homogeneous shearing deformation and to the heterogeneous and localized deformation of halite layer, respectively (*22*). The detailed analysis of this heterogeneous deformation is an important future task necessary for understanding the mechanism of seismogenic slip of a fault. The results in Figs. 1 through 3 are important with respect to the origin of large or great thrust-type earthquakes in subduction zones (*20*). Stability analyses of simulated fault are also needed to determine the fault constitutive laws in the brittle, semibrittle, and ductile regimes. These will provide rigorous information on necessary parameters in the modeling of fault motion at seismogenic depths and at deeper levels along plate boundaries. Existing fault constitutive laws (*5–7*) will need to be modified and extended to describe the fault motion in all of the deformation regimes [see also (*24*)].

The results in Figs. 2 and 3 have important implications concerning the long-term behavior of faults. Because all friction laws have been established empirically on the basis of short-term laboratory tests, there is no guarantee that they hold for slow natural deformation. However, halite data at slow rates (down to 10 cm/year) are encouraging since no peculiar long-term behavior has been observed. For instance, the logarithmic law with negative velocity dependency holds almost until the behavior changes into ductile shearing flow with decreasing velocity (Fig. 5). Perhaps most friciton laws are applicable to the slow motion of natural faults.

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26. I thank J. M. Logan and J. H. Dietrich for their review of the manuscript. Supported under U.S. Geological Survey contracts 14-18-0001-19293 and 14-08-0001-21181.

26 August 1985; accepted 7 November 1985

Palynological and Iridium Anomalies at Cretaceous-Tertiary Boundary, South-Central Saskatchewan

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The Cretaceous-Tertiary boundary in south-central Saskatchewan is marked by coincident anomalies in abundance of iridium and fern spores at the extinction level of a suite of Cretaceous pollen taxa. Evidence of disruption of the terrestrial flora includes the fern-spore abundance anomaly and local extinction of as much as 30 percent of angiosperm species. The reorganized earliest Tertiary flora is made up largely of surviving species that assumed new roles of dominance. Persistence of climatically sensitive taxa across the boundary indicates that if paleoclimate was altered by the terminal Cretaceous event, it returned quickly to the pre-event condition.

Orth *et al.* (*1*) recorded the occurrence of an anomalous concentration of iridium at the palynologically defined Cretaceous-Tertiary (K/T) boundary in a nonmarine stratigraphic sequence. According to Alvarez *et al.* (*2*), the excess iridium is of extraterrestrial origin and was deposited as a result of a large bolide impact. An alternative proposal (*3*) is that the iridium is of deep terrestrial origin and was deposited as a consequence of volcanism. The occurrence of the geochemical anomaly coincides with land-plant extinctions that mark the K/T boundary in western North America (*4, 5*). Irrespective of its cause, studies of the terminal Cretaceous event (TCE) and its effects on the nonmarine realm, with particular reference to effects on plants, are important because they have implications for possible analogies between impact and nuclear winter scenarios (*6*). Studies in nonmarine rocks in western North America (*7–10*) revealed the presence of the iridium anomaly at the palynologically defined K/T boundary at numerous sites in New Mexico, Colorado, and Montana.

We found sharply defined palynological and iridium anomalies at the K/T boundary near Morgan Creek, south-central Saskatchewan, about 165 km north of previously known sites in Montana and 1200 km north of the original site in New Mexico. The K/T boundary at Morgan Creek is characterized by extinctions of pollen taxa and the anomalous abundance of fern spores that are further evidence of an abrupt, continent-wide disturbance of the terrestrial ecosystem at the end of Cretaceous time (*4*). A second fern-spore abundance anomaly of uncertain significance is present more than 3 m above the boundary. Palynological data are evidence of paleoclimates immediately preceding and following the TCE, and they document major changes leading to the development of the earliest Tertiary flora. Geochemical data from this site bear on postdepositional behavior of iridium at the K/T boundary.

The K/T boundary in southern Saskatchewan is approximately at the contact between bentonitic mudstones and siltstones of the Frenchman Formation (late Maestrichtian) and the overlying Ravenscrag Formation (early Paleocene), which consists of sandstones, siltstones, mudstones, carbonaceous shales, and coals. These units were deposited in alluvial, lacustrine, and paludal environments associated with final retreat of the Cretaceous epicontinental sea. The Frenchman and Ravenscrag formations are, respectively, the stratigraphic equivalents of the Hell Creek and Fort Union formations in Montana. In these sequences the K/T boundary approximates the lithologic boundary between coal-bearing strata and

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strata below that lack coal but contain dinosaur bones. At Morgan Creek the palynologically and geochemically defined boundary is immediately below the base of the lowermost coal bed of the Ravenscrag Formation, locally known as the Ferris No. 1 coal. Dinosaur bone fragments are present on slopes of the Frenchman Formation near our measured sections (*11*), about 10 m below the K/T boundary.

Neutron activation and radiochemical separations were performed on 14 samples (Fig. 1). A 2-cm-thick layer of brown to black carbonaceous claystone immediately below the No. 1 coal yielded the greatest concentration of iridium [3 ng/g or 3000 parts per trillion (ppt)]. This bed is underlain by a 1.5-cm-thick layer of pinkish tan claystone that yielded 840 ppt of iridium. The peak of the iridium anomaly is about 100 times as great as that of the local background (which ranges from 5 to 60 ppt and averages 28 ppt for ten samples above and below the K/T boundary, excluding those within 10 cm of the peak).

By analogy with sites in New Mexico, Colorado, and Montana, the 1.5-cm and 2-cm claystones below the No. 1 coal represent the so-called K/T boundary clay. The boundary clay in Saskatchewan probably contains some detrital material, because titanium concentration is lower than observed at better preserved sites in Montana, Colorado, and New Mexico, where high titanium values characterize the boundary clay (*10*). From our samples, grains of quartz that exhibit multiple sets of planar microfractures were recovered; these features have been found only in minerals at meteorite impact or nuclear explosion sites. Our peak iridium anomaly occurs in the more carbonaceous layer of the boundary clay. Peak iridium anomalies measured in Italy, Denmark, Spain, New Zealand, and deep-sea-drilling-project cores occur in clay layers within carbonate sequences. The iridium concentration in nonmarine sections in western North America, however, peaks in carbonaceous matter immediately overlying or underlying clay, suggesting that iridium is postdepositionally mobilized to some degree toward organic-rich sediments (*12*).

Much similarity is evident between Maestrichtian palynomorph assemblages from Saskatchewan and Montana (*8, 13*), but there are important differences between these assemblages and those in New Mexico (*14*). Most notably, northern assemblages include higher percentages of *Aquilapollenites* and gymnosperm pollen than are found in those in the south. Our Maestrichtian assemblages are characterized by *Aquilapollenites* (seven species), *Proteacidites* spp., *Gunnera microreticulata, Cranwellia rumseyensis, Leptopecopites pocockii, Marsypiletes cretacea, Liliacidites complexus*, and *Ephedra cretacea*.

In the interval 0.1 to 12 m below the boundary clay, assemblages are dominated by angiosperm pollen (42 to 92 percent). Spores of pteridophytes, predominantly ferns, are common (5 to 46 percent) and pollen of gymnosperms, especially taxodiaceous or cupressaceous species, occurs consistently in low abundance (3 to 12 percent) in this interval. A major shift in palynomorph abundance takes place at the boundary level, and samples immediately above the boundary clay are overwhelmingly dominated by fern spores.

The anomalous abundance of fern spores at the K/T boundary in Saskatchewan is similar to that described in New Mexico and Montana (*1, 4, 9*). This "fern-spore spike" is characterized by low species diversity and high percentage abundance and is believed to reflect initial recolonization of the terrestrial environment following devastation by the TCE (*4*). The dominant species in Saskatchewan is *Laevigatosporites haardtii.* Total fern-spore abundance is 96.5 percent in the carbonaceous claystone immediately beneath the No. 1 coal seam. The percentage remains high (85 to 96 percent) in the basal 15 cm of the coal but declines rapidly in the upper part of the seam (Fig. 1), showing that the fern-spore spike is independent of lithology.

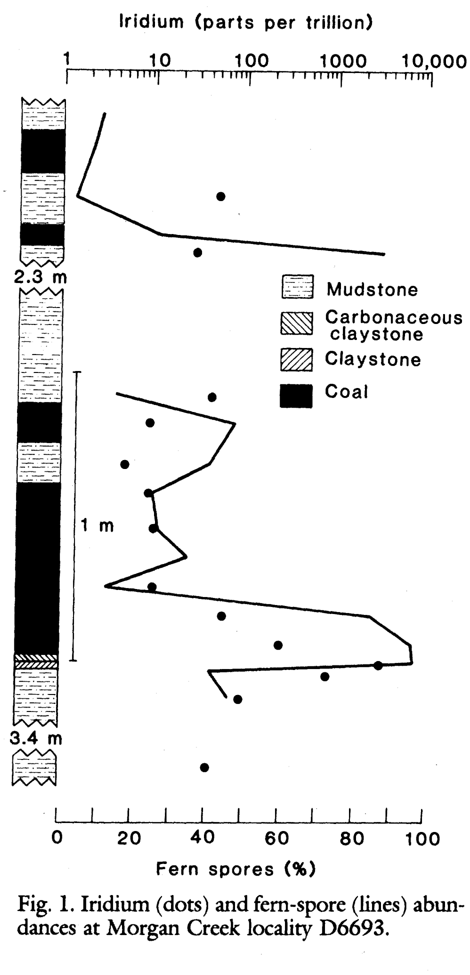

Fig. 1. Iridium (dots) and fern-spore (lines) abundances at Morgan Creek locality D6693.

By palynological evidence, the uppermost Cretaceous sample at Morgan Creek is the carbonaceous claystone that yielded the stratigraphically highest occurrence of *Aquilapollenites*, *Proteacidites*, and other typical Cretaceous taxa (as well as the iridium peak and fern-spore spike). Thus the K/T boundary is sharply defined between this sample and the immediately overlying coal seam. Our taxonomic studies are incomplete, but preliminary results indicate that as much as 30 percent of the palynoflora does not transcend the K/T boundary in south-central Saskatchewan. Local extinction primarily affected angiosperm taxa. The common Upper Cretaceous species *Wodehouseia spinata* persists into the lowermost Tertiary (Fig. 2), but *Aquilapollenites reticulatus*, which occurs consistently above the K/T boundary in southwestern Saskatchewan and Alberta (*15, 16*), is restricted to the Cretaceous in our sections (included in *Aquilapollenites* spp. in Fig. 2).

Tertiary samples from our sections yielded assemblages composed of species that survived the TCE and flourished as a reorganized flora. Only pollen referrable to *Triporopollenites* appears to be new in the flora of the lowermost Tertiary; species of the typically Paleocene genus *Momipites* occur 5.5 m above the boundary. Coal samples reflect swamp vegetation successively dominated by anemophilous dicot angiosperms (*Triporopollenites* and *Ulmipollenites* pollen) and monocots (*Arecipites* pollen). Gymnosperm pollen of taxodiaceous or cupressaceous affinity fluctuates in abundance and is dominant in some samples. Spores attributable to the bryophyte *Sphagnum* are conspicuous. With one exception, samples above the No. 1 coal yielded less than 50 percent fern spores.

The exception is mudstone 3.65 m above the boundary clay, immediately below a thin coal bed (Fig. 1). *Laevigatosporites haardtii* accounts for 87.5 percent of the assemblage in this low-diversity sample. No distinct clay layer analogous to the boundary clay is present at this stratigraphic horizon and iridium assay indicated a concentration of only 29 ppt. Relative abundance of fern spores decreases to 26.5 percent in the thin coal and to 3.5 percent in overlying mudstone. This second fern-spore abundance peak is unexplained at present. Occurrence of the peak in close association with a coal bed may be coincidental, because except here and at the boundary, samples directly beneath (or within) coals in our sections did not yield comparable abundances of fern spores. The second abundance peak may reflect a temporary disruption of communities dominated by higher plants—subsequent to the TCE. If so, it may be relevant to understanding the apparent continent-wide disruption of plant communities during the TCE.

According to the impact hypothesis of the TCE (*2*), the boundary clay layer was deposited as fallout from a globe-encircling dust cloud that would have blocked incident solar radiation; plants would have been subjected to a freezing "impact winter." Palynological evidence on latest Cretaceous and earliest Tertiary paleoclimates in western North America is meager. Previous studies (*17*) suggested that climatic deterioration was an aspect of the K/T transition in southern Canada and Montana on the basis of an observed shift from angiosperm-dominated to gymnosperm-dominated palynofloras. Gradual climatic deterioration may be an aspect of the K/T transition on a global scale, but the rapid shift in palynofloras in this region is more likely attributable (in part) to changes in local vegetation of the kind described by Hickey (*18*), in this instance associated with the change from fluvial channel-margin and levee (Hell Creek, Frenchman) to backswamp (Fort Union, Ravenscrag) sedimentation.

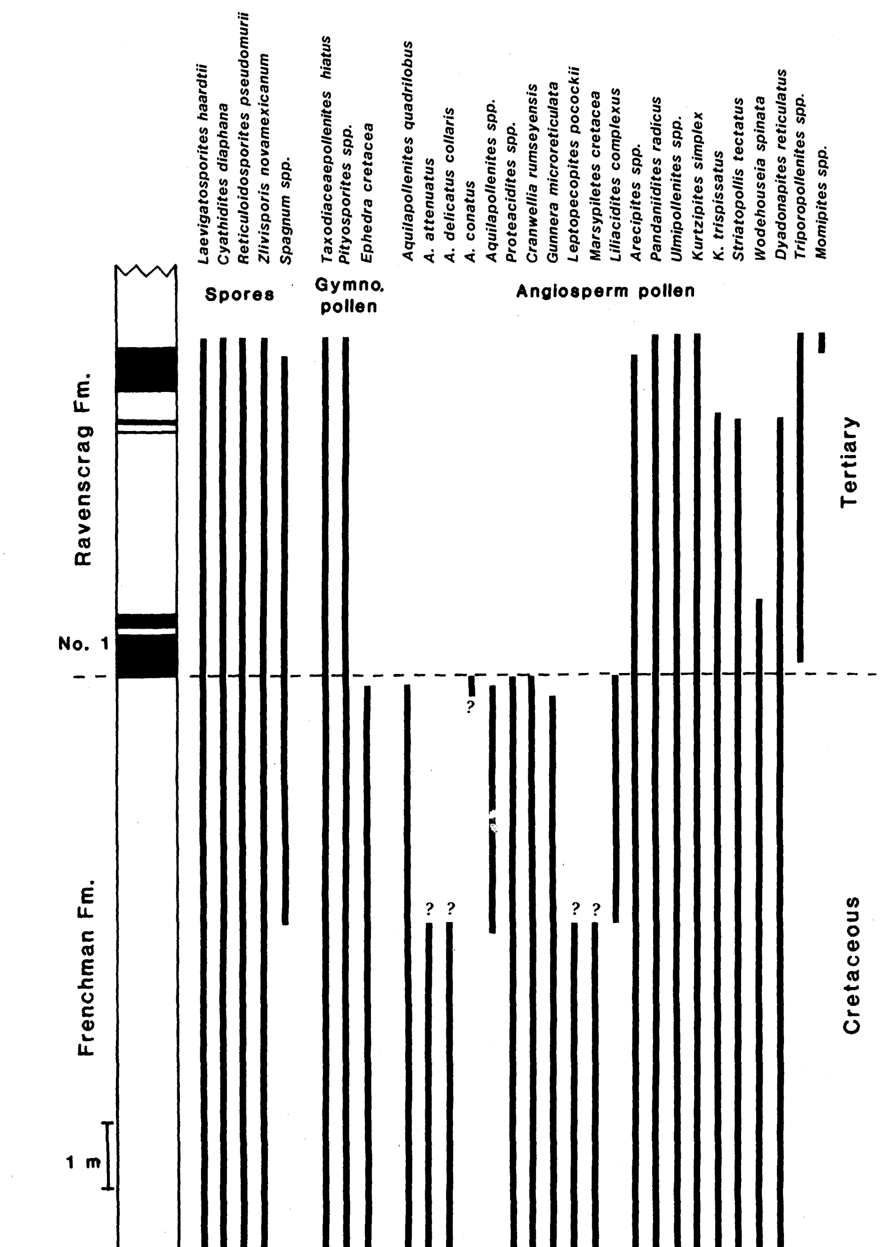

Fig. 2. Stratigraphic ranges of selected palynomorph taxa at Morgan Creek. Apparent range break within the Frenchman Formation may be due to sparse sample control. Lithology is not indicated, except for coal (black).

Changes that led to establishment of coal-depositional environments may explain shifts in floristic composition across the K/T boundary, but changes in sedimentation cannot account for the abrupt disappearance of the *Aquilapollenites-Proteacidites* palynomorph assemblage. That event is regionally independent of initiation of coal deposition. Although the extinction level is virtually coincident with the base of the Ferris No. 1 coal at the localities we studied, it occurs variously above or below the first coal bed in correlative sections elsewhere in Saskatchewan (*15*). Thus the Tertiary flora owes its composition in part to ecologic change and in part to extinction of certain Cretaceous plants.

Despite evidence of ecologic change and extinction at the K/T boundary in Saskatchewan, most plant taxa survived the TCE and some palynological data suggest that the regional paleoclimate remained essentially stable from latest Cretaceous to earliest Tertiary time. If paleoclimate was altered, it may have undergone only a brief change consistent with a 3- to 6-month period of darkness (*19*), after which it returned to the previous frost-free condition. Pollen of *Arecipites* and *Pandaniidites* occurs throughout the Cretaceous and Tertiary of the two sections we sampled. We interpret these species to represent thermophilic taxa—palms and screw pines—similar to those currently inhabiting southeast Asia and Indomalaysia (*20*). Their persistence across the K/T boundary suggests that no profound and lasting paleoclimatological change accompanied the TCE.

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11. Samples are from two sections in the Morgan Creek area, near Wood Mountain, Saskatchewan. One is National Museums of Canada Micropaleontology Locality 0136 (Sec. 14, T. 1, R. 5, west of the third meridian) and is described by Jarzen (*20*); the other is U.S. Geological Survey Paleobotany Locality D6693 (Sec. 23, T. 1, R. 5 W.). Palynological data described here were derived primarily from locality

D6693 and supplemented by samples from locality 0136; neutron activation analyses of trace elements were conducted on samples from locality D6693.
12. Data from Raton Basin sites (*10*) indicate that iridium moves preferably toward organic-rich sediments, upward where peak anomalies occur near or at the base of coal seams, but downward to the same extent where the boundary clay is surrounded by coal. Officer and Drake (*3*) may have overlooked or misinterpreted these data. Their conclusion that iridium moves upward as a result of bioturbation is dubious, at least for nonmarine environments.
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21. We thank R. F. Fleming and D. T. Pocknall for assistance in the field; the Los Alamos Research Reactor Group (INC-5) for neutron irradiations; R. H. Tschudy, J. A. Wolfe, D. A. Russell, and C. L. Pillmore for reviews and comments on the manuscript; and G. A. Izett who recovered the quartz grains showing shock lamellae from our samples. Two of us (C.J.O. and P.Q.O.) thank the U.S. Department of Energy for support.

3 June 1985; accepted 1 November 1985

Synthesis of Todorokite

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Todorokite of chemical composition $(Mg_{0.77}Na_{0.03})(Mg_{0.18}Mn^{2+}_{0.60}Mn^{4+}_{5.22})\ O_{12} \cdot 3.07\ H_2O$ was synthesized by a two-step procedure. First, sodium birnessite was synthesized and magnesium was exchanged for sodium to form magnesium birnessite, which was autoclaved under a saturated steam pressure at 155°C for 8 hours to form well-crystallized todorokite. Synthesized todorokite particles consisted of fibers extending from a central plate. The plate itself was made of twinned fibers forming a trilling pattern. The infrared spectra and x-ray diffraction patterns were similar to those of natural todorokite samples. Calcium birnessite and nickel birnessite, when autoclaved under conditions similar to those for magnesium birnessite, yielded a todorokite structure. However, the formation of todorokite from calcium and nickel birnessite was less extensive.

We report the synthesis of todorokite, which is formed principally in nature as an end product of oxidation of manganese (Mn^{2+}) in marine environments and under earth-surface conditions. There has been great interest in this tunnel-structured mineral because it is a major constituent of deep-sea manganese nodules (*1*) and has the potential of becoming a polymetallic resource of the twenty-first century (*2*). Knowing the chemistry of todorokite is important for understanding how nodules form and how they concentrate transition elements from ocean waters (*3*).

Todorokite was synthesized because natural samples of high purity are rare, and samples free of impurities and of high crystallinity are necessary for chemical and mineralogic studies. The synthesis involved a two-step procedure. First, sodium birnessite (*4*) was synthesized by oxidation of Mn^{2+} in an alkaline medium. The magnesium was then exchanged for sodium, and the magnesium birnessite was autoclaved at 155°C for 8 hours in an aqueous medium with or without excess $MgCl_2$ to obtain todorokite.

Infrared spectra of natural todorokite indicate that todorokite is not analogous to any of the synthetic phases (*5*) reported to be identical to todorokite (*6*). The largest tunnel structure reported for a synthetic manganese oxide (2 octahedra by 3 octahedra) is that of psilomelane (*7*). Tunnel-structured manganese minerals such as cryptomelane and hollandite have been synthesized by dry heating of birnessite saturated with the appropriate cations K^+ and Ba^{2+}, respectively, at 500° to 800°C (*8*). In the above syntheses, the size of the cation controls the dimensions of the tunnel (2 octahedra by 2 octahedra). However, the large size (ideally 3 octahedra by 3 octahedra) of the todorokite tunnel requires an unusually large cation. Because such an unhydrated inorganic cation does not exist, the large hydrated Mg^{2+} cation in aqueous solution was used in this preparation.

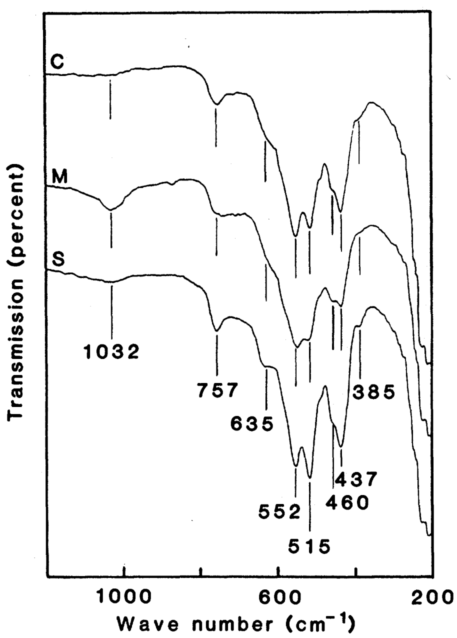

Fig. 1. Infrared spectra of synthetic todorokite (S) and natural todorokites from Montenegro mine, Cuba (M), and Charco Redondo, Cuba (C).

First, birnessite was synthesized by a modification of the procedure of Stähli (*9*). Manganese dichloride (200 ml, 0.5*M*) was placed in a 500-ml plastic beaker. Oxygen was then bubbled into the solution through a glass frit at a rate of 1.5 liters per minute [it was important to maintain this rate of oxygen flow to prevent the formation of hausmannite (Mn_3O_4)]. This was followed by the addition of 55 g of NaOH in 250 ml of H_2O.

After 5 hours oxygenation was stopped and the black precipitate (buserite) was washed with deionized water until the supernatant was salt-free. The product was freeze-dried, which dehydrated the buserite to birnessite, and stored. Infrared analysis, x-ray diffraction, and electron microscopy (*10*) indicated that birnessite was the only crystalline phase present.

In the second step, a 25-mg sample of the sodium birnessite was shaken with 20 ml of 1*N* $MgCl_2$ for 12 hours. The sample was then centrifuged and washed twice with 20-ml portions of distilled deionized water to remove the exchanged sodium. The magnesium birnessite synthesized was either dispersed in distilled water or fresh 1*N* $MgCl_2$ (20 ml). These mixtures were autoclaved at 155°C in a sealed 25-ml Teflon-lined stainless steel container under autogenous pressure for 8 hours. The container was then cooled to room temperature, and the contents were washed free of any excess $MgCl_2$ with water. The product was then freeze-dried and stored. Increased autoclaving time gives rise to slightly sharper x-ray diffraction peaks (*11*); however, it also causes the grad-

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