, area.

The K/T boundary, as defined palynologically, occurs in the lower coal zone of the Raton Formation of Cretaceous and Paleocene age (4-7). It lies at the top of a 1- to 2-cm-thick kaolinite-rich clay bed in an ordinary-appearing interval of carbonaceous shale and coal (Fig. 1). The first determination of the approximate position of the palynological boundary was described by Orth *et al.*

(4). This boundary is defined by the disappearance of several Cretaceous palynomorph taxa, chiefly *Proteacidites* spp. and *Tilia wodehousei* sensu Anderson, and often *Trisectoris* and *Trichopeltinites*. These taxa have not been found in samples overlying the boundary clay layer.

The disappearance of the taxa did not involve all of the plants represented by the Cretaceous palynomorph assemblage. Although the flora was decimated, some taxa apparently withstood the boundary event only to disappear during the early Paleocene (*Kurtzipites*); a few others have persisted to the present, relatively unchanged (*Ulmipollenites*).

The abrupt increase in the proportions of fern spores to angiosperm pollen at the palynological K/T boundary (4) may indicate a local abundance of fern plants at or near the deposition site or, if consistent and widespread, fern-spore dominance could reflect a pronounced change in the regional flora. We now also report fern-spore abundance peaks in samples

from Brownie Butte and Seven Blackfoot Creek localities (Hell Creek, Montana) more than 1000 km to the north; the samples were taken immediately above the palynological K/T boundary and the Ir-rich clay layer (8). The genera found in the Tertiary fern-spore abundance peaks are also present in terminal Cretaceous rocks as well as in other nearby localities (9).

Figure 2 shows the succession of rock types across the boundary in the representative Raton Basin section (the Starkville North site) (6). Observations of slides prepared from samples spanning the boundary reveal changes not only in the palynomorph content but also in the kind and abundance of accessory material present. The description below refers to the sampling intervals shown in Fig. 2 but generally represents the boundary interval throughout the Raton Basin.

In the lower part of the section, the samples from Cretaceous carbonaceous shales and shales with coal streaks commonly yield an abundance of cuticular material and epidermal tissue along with a suite of Cretaceous palynomorphs. Palynomorphs are sparse in the overlying boundary clay layer, but there are sufficient specimens to identify the assemblage and determine the fern-spore and angiosperm-pollen percentages. Even when the sample is dark, with an admixture of organic matter, palynomorphs are exiguous. The organic material commonly consists of sapropel and fragmented organic particles.

The overlying thin shale layer also contains scant palynomorphs. The flecks of organic material in this layer are often dark charcoal-like woody tissue consisting of fusinite and semifusinite. Fragmental particles of unidentifiable organic material commonly are present and, occasionally, a few algal spores are observed. The identifiable palynomorphs commonly are fern spores. In this layer, the first evidence of fern-spore dominance appears. The content of fern spores in latest Cretaceous samples from the Raton Basin varies from a few percent to a maximum of about 25 percent. Immediately above the palynological K/T boundary the proportion of fern spores increases to between 65 and 100 percent. For example, the fern-spore component of the assemblage shown in Fig. 2 changes abruptly within less than a centimeter from about 20 to almost 100 percent. This fern-spore dominance immediately above the boundary is present in all Raton Basin K/T boundary localities examined where Ir anomalies have been found. Fern-spore dominance is generally not associated with other thin ash falls

Fig. 1. Photograph of the K/T boundary interval at the Starkville North site near Trinidad, Colorado (6). The fossil-pollen-defined boundary is at the top of a white-weathering, kaolinitic claystone bed beneath the dark coal layer. The claystone consists of finely crystalline to amorphous kaolinite with scattered fragments of quartz and feldspar. It contains abundance anomalies of Ir (6 ng/g) and other elements, including Sc, Ti, V, Cr, and Sb, that distinguish it from other nonboundary kaolinitic clay beds that occur in coaly sequences (14). A thin, flaky, dark shale separates the kaolinitic claystone from the overlying thin coal bed.



(tonsteins) in either Cretaceous or Tertiary rocks near the boundary.

In the thin coal layer immediately above the boundary clay, fern spores are dominant at most sites. Palynological residues from the basal part of the coal show an absence of cuticular material and contain large amounts of fusinite, commonly abundant enough to partially obscure the fern spores. In the upper part of the coal, residues contain degraded organic material, some cuticles, fusinite, and sometimes abundant fungus spores.

There are high percentages of fern spores in the lower and middle parts of the shale above the coal and some cuticular material and fusinite, indicating that the high fern-spore spike does not accompany only depositional conditions associated with coal. The upper part of the shale above the coal yields a low fern spore-high angiosperm ratio. The fern spore-angiosperm pollen percentage reversal occurs about 10 cm above the boundary clay. Fusinite and unidentified organic material are also present.

Sample D6411 (Fig. 2) from about 4 m above the boundary clay has abundant palynomorphs also dominated by angiosperm pollen plus some cuticle and degraded organic material. Thus, the two stratigraphically highest samples in this section reveal a return to the normal angiosperm percentages. This angiosperm recovery was observed in all boundary sections examined. The widespread but temporally brief dominance of ferns followed by very rapid angiosperm recovery is always recorded within less than 15 cm of sediment (10).

At the end of the Cretaceous, all plant life in the western interior apparently suffered a profound ecologic shock, resulting in the extinction of some species. During the deposition of the boundary clay, few spores or pollen grains were deposited in the sediment, possibly because of a rapid deposition rate or, more probably, because of the sparsity of living plants. In the shale above the clay layer, scarcity of pollen grains and the presence of algal spores and sapropel suggest some areas of freshwater, possibly lacustrine, deposition accompanied by decomposing organic matter. The dominance of fern spores in the sediment above the boundary clay heralds the beginning of repopulation of the area. The abundance of fusinite and the absence of cuticular material possibly indicate periods of fire consuming the vestigial or dead organic matter. After the devastating ecologic disturbance the vegetation recovered rapidly, in geologic terms, although the succeeding floral

complex was distinctly different from the preceding Cretaceous flora.

A possible model of a similar recent ecological crisis is recorded in studies of the recolonization of the island volcano Krakatau, situated in the straits between Java and Sumatra. The catastrophic eruption of 1883 destroyed most of the island, and the surviving parts were covered with volcanic debris to a depth of about 30 m. Richards (11) noted that in 1884 "the most striking feature of the vegetation was the abundance of ferns." However, as early as 1919, ferns were no longer dominant, although a climax vegetation cover had not yet been reestablished. The temporary dominance of ferns at Krakatau and at the K/T boundary in continental rocks may perhaps be attributed to the early arrival of wind-dispersed spores, the removal of competitors, and the known tolerance of ferns to soils deficient in mineral nutrients.

In summary, palynological data indicate that the Cretaceous flora of the western interior was profoundly disturbed at the time that the Ir-bearing layer was deposited. These data include the following: (i) the Cretaceous flora was decimated and some plant taxa abruptly became extinct exactly at the level of the Ir anomaly; (ii) high fern spore-low angiosperm pollen percentages are present immediately above the boundary layer; (iii) fusinite and macerated organic material, including sapropel, is present in most samples from the boundary clay layer as well as from samples of the overlying coal layer; and (iv) recovery of the flora to its original low fern spore-high angiosperm pollen percentages occurs within a few centimeters above the boundary layer.

These observations lead us to conclude that some major catastrophic event at the end of the Cretaceous was responsible for massive destruction of the vege-

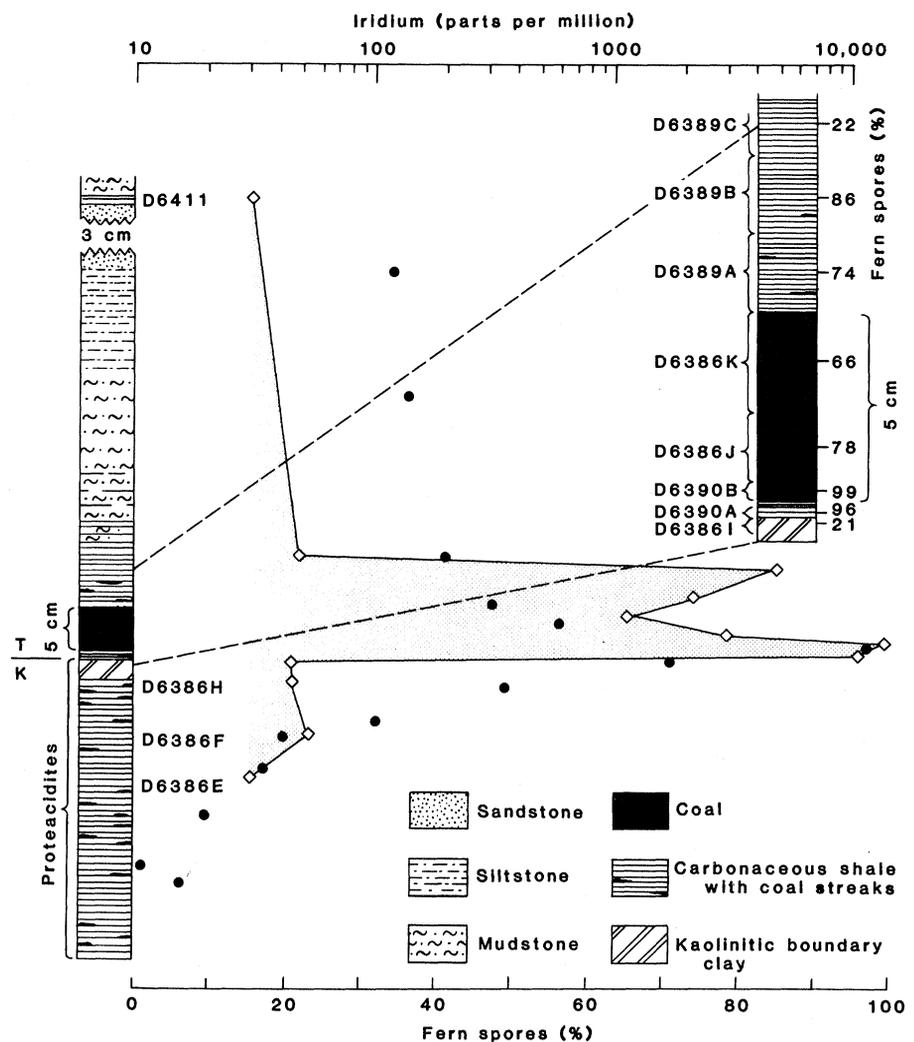


Fig. 2. Diagram showing the lithology of the K/T boundary interval at the Starkville North site, 5 km south of Trinidad, Colorado. The large black dots show the variation in Ir concentrations, the solid line and diamonds show the fern-spore percentages, and the inset shows the detail of the boundary interval. The USGS locality numbers are shown adjacent to the columns.

tation and the abrupt extinction of a few plant species. The destruction of plant life produced vacant vegetal niches, or what may be termed a partial ecological desert. Plant destruction was not total; refugia remained, possibly in widely scattered localities providing nuclei for recolonization. Ferns were the first invaders or colonizers. These were rapidly crowded out as those angiosperms that survived the boundary event gradually reestablished dominance. The succeeding climax vegetation following any major ecological crisis such as a volcanic eruption, flood, or forest fire (12, 13) would not be the same as it was previously. Such a crisis also provides the opportunity for new biotic radiations; the resulting plant community can be vastly different from the preceding one, as was the case during the early Paleocene in the western interior.

R. H. TSCHUDY
C. L. PILLMORE

U.S. Geological Survey,
Denver, Colorado 80225

C. J. ORTH
J. S. GILMORE
J. D. KNIGHT

Los Alamos National Laboratory,
Los Alamos, New Mexico 87545

References and Notes

1. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208**, 1095 (1980).
2. W. Alvarez, L. W. Alvarez, F. Asaro, H. V. Michel, *Geol. Soc. Am. Spec. Pap.* **190**, 305 (1982).
3. W. Alvarez, unpublished observations.
4. C. J. Orth, J. S. Gilmore, J. D. Knight, C. L. Pillmore, R. H. Tschudy, J. E. Fassett, *Science* **214**, 1341 (1981).
5. R. H. Tschudy, in *Cretaceous and Tertiary Rocks of the Southern Colorado Plateau*, J. E. Fassett, Ed. (Four Corners Geological Society Memoir, Farmington, N.M., 1973), p. 131.
6. C. L. Pillmore, R. H. Tschudy, C. J. Orth, J. S. Gilmore, J. D. Knight, *Science* **223**, 1180 (1984).
7. W. T. Lee, *U.S. Geol. Surv. Prof. Pap.* **101**, 1 (1917).
8. B. F. Bohor, E. E. Foord, P. J. Modreski, D. M. Triplehorn, *Science* **224**, 867 (1984).
9. C. Hotten, *Programs and Abstracts of the American Association of Stratigraphic Palynologists, 16th Annual Meeting*, San Francisco, Calif., 1983, abstract, p. 21; unpublished observations.
10. The pollen record indicates that the ecological system was disrupted for a period as short as a few thousand years. Sample increments necessary to perceive these changes must be on the order of 10 cm, or the changes could easily be overlooked. If observations across the K/T boundary are made on wider spaced sample increments, evidence of the disruption will be missed.
11. P. W. Richards, *The Tropical Rain Forest, an Ecological Study* (Cambridge Univ. Press, Cambridge, 1952), p. 271.
12. R. E. Taggart and A. T. Cross, in *Biostratigraphy of Fossil Plants*, D. L. Dilcher and T. N. Taylor, Eds. (Dowden, Hutchinson & Ross, Stroudsburg, Pa., 1980), pp. 186-200.
13. A. T. Cross, R. E. Taggart, *Ann. Missouri Bot. Gard.* **69**, 676 (1980).
14. J. S. Gilmore, C. J. Orth, J. D. Knight, C. L. Pillmore, R. H. Tschudy, *Nature (London)* **307**, 224 (1984).
15. We thank D. Nichols and G. Scott for their critical reviews of the manuscript; S. Van Loenen for preparation of pollen samples; and V. Sable for helpful comments and assistance. Supported by the Department of Energy.

31 January 1984; accepted 12 April 1984

Inhibition of Human Estrogen Synthetase (Aromatase) by Flavones

Abstract. Several naturally occurring and synthetic flavones were found to inhibit the aromatization of androstenedione and testosterone to estrogens catalyzed by human placental and ovarian microsomes. These flavones include (in order of decreasing potency) 7,8-benzoflavone, chrysin, apigenin, flavone, flavanone, and quercetin; 5,6-benzoflavone was not inhibitory. 7,8-Benzoflavone and chrysin were potent competitive inhibitors and induced spectral changes in the aromatase cytochrome P-450 indicative of substrate displacement. Flavones may thus compete with steroids in their interaction with certain monooxygenases and thereby alter steroid hormone metabolism.

Flavonoids are 2-phenyl-1,4-benzopyrone derivatives that are found throughout the plant kingdom (1). They occur in many human foods and have been used as drugs or food supplements (2). The physiological role of the naturally occurring flavonoids is not known, but they have been reported to exhibit anti-oxidant, antibacterial, and antiviral properties.

Two synthetic flavones, 5,6-benzoflavone (β -naphthoflavone) and 7,8-benzoflavone (α -naphthoflavone), have also

attracted considerable interest. These derivatives can modify the metabolism of polycyclic aromatic hydrocarbons and other xenobiotics and thereby alter their toxicity and carcinogenicity (3). 5,6-Benzoflavone appears to act indirectly, inducing synthesis of specific cytochrome P-450 isozymes (4). 7,8-Benzoflavone, on the other hand, directly affects the activity of hepatic P-450 enzymes, inhibiting some forms (5) and activating others (6); these effects are complex and vary with the concentration of 7,8-ben-

Fig. 1. Dose-response curves for flavone inhibition of androstenedione aromatization by human placental microsomes. The 1-ml reaction mixture contained 0.04 μ M androstenedione, 0.1 mg of protein, 2.5 mM glucose-6-phosphate, 0.25 unit of glucose-6-phosphate dehydrogenase, and 100 μ M reduced nicotinamide adenine dinucleotide phosphate in 0.05M sodium phosphate (pH 7.2). Incubations were for 6 minutes at 37°C; control activities (100 percent) averaged 16 pmol per milligram of protein per minute. Curves shown were calculated (11) by assuming I_{50} values of 0.07, 8, and 500 μ M.

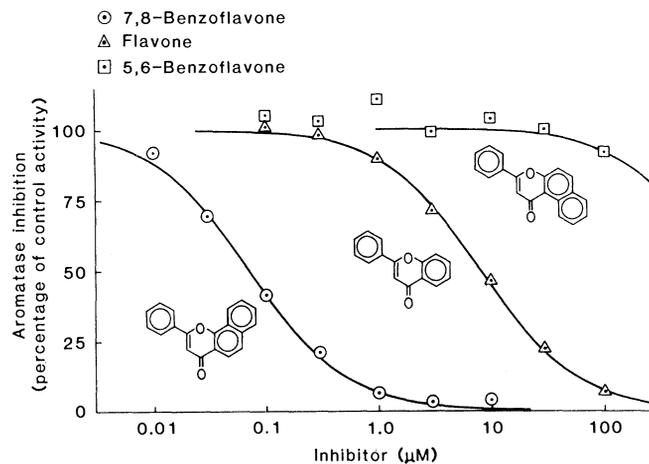


Fig. 2. Kinetic analysis of the mechanism of inhibition of aromatase by 7,8-benzoflavone. (Right) Double-reciprocal plot of reaction velocity (V) versus the substrate concentration. (Left) Slope of lines at right versus inhibitor concentration. Assay conditions are as described in the legend to Fig. 1.

