STABLE ISOTOPE EVIDENCE FOR GRADUAL ENVIRONMENTAL CHANGES AND SPECIES SURVIVORSHIP ACROSS THE CRETACEOUS/ TERTIARY BOUNDARY

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<u>Abstract</u>. High-resolution δ^{13} C and δ^{18} O records have been generated from analyses of the planktonic foraminiferal species Heterohelix globulosa and the benthonic foraminiferal taxon <u>Lenticulina</u> spp from 3 m of a cored section spanning the Cretaceous/Tertiary (K/T) boundary at Brazos River, Texas. These are the first stable isotope records across the K/T boundary based on monospecific and monogeneric foraminiferal samples. They show a gradual decrease in δ^{13} C values of about 2.5 permil beginning at the K/T boundary, as defined by the first appearance of Tertiary planktonic foraminifera, and continuing 17-20 cm above the boundary, approximately 40,000 years later. Gradual ¹³C depletion contrasts with the sudden δ^{13} C drop at the K/T boundary observed in many deep-sea sections. The surface-to-bottom $\delta^{13}C$ gradient decreased to less than zero approximately 25,000-30,000 years after the K/T boundary and remained negative for at least the next 140,000 years. Concomitant with change in $\delta^{13}C$ values is a gradual decrease of about 2.5 permil in δ^{18} O values which has not been observed at other localities. This ¹⁸0 depletion suggests changes in temperature and/or salinity in

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the earliest Paleocene Gulf of Mexico. No extinction of foraminiferal species is associated with the K/T boundary or the onset of ¹⁸O and ¹³C depletions. Instead, two phases of Cretaceous species extinctions occur. One extinction phase is below the K/T boundary and below the tsunami bed of Bourgeois et al. [1988] and may be linked to sea level regression and environmental perturbations. The second extinction phase coincides with the minimum in δ^{13} C and δ^{18} O values in the Early Danian (Zone PO/Pla) and appears directly related to environmental changes reflected in the isotopic record. <u>H. globulosa</u>, which is commonly present in Maastrichtian and Danian sediments, exhibits significantly lower $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in Tertiary sediments relative to specimens from Maastrichtian sediments, demonstrating the survival of this important Cretaceous taxon after the K/T boundary event.

INTRODUCTION

The Cretaceous/Tertiary boundary transition in deep-sea sections is generally characterized by an anomalously high concentration in iridium (Ir), a sudden decline in δ^{13} C values of carbonate from surface waters, and the simultaneous mass extinction of all but one Cretaceous planktonic foraminiferal species. These geochemical and faunal anomalies are commonly interpreted to have been caused by an extraterrestrial bolide impact [e.g., Alvarez et al., 1980; Hsü et al., 1982]. This paper examines the stable isotope records and the nature of the foraminiferal mass extinction across the K/T boundary transition in a shallow epicontinental sea environment at Brazos River, Texas.

The δ^{13} C records of surface water microfossils in K/T boundary sections show a sudden 13 C depletion ranging from about 1 to 2.5 permil at the boundary transition [Hsü et al., 1982; Shackleton et al., 1984; Shackleton and Hall, 1984; Zachos and Arthur, 1986]. Because photosynthesizing organisms in the photic zone preferentially incorporate ¹²C in organic matter and return this carbon to the ocean by its oxidation at depth [Deuser and Hunt, 1969; Kroopnick, 1974], the total dissolved carbon (TDC) of surface waters has higher δ^{13} C values than that of deep waters. The reduction of the surface-to-bottom $\delta^{13}C$ gradient to values near or below zero, from the decrease in planktonic microfossil $\delta^{13}C$ values relative to those of benthonic microfossils at the K/T boundary, has been interpreted as evidence for a sudden drop in surface water productivity [Broecker and Peng, 1982; Hsü et al., 1982; Shackleton et al., 1984; Shackleton and Hall, 1984; Zachos and Arthur, 1986] possibly caused by a catastrophic event such as an extraterrestrial bolide impact [Hsü et al., 1982]. In this scenario, marine productivity declined with the near cessation of photosynthesis in marine plankton as a result of the temporary blocking of sunlight by a dust cloud generated by a bolide impact at the K/T boundary [Alvarez et al., 1980; Hsü et al., 1982]. This hypothesis has been based on results from sections with a very condensed early Danian record with the earliest Tertiary planktonic foraminiferal Zone Guembelitria cretacea (PO) missing in all deep-sea sequences and the succeeding <u>'Globigerina'</u> eugubina Zone (Pla) frequently represented by only a few centimeters of sediments [Smit, 1982; Keller, 1988, 1989a]. The expanded sedimentary record in a Brazos River core with a 20-cm-thick Zone PO provides the opportunity to study the nature and sequence of events and environmental effects of the K/T boundary event as well as raises questions regarding the dust cloud darkness scenario [Alvarez et al., 1980; Wolbach et al., 1985, 1988].

Until recently, there has been little challenge to the general notion that all but one Cretaceous planktonic foraminiferal

species (i.e., <u>Guembelitria</u> <u>cretacea</u>) suddenly became extinct at the K/T boundary [Smit, 1982; Smit and Romein, 1985]. Careful documentation of stratigraphic ranges and changes in population on the centimeter scale across the K/T boundary in epicontinental sea and continental shelf sections with high sedimentation rates (El Kef, Tunisia, and Brazos River, Texas) illustrates a different mass extinction pattern [Keller, 1988, 1989a]. In these sections, between 30% and 45% of the species disappear during the latest Cretaceous prior to the K/T boundary [Keller, 1989b]. Up to 30% of Cretaceous species appear to have survived the boundary event and disappear during the first 250,000 years of the Tertiary. Their survivorship has been inferred by their common presence in Danian sediments [Keller, 1988, 1989a,b].

In this paper, we provide stable isotope evidence of a gradual depletion in $\delta^{13}C$ values over tens of thousand of years in the post-K/T boundary environment (Zone PO) based on analyses of the benthonic foraminifer Lenticulina spp. and the Cretaceous planktonic foraminifer <u>Heterohelix</u> globulosa. The δ^{13} C values of <u>H. globulosa</u> become lower than those of Lenticulina spp. about 25,000 to 30,000 vears after the K/T boundary and continued low for at least the next 140,000 years. Moreover, we provide the first unequivocal evidence of Cretaceous species survivorship well after the K/T boundary based on the stable isotope composition of a Cretaceous survivor species. In addition, we present evidence that the K/T boundary event at Brazos River did not cause geologically instantaneous species extinctions, but instead resulted in a slow decline in Cretaceous foraminiferal populations parallel to depletion in δ^{13} C values.

THE BRAZOS CORE SECTION

Lithology and Environment of Deposition

The Brazos River section, isotopically investigated in this study, was drilled with a 5-cm-diameter core (henceforth labeled Brazos core) at the location of a small tributary to the Brazos River informally known as Cottonmouth Creek about 1/2 mile (0.8 km) upstream from its intersection with the Brazos River and the locality known as Brazos 3 of Hansen et al. [1984]. The lithology of the core is

similar to that of nearby Brazos outcrops, all of which have been described in detail by Hansen et al. [1984, 1987], Jiang and Gartner [1986], and Bourgeois et al. [1988]. The Brazos core contains 23.5 m of Upper Maastrichtian sediment consisting of grey calcareous claystone of the Corsicana Formation and 2 m of grey calcareous clay of the Paleocene Kincaid Formation. (The total thickness of Paleocene sediments overlying Maastrichtian units is more than 5 m.) These two rock units are separated by a coarse-grained lithologic unit which spans about 20 cm in the core, and varies from 20 cm to 1 m in nearby outcrops [Hansen et al., 1984, 1987; Jiang and Gartner, 1986; Keller, 1989a]. A sandy shell-hash bed with an irregular scoured contact and rip-up clasts characterizes the base of this unit and indicates the presence of a hiatus as discussed later [Hansen et al., 1987; Keller, 1989a]. Sediments overlying this contact grade upwards into silty sandstone, sandy claystone, calcareous siltstone or chalk, massive gray clay, clay with sand

laminations, and silt-clay, respectively. This sedimentary deposit up to the top of the calcareous siltstone or chalk layer has been interpreted as generated by either a storm event [Hansen et al., 1987] or a tsunami wave [Bourgeois et al., 1988]. In this paper we will refer to it as the "tsunami deposit".

Detailed sedimentological data of the 3 m of the Brazos core section spanning the K/T boundary do not indicate a radical change in the physical environment during deposition of these sediments. Results of the mineralogy, and organic carbon and carbonate contents are tabulated in Tables 1 and 2, respectively (see, Figures 1 and 2 for the stratigraphic position of samples). Sand grains, most of which are quartz, increase in abundance only within the tsunami deposit. Danian sediments have a higher carbonate content relative to those of Maastrichtian age (Figure 6 and Table 2), in part due to the presence of authigenic dolomite (Table 1). The latter suggests that fine-grained biogenic carbonate has likely been affected by

TABLE 1.Mineralogy of the Upper Maastrichtian and Lower Tertiary
Sediments of the Brazos Core Section.

Sample	Data				Minera	logy a	and Ab	undance	:	
		Qtz	Fld	Mic	I/S	111	Kao	Ca	Dol	Pyr
289	XRD	**	*		***	*	*	****	*	*
279	XRD, TS	**	**	*	***	*	*	**	***	*
274	TS	**	*	*	***	*				*
269	XRD, TS	**	*	-	***	*	*	***	**	*
265	TS	**	*	-	***	*				*
262	TS	**	*	-	***	*				*
260	XRD, TS	*	*	-	***	*	*	***	**	*
257	XRD, TS	**	*	*	****	*	*	**	**	**
255	XRD, TS	**	*	-	****	*	*	**	**	**
252	XRD, TS	*	*	-	****	**	*	**	*	**
248	XRD, TS	***	*	-	****	**	*	**	*	**
247	TS	***	*	-	****	*				*
244	XRD, TS	***	*	*	****	*	*	**	-	*
236	XRD, TS	**	*	*	****	*	*	**	-	*
226	XRD, TS	**	*	*	****	*	*	**	-	*
217	XRD, TS	**	*	-	****	*	*	**	-	*

Mineralogy and abundance are based on X ray diffraction patterns (XRD) and/ or thin section observations (TS). Abbreviations are as following: Qtz, quartz; Fld, feldspar; Mic, micas; I/S, illite/smectite (20% illite); Ill, glauconite and/or illite; Kao, kaolinite; Ca, calcite; Dol, dolomite and/or ankerite; Pyr, pyrite. Abundances are as follow: **** = very abundant; *** = abundant; ** = minor; * = rare; - = absent; ? = undetermined.

and	
Samples	
Carbonate	
ind Bulk	Section
Species a	zaos Core
Foraminiferal	on From the Br
of Selected	Drganic Carb
Values	ite and (
Isotopic	Carbonā
Carbon 1	Percent
and	
Oxygen	
TABLE 2.	

Sample Depth	Depth m	Foram Zone			Species				Bulk Ca	rbonate	Carbonate	Organic Carbon
,			Lenticu	lina spp.	Lenticuli	na spp.*	Heterohelix g	lobulosa				
			Š ¹⁸ O	§ 13C	Š ¹⁶ O	S 13C	δ ^{1θ} Ο	§ ¹³ C	δ ¹⁸ Ο	§ 13C	Percent	Percent
289	1.75	Plb	-4.123	-2.126	-1.632	-0.337						
288	1.65	Plb	-3.821	-1.961	-3.853	-1.561					21.75	1.79
287	1.45	PID	-3.946	-1.529	-3.792	-1.346						
283	1.15	qIa	-3.185	-1.841	-1.857	-0.573					14.99	2.41
279	1.05	qIq	-2.576	-0.806								
275	0.95	ALT	-3.821	-1.856	-3.297	-1.638			-2.005	-2.699	13.08	2.41
274	0.93	dIg	-3.441	-0.854	-3.581	-1.533						
271	0.85	Plb	-4.299	-2.318	-4.159	-2.175	-5.411	-2.976			24.16	
270	0.87	Pla	-3.732	-1.986	-4.038	-1.951			-3.245	-6.718	16.08	2.55
269	0.80	Pla	-3.521	-1.151	-4.163	-2.041						
268	0.77	Pla	-3.505	-1.955							17.25	1.93
266	0.73	Fla	-4.121	-2.526	-3.971	-2.154			-2.463	-5.747	20.08	2.26
265	0.70	Pla	-4.099	-2.526	-4.076	-2.253				•	24.42	2.28
264	0.68	Pla	-4.301	-2.319	-3.453	-1.824			-2.776	-2.279	23.58	
262	0.62	Pla	-4.514	-1.812					-2.058	-1.882	25.75	2.54
261	0.48	Pla	-4.877	-2.548					-1.796	-3.178	27.25	2.33
260	0.45	PO	-4.336	-2.237	-3.814	-2.001			-2.402	-2.451	25.08	2.16
259	0.42	PO	-4.541	-2.193	-4.053	-2.136	-5.354	-2.998	-2.871	-6.391		
257	0.38	РО	-3.642	-1.935	-3.562	-1.514	-4.793	-2.656	-2.889	-5.184	12.51	2.75
256	0.35	PO	-3.377	-1.525	-3.779	-1.324	-4.393	-0.998	-2.681	-4.490		
255	0.32	PO	-2.008	-0.871	-2.953	-0.741	-3.656	-0.563	-1.958	-1.747	10.75	
253	0.27	PO	-1.734	-0.116	-3.409	-0.527	-2.449	-0.296	-3.071	-1.391		
252	0.25	P. def.	-1.864	-0.555	-3.015	-0.707	-2.876	-0.291	-2.864	-0.141	6.16	2.72
248	0.15	P. def.	-1.541	-0.286			-2.371	0.003			7.58	2.52
247	0.10	P. def.	-1.821	-0.101			-3.935	-0.349	-2.522	-0.708	9.08	2.41
246	0.07	P. def.	-1.518	-0.801			-2.997	-0.157			27.66	1.89
244	0.02	P. def.	-1.721	-0.345			-2.533	-0.215			8.92	3.14
240	-0.07	P. def.	-1.494	-0.481			-2.391	-0.187			8.16	2.93
238	-0.10	P. def.	-1.661	0.261			-2.598	0.161			9.58	
236	-0.15	P. def.	-2.026	-0.402			-3.157	-0.111				
234	-0.20	P. def.	-1.609	-0.243					-2.248	-0.141	9.16	1.81

					TABLE	2. (continued)					
Sample	Depth	Foram								Carbonate	Organic
Depth	E	Zone			Species			Bulk Car	cbonate		Carbon
			Lenticu	lina spp.	Lenticulina spp	.* Heterohe	lix globulosa				
			δ 18O	δ 13C	8 ¹⁸ O 8 ¹³ C	Š ¹⁸ O	<u>813C</u>	δ ¹⁸ Ο	§ 13C	Percent	Percent
229	-0.32	P. def.	-1.749	-0.496		-3.176	-0.139			10.42	1.68
226	-0.45	P. def.	-1.688	0.083		-2.410	0.324				
223	-0.60	P. def.	-1.894	-0.788		-2.875	-0.437	-1.906	-1.077	10.66	1.69
223	-0.60	P. def.	-1.356	0.285						• • •	
221	-0.70	P. def.	-1.548	0.007		-2.354	0.178			9.75	1.67
217	-1.05	P. def.	-1.481	0.061							•
217	-1.05	P. def.	-1.134	0.655							
217	-1.05	P. def.	-1.307	0.358		-2.354	0.178				
214	-1.20	P. def.	-1.706	-0.402							
214	-1.20	P. def.	-1.822	-0.505		-3.344	0.264			8.16	3.43
209	-1.45	P. def.	-1.773	-0.239		-3.052	0.693			8.42	3.47
209	-1.45	P. def.	-1.669	-0.381							•
205	-1.65	P. def.	-1.684	-0.732		-2.703	0.207				

solution-reprecipitation processes in this interval. Tertiary sediments also have a slightly higher organic matter content (between 1.3 and 1 wt %) than older sediments (< 1 wt %) reflecting reducing conditions during deposition. The dominant clay phase, highly smectitic illite/ smectite (I/S) mixed-layer (20% illite), is significantly less abundant in the Tertiary than in the Maastrichtian interval. The relative abundance of other components such as illite and/or glauconite and kaolinite does not vary. The presence of glauconite is indicative of deposition in an open marine environment characterized by low sedimentation rates and shallow water depths [Odin and Matter, 1981]. In fact, benthonic foraminiferal and molluscan assemblages indicate that water depth was less than 150 m [Hansen et al., 1987; Keller, 1989a] during deposition of the K/T boundary sequence.

No trace element analyses are available for the Brazos core. However, trace element analyses have been published by Ganapathy et al. [1981] and Asaro et al. [1982] for the Brazos River section also known as Brazos 1 [Hansen et al., 1984, 1987; Keller 1989a] located about 1 mile (1.6 km) upstream from the Brazos core. Figure 1 illustrates lithology, including the tsunami bed and the Ir concentration of Ganapathy et al. [1981] of the Brazos 1 section, and the correlation of Brazos 1 with the Brazos core. The two sections contain essentially identical foraminiferal records as discussed by Keller [1989a]. Trace element analysis shows a first increase in Ir to 1 part per billion (ppb) just below the 10-cm-thick calcareous siltstone or chalk layer. A second increase in Ir to 2.1 ppb occurs about 17 cm above this chalk layer in an inconspicuous thin clayey bed which marks the first appearance of Tertiary planktonic foraminifera [Keller, 1989a] and nannofossils [Jiang and Gartner, 1986, also personal communication, 19881.

<u>Biostratigraphy: The K/T Boundary</u> <u>Transition</u>

one specimen

*Indicates analysis of

Foraminiferal biostratigraphy of the Brazos core and nearby outcrops and detailed census of foraminiferal faunas have been discussed in detail by Keller [1989a]. The K/T boundary in marine deposits is generally defined by the simultaneous extinction of most Cretaceous planktonic foraminifera, or the first



Fig. 1. Iridium concentration in parts per billion at the Brazos 1 section, and litholology of the Brazos 1 and Brazos core. Note, the first appearance of Tertiary planktonic species coincides with a thin clay layer and the second iridium peak. The tsunami deposit is slightly thicker in the core. Data from Hansen et al. [1984] and Ganapathy et al. [1981].

appearance of Tertiary species. The latter is the preferred boundary marker because of possible upward reworking of older specimens. Downward reworking of younger specimens is considered less likely. In the Brazos core the first Paleocene planktonic foraminiferal species (Globigerina fringa, Woodringina hornerstownensis and Globastica sp.) are found 17 and 20 cm, respectively, above the tsunami deposit (samples 253-256, Figures 1, 2, and 3) near the thin brown clay layer, which contains the uppermost Ir peak in the nearby Brazos 1 outcrop. The first Tertiary nannofossils are found near this clay layer in Brazos 1 [Jiang and Gartner, 1986]. The first appearance of Tertiary nannofossils and planktonic foraminifers thus characterize the K/T boundary in Brazos River sections and at other high sedimentation boundary transitions such as those at El Kef, Tunisia, and Caravaca and Agost in Spain [Smit, 1982, 1989; Keller, 1988; Brinkhuis and Zachariasse, 1988]. The first appearance of 'Globigerina' eugubina, which defines the base of foraminiferal Zone Pla occurs at 47.5 cm above the tsunami deposit (in sample 261, Figures 2 and 3). The last occurrence of 'G', eugubina, which was used to mark the Pla/Plb boundary is at 105 cm above the tsunami deposit (sample 279

[Keller, 1989a]). The top of the foraminiferal Subzone Pla ('G', eugubina) coincides with the top of Chron C29R estimated at 66.17 Ma and the K/T boundary is estimated at 66.4 Ma by Berggren et al. [1985]. Zones PO-Pla therefore span about 230,000 years. Since Zone PO spans about 50,000 years based on the first appearance datum of <u>Globigerina</u> eugubina at 66.35 Ma [Berggren et al., 1985], a sedimentation rate of 0.4 cm/1000 years is estimated for this zone in the core. Comparison with the other Brazos sections suggests that an interval representing about 80,000 years is missing in the upper part of Zone Pla in the cored section, assuming that the same average sedimentation rates continued through Subzone Pla [Keller, 1989a]. This short hiatus is well above the K/T boundary at the top of the paleomagnetic Chron C29R and therefore in no way hinders accurate placement of the boundary.

The section just below the microfossil defined K/T boundary belongs to the latest Maastrichtian <u>Pseudotextularia</u> <u>deformis</u> Zone [Keller, 1988]. Assuming that the sediment accumulation rate above and below the tsunami bed remained constant through Chron C29R, because average rates in Zone P0 and Chron C30N are similar, Keller [1989a] estimated that about 295,000 years



γd Hiatuses are marked wiggly lines: a short hiatus of about 80,000 years appears to be present at the Pla/Plb Subzone boundary and another hiatus of about 295,000 years is present at the base of the tsunami deposit. Numbers and ticks to the right of the lithological column represent samples. Black intervals in the core indicate missing section. Thick lines mark the Planktonic foraminiferal species ranges, oxygen and carbon isotope compositions of selected species, and relative abundance of <u>Heverohelix</u> <u>globulosa</u> across the K/T boundary interval in the Brazos core. actual occurrence of species in the section. Faunal data from Keller [1989a]. Fig. 2.



Fig. 3. Expanded K/T boundary record detailing foraminiferal δ^{13} C data and ranges of key planktonic foraminiferal species plotted versus thousand of years before and after the K/T boundary event in the Brazos core. Species ranges: 1, <u>H. striata; 2, P. excolata; 3, R. macrocephala; 4, R. rugosa; 5, P. kempensis;</u> 6, <u>P. costulata; 7, H. pulchra; 8, H. americana; 9, R. hexacamerata; 10, G. fringa; 11, W. hornerstownensis; 12, Globastica sp; 13, <u>E. simplicissima;</u> 14, <u>G. eugubina sl; 15, G. conusa; 16, G. edita; 17, G. daubjergensis;</u> 18, <u>G.</u> triloculinoides; 19, <u>G. taurica</u>.</u>

are missing at the scoured surface where the tsunami deposit rests. The complete sequence of earliest Tertiary foraminiferal and nannofossil species present above the tsunami bed indicates that this hiatus only affects latest Maastrichtian sediments and does not hinder the accurate placement of the K/T boundary [Jiang and Gartner, 1986; Keller, 1989a].

Maastrichtian foraminiferal assemblages change in the last 310,000 years before the appearance of the first Tertiary species (based on estimated sedimentation rates) beginning about 15-25 cm below the tsunami deposit and terminating at the scoured surface at the base of the tsunami deposit (Figure 2). In this interval, 15 species disappear from the record. There is no drastic change in the assemblage composition at the microfossil K/T boundary. However, near the PO/Pla Zonal boundary, nine Cretaceous species disappear from the record. The remaining seven Cretaceous species disappear gradually through Zone Pla and into the lower part of Zone Plb (Figure 2), or between 100,000 and 250,000 years into the Paleocene [Keller, 1989a].

Placement of K/T boundary

There has been some disagreement as to the placement of the K/T boundary in Brazos River sections. Microfossil workers place the K/T boundary at the first appearance of Tertiary planktonic foraminiferal and nannofossil species in agreement with the placement of this boundary in sections globally [Jiang and Gartner, 1986; Smit, 1982, 1989; Brinkhuis and Zachariasse, 1988; Keller, 1988, 1989a,b]. In the Brazos River sections, Hansen et al. [1987] and Bourgeois et al. [1988] place the K/T boundary at the top of the tsunami deposit based on the reasoning that this deposit was caused by a tsunami wave generated by the hypothesized K/T bolide impact and that most macrofossils disappear at or below the scoured base of the tsunami deposit.

In the Brazos River sections the microfossil defined boundary coincides with the thin brown clay layer and upper Ir peak in the Brazos 1 section [Ganapathy et al. 1981] (Figure 1). The lower Ir peak occurs just below the calcareous siltstone or chalk bed that marks the top of the tsunami deposit [Hansen et al., 1984, 1987] (Figure 1). It has been argued that the intervening 17-20 cm of sediment between the top of the tsunami deposit and the microfossil defined K/T boundary are resuspended sediment that settled from the water column after the tsunami event and hence represent the same event [Hansen et al., 1987; Bourgeois et al., 1988]. Keller [1989a] argued that the absence of grain size grading and reworked Maastrichtian species in these sediments (although they are present at the base and below the tsunami bed), and the continued presence of abundant small Cretaceous species up to 1 m to 1.5 m above the tsunami deposit does not support this interpretation.

To clarify this disagreement and to determine the location of the K/T boundary independent of microfossil biostratigraphy, we measured $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios of monospecific foraminiferal and bulk carbonate samples across a 3-m interval spanning both the tsunami deposit and the microfossil defined boundary. The δ^{13} C results show a gradual decrease beginning at the first appearance of Tertiary planktonic foraminifera in the Brazos core section, correlative in the Brazos 1 section with a foraminiferal ¹³C depletion (M. Lindinger and G. Keller, unpublished data, 1987) and the upper of two Ir peaks [Ganapathy et al., 1981] (Figure 1). The

juxtaposition of the decrease in δ^{13} C values and the evolution of the first Tertiary plankton is widely accepted as defining criteria for the K/T boundary. This same relationship characterizes the K/T boundary in the most complete sections such as those at El Kef, Caravaca, and Agost where Ir anomalies also mark this interval [Smit, 1982, 1989; Keller, 1988; Lindinger, 1988].

The first appearances of Tertiary planktonic foraminifera and nannofossils coincident with the onset of the ¹³C depletion in the Brazos core section therefore unequivocally place the K/T boundary 17 cm above the 10-cm-thick calcareous siltstone or chalk that originally defined the top of the tsunami deposit [Hansen et al., 1987; Bourgeois et al., 1988]. The issue that has not been resolved is whether the 17 cm of uniform fine-grained shaly sediments are part of the tsunami event representing a later stage settling from the water column despite absence of characteristic grading features or the characteristic Maastrichtian planktonic foraminifers present at the scoured surface at the base of the tsunami deposit. There is also no consensus as to the origin of this "tsunami deposit." At Brazos River the tsunami deposit could be a submarine shelf channel deposit or a shelf fan deposit [Jiang and Gartner, 1986; G. Baum, written communication, 1988]. Coarse sediment deposits at or near the K/T boundary in the sections at Deep Sea Drilling Project (DSDP) sites 151 and 153 in the Caribbean and in onshore deposits in Cuba have recently been interpreted as having been generated by a tsunami wave after a bolide impact and to be correlative with the tsunami deposit at Brazos River [Hildebrand and Boynton, 1990]. This and other evidence has been used to suggest that the site of the K/T boundary bolide impact was between North and South America [Hildebrand and Boynton, 1990]. The stratigraphy of these Caribbean deposits, however, is still poorly resolved. Although the question of the origin of the tsunami deposit at Brazos River is beyond the scope of this paper, there is enough uncertainty that it should be divorced from the definition or characterization of the K/T boundary.

Unfortunately, trace element analysis of the Brazos River section does not clarify placement of the K/T boundary. The double Ir peaks of Ganapathy et al. [1981] in the tsunami deposit (1ppb) and at the microfossil defined boundary (2.1 ppb), and a possibly third smaller peak at the base of the tsunami deposit reported by Asaro et al. [1982] are much smaller than Ir anomalies reported for other sequences. Moreover, multiple Ir anomalies have been reported from a number of sections including DSDP site 577 [Michel et al., 1985], the Alps [Graup and Spettel, 1989] and Sopelana, Spain [Rocchia et al., 1988]. In the Lettengebirge section, Graup and Spettel [1989] found the multiple Ir enrichments associated with chalcophile trace elements primarily contained in sulfides, which they believe points to a volcanic origin and unrelated to an extraterrestrial impact. In contrast, Rocchia et al. [1988] and Michel et al. [1985] favor an extraterrestrial source with postdepositional sedimentary changes due to biochemical or geochemical activity related to the major faunal and environmental changes associated with the K/T boundary catastrophe. Until the origin of Ir enrichments and the postdepositional behavior of Ir are better understood, the Ir anomaly, especially when there are multiple enrichments, is a poor indicator for the placement of the K/T boundary.

Cretaceous Survivors

There are some doubts as to whether Cretaceous species reported by Keller [1988, 1989a] from Danian sediments represent in situ fauna (i.e., Cretaceous survivors), or older redeposited specimens from Cretaceous sediments [Smit, 1982; Smit and Romein, 1985]. Earlier workers have observed Cretaceous species in early Paleocene sediments [Smit, 1977; Gerstel et al., 1986], but their presence was frequently interpreted as being due to redeposition of Cretaceous sediments. The main problem has been the difficulty in identifying in situ versus redeposited specimens. Redeposited specimens are generally identified by their poorer preservation relative to the in situ fauna and by their presence in younger sediments than the age of their supposed disappearance from the record. The later criterium is a hindrance in Danian sediments because it assumes that all Cretaceous species went extinct at the K/T boundary.

Foraminiferal stable isotope results provide independent means of testing whether the Cretaceous species present in Danian sediments are survivors. Because of the large 13 C depletion of surface water total dissolved carbon after the K/T boundary, Cretaceous species living after the event must have lower 13 C/ 12 C ratios relative to their Cretaceous relatives. Indeed, stable isotope results of the Cretaceous species <u>H. globulosa</u> from Cretaceous and Danian sediments in the Brazos core exhibit this pattern which demonstrates the survival of this species after the boundary event.

MATERIALS AND METHODS

Foraminiferal and sediment samples analyzed in this study were taken from the stratigraphic levels in the core indicated in Figure 2 and listed in Table 2. We isotopically analyzed specimens of the planktonic foraminiferal species Heterohelix globulosa in the size fraction between 150 and 65 μ m, whereas those of the benthonic foraminifera Lenticulina spp were larger than 250 μ m. Isotopic analyses of Lenticulina spp were done on samples containing multiple specimens as well as a single specimen. Those tests with the best preservation, as discussed below, were selected for isotopic analysis. It was not possible to isolate sufficient nannofossils from the sediment for isotopic measurement and to obtain an additional record of nearsurface water conditions. Instead undifferentiated carbonate in sediment samples referred as "bulk carbonate" was analyzed. Thin section observations indicate that this material represents a variable mixture of foraminifera, nannofossils and diagenetic carbonate particles, with the later increasing in abundance in uppermost Maastrichtian and Tertiary sediments (Table 1).

Sediment samples were processed according to standard micropaleontological techniques [Keller, 1986]. Before isotopic analysis, extraneous material inside foraminiferal chambers was removed by ultrasonic agitation of the tests in distilled water. This was not possible when only one specimen was analyzed and consequently, we selected specimens that contained little infilling material. For analysis of bulk carbonate, sediment samples were crushed to a fine powder and roasted in vacuum at 400°C for one hour. Bulk samples were reacted in 100% H₃PO4 at 25°C for several hours and the evolved CO₂ was isolated for analysis in a Finnigan MAT model DELTA S mass spectrometer.

Foraminifer isotopic analyses were made on a Finnigan MAT 251 mass spectrometer using an automatic carbonate preparation device (Kiel device), where samples are reacted individually with 100% H_3PO_4 at 75°C. Data are reported in δ notation as permil deviations from the Peedee belemnite standard (PDB). Nineteen samples of National Bureau of Standards (NBS) Isotopic Reference Material 20 (Solenhofen limestone) of weight similar to that of the analyzed foraminiferal samples measured -4.157±0.139 permil (2 σ) for δ^{18} 0 and -1.105±0.062 permil (2 σ) for δ^{13} C. NBS 20 is assumed to have values of -4.14 per mil $(\delta^{18}O)$ and -1.06 per mil $(\delta^{13}C)$ [Craig, 1957].

Semiquantitative determinations of the mineralogical composition of the sediments were made by thin section observations and X ray diffraction patterns. Percent $CaCO_3$ of bulk samples, previously powdered and dried, was measured with a Coulometric Carbonate-Carbon Analyzer. Determination of percent organic matter were estimated by weight after combustion of the organic matter at approximately $400^{\circ}C$.

Foraminiferal Preservation

The preservation of most foraminiferal taxa selected for isotopic analysis was judged excellent based on (1) visual inspection of tests under the binocular microscope; (2) scanning electron microscope (SEM) observation of the wall structure, and interior and exterior chamber surfaces which showed no secondary and/or overgrowth calcite precipitation and (3) lack of luminescence of the wall observed under the cathodoluminescent microscope indicating that the original calcite has not been replaced by diagenetic calcite. Most Cretaceous specimens from sample 253 and lower levels, and Tertiary specimens above sample 269 (Figure 2) present no overgrowth on chamber surfaces (Figures 4a and 4b and Figures 5c and 5f) and test walls have not been replaced by secondary calcite as evidenced by the preservation of fine pores and wall structures (Figures 4c and 5c), and absence of luminescence, although matrix infilling of some of these Tertiary specimens was brightly luminescent. SEM observation of earliest Danian benthonic and planktonic specimens from samples 256 through 268 (Figures 2, 3, and 4d-4f, 5g-5i), show that wall structures were affected by solution processes, which have also erased

distinctive features of the test surfaces. In addition, chamber walls of these specimens were luminescent indicating diagenetic replacement of foraminiferal calcite. Nearly all of the samples from this interval were infilled by brightly luminescent carbonate. The wall of these tests also had a massive appearance (Figure 4f) and original tests structures such as fine pore spaces observed in surfaces and walls of well-preserved older and younger specimens (Figure 4c) were partially filled with diagenetic calcite, or not apparent in most tests from this interval.

FORAMINIFERAL ISOTOPIC SYSTEMATICS AND PALEOECOLOGY

Cretaceous-Paleocene Lenticulina spp. have modern representatives only at the genus level. Consequently, it is impossible to ascertain whether the isotopic compositions of these extinct taxa reflect equilibrium precipitation. Nevertheless, Cretaceous Lenticulina spp. are believed to have inhabited shallow water environments similar to their modern counterparts, which are depleted in ¹⁸0 by a few tenths to about 1 permil and in ^{13}C up to about 2 permil from equilibrium values [Grossman, 1987]. It is probable that δ^{18} O and δ^{13} C compositions of species of Lenticulina from Brazos sediments are likewise depleted from equilibrium values. For example, Maastrichtian L. macrodisca from shelf sediments on Seymour Island, Antarctica, have $\delta^{18}O$ and $\delta^{13}C$ values lower by 0.3 permil than species of <u>Cibicides</u> [Barrera et al., 1987], whose modern counterparts also have $\delta^{13}C$ and $\delta^{18}O$ compositions lower than and somewhat similar to equilibrium values, respectively [Grossman, 1987].

Today, planktonic foraminiferal forms distantly related to <u>H.</u> globulosa exist in restricted areas of the Indian and Pacific Oceans [Boersma and Premoli Silva, 1989]. The isotopic systematic of these taxa has not been studied. In Late Cretaceous times, biserial heterohelicids such as H. globulosa were opportunistic forms that thrived in epicontinental seas in waters of low oxygen content and high salinity and apparently continued to thrive in similar conditions during the Paleogene [Hamaoui, 1966; Lindsay and McGowran, 1986; Boersma and Premoli Silva, 1989]. Paleogene biserial heterohelicids have been found to have the lowest $\delta^{13}C$ values and intermediate δ^{18} O values relative to other



Fig. 4. (Opposite) (a) Lenticulina spp. Brazos core sample 240, Late Mastrichtian Zone <u>P. deformis</u>, magnification X100, scale bar = 100 μ m. (b) Fractured test of the Lenticulina spp. specimen in Figure 4a, showing absence of overgrowth or infilling material on interior chamber surfaces, magnification X170, scale bar = 58 μ m. (c) Aspect of the chamber wall of the Lenticulina spp specimen in Figures 4a and 4b showing excellent preservation of structures and pores, magnification X3500, scale bar = 3 μ m. (d) Lenticulina spp. Brazos core sample 259, early Danian Zone



P0, showing lack of chamber sutures and other solution features, magnification X100, scale bar = 100 μ m. (e) Fractured test of the <u>Lenticulina</u> spp specimen in Figure 4d, showing chambers entirely filled by diagenetic calcite, magnification X100, scale bar = 100 μ m. (f) Aspect of the chamber wall of the <u>Lenticulina</u> spp specimen in Figures 4d and 4e, showing massive aspect of wall replaced by secondary calcite, and chamber filled by diagenetic calcite, magnification X5000, scale bar = 2 μ m.



Fig. 5. (Opposite) (a) Lenticulina spp. Brazos core sample 269, early Danian Subzone Pla, magnification X200, scale bar = 50 μ m. (b) Fractured test of the Lenticulina spp. specimen in Figure 5(a), showing some chambers partially filled by diagenetic calcite, magnification X500, scale bar = 20 μ m. (c) Aspect of the chamber wall of the Lenticulina spp. specimen in Figures 5(a) and (b), showing excellent preservation of non-luminescent calcite structure and pores, magnification X12000, scale bar = 0.8 μ m. (d) <u>Heterohelix</u> globulosa Brazos core sample 240, late Maastrichtian Zone <u>P.</u> <u>deformis</u>, magnification X400, scale bar = 30 μ m. (e) <u>H. globulosa</u> showing interior surface free of secondary overgrowth calcite, Brazos core sample 240, late Maastrichtian Zone P. deformis, magnification X400, scale

bar = 30 μ m. (f) Wall structure of <u>H</u>. globulosa composed of fine cristallite units and showing preserved pore spaces and no secondary overgrowth on interior surfaces, Brazos core sample 240, late Maastrichtian Zone P. deformis, magnification X 5500, scale bar = 2.5 μ m. (g) <u>H. globulosa</u> showing partial solution of chamber exterior surface, note smaller size of test relative to specimen in Figure 5(d), Brazos core sample 259, early Danian Zone PO, magnification X400, scale bar = 30 μ m. (h) <u>H. globulosa</u>, Brazos core sample 261, early Danian Zone PO, magnification X400, scale bar = 30 μ m. (i) Interior of chamber of <u>H. globulosa</u> showing little overgrowth on surfaces, Brazos core sample 261, early Danian Zone PO, magnification X1700, scale bar = 10 μ m.

planktonic foraminiferal species [Boersma and Premoli-Silva, 1989]. Based on this isotopic ranking, they are inferred to have lived within the oxygen minimum zone in pelagic environments [Boersma and Premoli Silva, 1988]. Isotopic values of Cretaceous <u>H. globulosa</u> from shallow-water shelf environments are first presented here.

ISOTOPIC RESULTS

Stable isotopic results from the Brazos Core across the K/T boundary are tabulated in Table 2 and illustrated in Figure 2 along with species range data and relative abundance of <u>H.</u> <u>globulosa</u>. Figure 3 shows expanded details of foraminiferal δ^{13} C values and species ranges across the K/T boundary. The δ^{18} O and δ^{13} C values of the biserial planktonic foraminifera H. globulosa and the benthonic foraminifera Lenticulina spp. exhibit similar trends. Maastrichtian δ^{13} C values (samples 217-252) are stable with values of <u>Lenticulina</u> spp averaging -0.25±0.34 or 0.15 permil lower than mean values of <u>H.</u> globulosa (-0.10 ± 0.23) . This small δ^{13} C difference between planktonic and benthonic values may reflect H. globulosa's habitat within an oxygen deficient layer in the water column and/or disequilibrium precipitation of either H. globulosa or Lenticulina spp. The average of Maastrichtian δ^{18} O values of Lenticulina spp (-1.66±0.17) is 1.14 permil higher than that for <u>H.</u> globulosa (-2.80±0.46) (Figure 2). The range of δ^{18} O values of <u>H.</u> globulosa (1.58 permil) is greater than that of the benthonic taxon (0.67 permil) and probably caused by the greater variability in surface water conditions. These patterns are expected for normal marine settings where surface waters are warmer, less dense, and enriched in ¹³C relative to deeper waters.

In contrast, Tertiary δ^{18} O and δ^{13} C values are lower and significantly more variable than Maastrichtian values. A gradual decrease of about 2-3 permil in both δ^{18} O and δ^{13} C values begins in sample 253 coincident with the first appearance of Tertiary foraminiferal taxa (<u>Globigerina fringa</u> and <u>Woodringina</u> <u>hornerstownensis</u>, Figures 2 and 3), which mark the K/T boundary. The depletion follows a continuous trend with each successive sample more depleted than the preceding sample and reaches a minimum in sample 261 about 20 cm above the K/T boundary (Figure 3). The gradual ¹³C depletion thus spans the earliest Tertiary foraminiferal Zone PO. The $^{13}\mathrm{C}$ depletion within Zone PO is greater for the planktonic <u>H. globulosa</u> than for the benthonic Lenticulina spp., but depletion in ¹⁸0 is about of the same magnitude for both taxa (Figure 2). For instance, <u>H.</u> globulosa δ^{18} 0 values average -4.34±1.13 and are 1.08 permil lower than benthonic values (-3.26±1.16) from the same samples (253-259, 271). Thus the difference between δ^{18} O values of benthonic and planktonic foraminifera in the same samples appears to be approximately the same in the earliest Danian (Zone PO) as in Maastrichtian sediments. There is also no significant change in the difference between $\delta^{13}C$ values of planktonic and benthonic foraminifera from Maastrichtian and basal Danian samples (253-256). However, there is a reversal in δ^{13} C values of younger samples (257,259,271) where planktonic foraminifera are on the average more depleted in ¹³C by 0.73 permil than benthonic foraminifera (Figures 2 and 3). Absolute δ^{13} C values of single specimens of Tertiary Lenticulina spp. are similar to those of multiple specimens (Figure 3), but δ^{18} 0 values are significantly different from multiple specimens results particularly in the earliest Danian.

After the gradual K/T boundary depletion in both ¹³C and ¹⁸O, foraminiferal isotopic values remain low during the Danian Zone Pla or upper part of Chron 29R (Figure 2). Higher, but much more variable, δ^{18} O and δ^{13} C values characterize the lower part of Chron 29N (Zone Plb) followed by a return to lower values in the upper part of Chron 29N and lower part of Chron 28R (Zone Plb, Figure 2).

The δ^{16} O values of bulk carbonate samples across the K/T boundary transition do not exhibit the same trend as those of foraminifera (Figure 6). Most Maastrichtian and Tertiary values range between -2 and -3 permil. In contrast, Maastrichtian bulk carbonate δ^{13} C values are somewhat similar to those of foraminifera but Tertiary bulk carbonate values are for the most part very different and extremely variable (Figure 6). Within foraminifera Zone PO, they decrease gradually by 6.5 permil and subsequently increase by 4 permil. The lowest δ^{13} C value across the K/T boundary occurs earlier (sample 259) than in the foraminiferal records (sample 261). Across subzones Pla and Plb, there is a decrease of about 5 permil followed by a 4 permil increase.

The foraminiferal stable isotope data contrast with published K/T boundary transition records on several points: (1) gradual or over several thousand years rather than sudden or instantaneous decrease in δ^{13} C values; (2) gradual 13 C depletion in both benthonic and planktonic values, rather than depletion restricted to the plankton record; (3) simultaneous gradual decrease in both $\delta^{18}{\rm O}$ and $\delta^{13}{\rm C}$ records of planktonic and benthonic foraminifera; and (4) planktonic for minifera δ^{13} C values become more negative than benthonic values 20,000-30,000 years after K/T boundary event and for at least the next 140,000 years, whereas planktonic-benthonic δ^{18} O differences are similar in Maastrichtian and early Paleocene sediments. In the following pages we will discuss each of these features of the Brazos core stable isotope records. First, however, we will present evidence in support of the idea that the Brazos River K/T boundary $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios provide insights into the

environmental conditions near the Brazos in the Gulf of Mexico and globally during the boundary event and that published K/T boundary isotopic records are generally incomplete at the K/T boundary and in the earliest Danian Zone PO, and often reflect diagenetic or species compositional effects.

HIATUS, COMPOSITIONAL, AND DIAGENETIC EFFECTS UPON K/T BOUNDARY STABLE ISOTOPE RECORD

Why are both the faunal and foraminiferal stable isotope records from the Brazos River sections different from the deep-sea records? Perhaps the major difference is the incompleteness of the stratigraphic record in the earliest Danian and across the K/T boundary in the deep sea [Perch-Nielsen et al., 1982; Officer and Drake, 1985; Keller, 1988, 1989b; MacLeod and Keller, 1990]. Over 90% of all sections contain hiatuses or extremely reduced



Fig. 6. Oxygen and carbon isotopic compositions of selected foraminiferal species and and bulk carbonate samples, and percent carbonate content across the K/T boundary in the Brazos core. Symbols in the isotopic records are solid triangles, bulk carbonate samples; crosses, <u>H. globulosa</u>; squares, multiple specimens of <u>Lenticulina</u> spp.

sedimentation at the boundary resulting in the absence of one and frequently two foraminiferal zones (Guembelitria cretacea (PO) and '<u>Globigerina' eugubina</u> (Pla)) in the early Danian. In contrast, shallow epicontinental sea and continental shelf sections such as Brazos River, Texas, and El Kef, Tunisia, as well as the deeper water sections of Caravaca and Agost in Spain have high rates of sediment deposition resulting in expansion of the stratigraphic record [Perch-Nielsen et al., 1982; Smit, 1982, 1989; Brinkhuis and Zachariasse, 1988; Keller, 1988, 1989a]. Therefore, the sudden decrease in $\delta^{13}C$ values at the K/T boundary in deep-sea sections is most likely the result of an incomplete stratigraphic record, whereas at Brazos River sediments which record the gradual depletion in ¹³C represent the missing record. The hiatuses at the top of the Zone Pla and at the base of the tsunami deposit at Brazos River do not affect the earliest Danian record.

Even if the stratigraphic record is relatively complete as indicated by the presence of planktonic foraminiferal Zones PO and Pla, polytaxic compositional effects or diagenesis of carbonate may influence the isotopic record. Paull and Thierstein [1987] report that species compositional effects as a result of the polyspecific nature of carbonate ooze may introduce a systematic variation over a range of 1.25-4 permil for δ^{18} and δ^{13} C in measurements of Holocene and Pleistocene sediments. Such isotopic variations may not be large enough to obliterate, but only to modify, isotopic signatures of major oceanographic events. Published K/T boundary stable isotope records are generally based on analysis of bulk carbonate or fine-fraction carbonate as a surface-water signal and benthonic foraminifera as a deep water signal [Hsü et al., 1982; Zachos and Arthur, 1986; Keller and Lindinger, 1989]. All of these surface water δ^{13} C and δ^{18} O records may contain significant compositional effects in addition to diagenetic overprints. For example, isotopic values of bulk carbonate across the K/T boundary in the Brazos core reflect the relative proportion and isotopic compositions of biogenic and secondary carbonate. Because Brazos core foraminiferal isotopic analyses were performed on monospecific and monogeneric planktonic and benthonic samples, these data do not contain polyspecific compositional effects, or they are minor in the case of monogeneric samples.

Burial diagenesis and lithification of sediments observed to a variable degree in nearly all marine sediments is likely responsible for some of the inconsistencies in deep-sea δ^{18} O records across the K/T boundary [Zachos and Arthur, 1986]. In deep-sea sections, $^{18}O/^{16}O$ ratios can be significantly altered with carbonate dissolution and reprecipitation [Margolis et al., 1987; Williams et al., 1985], whereas original ${}^{13}C/{}^{12}C$ ratios will remain essentially unchanged by diagenesis in sediments with low organic carbon content. Except for earliest Danian samples, Brazos core foraminiferal carbonate exhibits excellent preservation and no evidence of replacement by secondary calcite. The $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios of these samples represent original isotopic compositions. Conversely, isotopic ratios of earliest Danian foraminiferal samples have likely been affected by carbonate dissolution/ reprecipitation.

EFFECT OF DIAGENETIC ALTERATION ON BRAZOS CORE ISOTOPIC RECORDS

Diagenetic alteration of original foraminiferal isotopic signatures could be invoked as a cause of the K/T boundary decrease in δ^{18} O and δ^{13} C because calcite in foraminiferal walls of earliest Danian samples (samples 256-268) has been replaced to a large extent by secondary calcite, as evidenced by SEM (Figures 4e and 4f) and cathodoluminescent observations. Replacement of original foraminiferal calcite by secondary calcite is expected to change δ^{16} of and δ^{13} cvalues of different taxa and make them either more similar or more dissimilar, depending on whether different taxa are simultaneously affected to the same extend or whether alteration occurred differentially affecting some species more than others. A possible but less likely case is that diagenetic alteration caused shifts of the same magnitude in isotopic signatures of all the taxa. In the Brazos core, the thinner walled <u>H. globulosa</u> should have been more readily affected by dissolution/ reprecipitation processes than the thick walled Lenticulina spp., modifying original interspecific differences between these taxa. The δ^{18} O differences between <u>H.</u> globulosa and multiple specimen results of Lenticulina spp. are about the same below and above the K/T boundary (Figures 2 and 6 and Table 2). Interspecific $\delta^{13}C$

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differences are also somewhat similar for Maastrichtian and earliest Danian foraminifera (below sample 256). In the early Danian (beginning at sample 257 and above) δ^{13} C values of <u>H</u>. globulosa become more negative than those of Lenticulina spp. (Figures 2 and 3), a pattern that has been observed in planktonic and benthonic microfossil records at some deep-sea sites and is discussed in more detail later. It is also apparent that δ^{13} C and δ^{18} O values of Tertiary foraminifera were lower than Maastrichtian values because well-preserved Lenticulina spp. above sample 268 have lower values than Maastrichtian specimens (Figures 2 and 6). The retention of interspecific isotopic differences indicates that in spite of test replacement by secondary calcite, original foraminiferal $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios have not been extensively modified through the boundary transition. Moreover, it is unlikely that diagenesis could have fortuitously lowered planktonic δ^{13} C values in Foraminiferal Zone PO below those of the benthonic taxa mimicking the pattern observed in other K/T boundary sections. This pattern persists in subzone Plb (sample 271) in the Brazos core where specimens are well preserved (Figure 3). Diagenetic alteration of foraminiferal calcite from the Brazos core could have occurred with limited interaction with pore waters in which the isotopic composition of the reprecipitated carbonate is not very different from that of the pristine foraminifera.

Comparison with isotopic compositions of bulk carbonate samples also provides information on the preservation of foraminiferal isotopic signatures. Bulk carbonate δ^{18} O and δ^{13} C values in the Brazos core should be closer to the average composition of diagenetic carbonate as evidenced by the presence of secondary foraminiferal calcite, brightly luminescent calcite inside foraminiferal chambers, authigenic dolomite rhombus and highly reactive fine carbonate particles, all of which increase in abundance in the Tertiary interval. The δ^{18} O values of these samples do not systematically change across the K/T boundary and range between about -2 and -3 permil in the entire section (Figure 6). These values are not very different from Maastrichtian foraminifera δ^{18} 0 but are several permil higher than those of Tertiary foraminifera. Bulk carbonate $\delta^{13}C$ are not very different from those of the foraminifera, except for the extremely

depleted isotopic compositions within foraminiferal Zone PO and at the top of subzone Pla. This similarity between foraminifera and bulk carbonate compositions suggests that bulk $\delta^{13}C$ values, which are usually less affected by diagenetic processes than $^{18}O/^{16}O$ ratios [Margolis et al., 1987; Williams et al., 1985], may be close to the average original composition of bulk carbonate. The very low δ^{13} C values could reflect carbonate exchange with marine pore waters depleted in ^{13}C from the oxidation of organic matter, although no correlation exists between percent amount of organic carbon or carbonate (see Table 2 and Figure 6) in the sediment and $\delta^{13}C$. Alternatively, they could be the result of extensive carbonate exchange with meteoric waters, in the more permeable Tertiary sediments with lower clay and higher carbonate content than Maastrichtian sediments (Figure 6) Unfortunately, bulk carbonate ¹⁸0/¹⁶0 ratios do not help to discriminate between these two scenarios. Nevertheless, if Tertiary for a miniferal δ^{18} O values significantly reflected diagenetic processes, they would be more similar to bulk carbonate values. This, in fact, explains the more positive δ^{18} O results of single specimens of Lenticulina spp. in comparison with analyses of multiple specimens. In the single specimen measurements, matrix and diagenetic carbonate formed inside foraminiferal chambers could have subsequently exchanged with pore waters shifting foraminiferal δ^{18} O values in the positive direction toward the composition of the bulk carbonate. The ${}^{13}C/{}^{12}C$ ratio of the single specimen, however, may remain similar to that originally in the test.

If isotopic compositions of foraminiferal calcite in earliest Danian sediment had been diagenetically modified, original δ^{18} O values could have been lower and δ^{13} C values would have been higher than we measured. Although difficult to ascertain and quantify, this possibility cannot be ruled out. However, the issues raised above support the argument that the patterns of gradual decrease and subsequent low isotopic values in the earliest Danian are not entirely the result of postdepositional diagenetic processes.

DISCUSSION

Brazos River δ¹³C Record

Gradual ¹³C depletion in monospecific

planktonic foraminifera observed in the Brazos Core is in contrast to the sudden ¹³C depletion observed in bulk or fine fraction carbonates in nearly all known K/T boundary transitions [Hsü et al., 1982; Zachos and Arthur, 1986; Arthur et al., 1987; Keller and Lindinger, 1989]. As discussed above for most K/T boundary sections the difference could be primarily attributed to an incomplete or highly condensed stratigraphic record and secondarily to polytaxic compositional and diagenetic effects. Neither of these appear to affect seriously the foraminifer stable isotope record at Brazos River. The gradual decrease of δ^{13} C values of single specimens of Lenticulina spp. across the K/T boundary transition (Figures 2 and 3) shows that this pattern, in which each sample of single and multiple specimens is successively more depleted than previous samples, is not the result of either upward or downward reworking of sediments. We propose that the onset of the gradual δ^{13} C decline in conjunction with the first appearance of Tertiary planktonic foraminifera in the Brazos core represents evidence for the placement of the K/T boundary at this horizon because the same characteristics have been observed in all relatively complete K/T boundary sections (e.g., El Kef, Caravaca, Agost) as discussed earlier.

At Brazos River, both planktonic and benthonic foraminifera δ^{13} C values decrease gradually beginning at the K/T boundary and ending 17-20 cm above (top of Zone PO; Figures 2 and 3), and stay low for the rest of the Tertiary. In no other K/T boundary section have benthonic foraminifera exhibited this ¹³C depletion. The foraminiferal isotopic pattern at Brazos can be interpreted as a decline in δ^{13} C of TDC affecting the entire water column. An increase in the flux of fresh water into the area beginning at the K/T boundary could have lowered the foraminifera δ^{13} C and δ^{18} O values as observed. However, to account for the δ^{18} O variation, a change in salinity of about 8-10 permil is required, which is not consistent with the absence of change in molluscan assemblages and of colonization by taxa adapted to significantly lower salinity levels in the Tertiary [Hansen et al., 1987]. Moreover, the decrease of surface waters δ^{13} C below that of bottom shelf waters shortly after the K/T boundary (Figure 3) requires a substantial long-term decrease in surface water salinity relative to shelf bottom

waters that is not seen in the δ^{10} record. Although small salinity variations may have occurred at Brazos, this is not the apparent cause of the isotopic change after the K/T boundary.

Alternatively, the foraminiferal gradual δ^{13} C decline at Brazos is related to the global δ^{13} C decrease of surface water TDC recorded at the K/T boundary in other sections. This δ^{13} C change was also recorded by the benthonic foraminifera at Brazos because of the shallow water depth of deposition estimated at less than 150 m [Hansen et al., 1987; Keller, 1989a]. For example, in deeper water sections such as the continental shelf deposit at El Kef deposited at a depth of less than 300 m [Peypouquet et al., 1986; Brinkhuis and Zachariasse, 1988; Keller, 1988] and in deep-sea sections, δ^{13} C values of benthonic foraminifera change little across the boundary interval [Keller and Lindinger, 1989; Zachos and Arthur, 1986]. Therefore, the Brazos River section confirms that the decrease in δ^{13} C of surface water TDC associated with K/T boundary event was indeed restricted to the upper portion of the water column and did not affect deeper waters. Moreover, the greater ¹³C depletion of planktonic foraminiferal values relative to those of the benthonic taxa shortly after the K/T boundary at Brazos is similar to that observed at other sections (i.e., DSDP sites 356, 465, 524, and 577 [Boersma and Shackleton, 1981; Zachos and Arthur, 1986] and interpreted to reflect reduced surface water productivity [Broecker and Peng, 1982] lasting for about 0.5 m.y [Zachos et al., 1989]. In the pelagic environment a drop to low productivity of surface waters appears to occur geologically instantaneous at the K/T boundary event [Zachos and Arthur, 1986; Zachos et al., 1989]. In contrast, in the expanded (17-20 cm) sedimentary record at Brazos, the same global event occurs over a longer time span. The gradual decline in $\delta^{13}C$ of surface TDC began at the K/T boundary and reached a minimum 40,000-50,000 years after the event (sedimentation rate 0.4 cm/1000 years [Keller, 1989a], whereas the surface-to-bottom δ^{13} C gradient at Brazos changed as evidenced by planktonic $\delta^{13}C$ values becoming more negative than benthonic values in less than 10,000 years about 25,000 years after the K/T boundary event and continued low for at least the next 140,000 years. The difference between the records of deep-sea and shallow water sections appears to be

due to a short hiatus or condensed interval in the deep sea [MacLeod and Keller, 1990].

The similarity between the observed patterns in deep-sea δ^{13} C records and the stratigraphically expanded record of the Brazos core is evidence that the latter reflects to a large extent the global event associated with the K/T boundary. Significant differences exist, however, between the pelagic and Brazos records which are attributable to the influence of local factors at Brazos as well as the analysis of taxa atypical of the pelagic environment and with unknown isotopic systematics. For example, the Brazos for a miniferal δ^{18} O record discussed in the following section probably reflects regional conditions since a similar trend across the K/T boundary transition has not been observed elsewhere. Absolute δ^{18} O and δ^{13} C values are also lower than isotopic ratios from deep sea K/T boundary sections but are close to those measured in lowlatitude continental margin sections [Keller and Lindinger, 1989]. The small difference between $\delta^{13}C$ values of Maastrichtian <u>H.</u> globulosa and <u>Lenticulina</u> spp. can be interpreted as indicative of no δ^{13} C stratification within the water column at Brazos, a pattern very different from that measured in δ^{13} C records from pelagic settings. This apparent absence of $\delta^{13}C$ stratification may result from the habitat of the planktonic taxon within an oxygen deficient layer in the water column and/or vital effects of either taxon. However, the direction of the change in the $\delta^{13}C$ difference between planktonic and benthonic taxa in early Danian sediments at Brazos is similar to that in other K/T boundary sections arguing for a common cause. We propose that this change in the surface-tobottom δ^{13} C gradient at Brazos reflect a decline in productivity of surface waters in the Gulf of Mexico as previously inferred from δ^{13} C records of other shallow water and pelagic sections [Broecker and Peng, 1982; Hsü et al., 1982; Zachos and Arthur, 1986; Keller and Lindinger, 1989].

This interpretation of the Brazos core foraminiferal δ^{13} C record based on the evidence listed above implies that a sharp decline in surface water productivity occurred either instantaneously or within a few thousand years, but more than 20,000 years after the K/T boundary event. This is not consistent with the impact hypothesis that predicts the demise of marine plankton due to darkness, cold and acid rain as a result of rock dust ejecta from the impact and soot from wild fires in the atmosphere [Wolbach et al., 1985, 1988; Gilmour et al., 1988]. Furthermore, the relative increase in carbonate content of Danian sediments at Brazos (Table 2 and Figure 6) suggests that carbonate dissolution at the K/T boundary transition may have been restricted to deep waters and that surface waters did not increase in their acid content as would be expected from acid rain.

Finally, we have used stable isotope analysis to address the question of Cretaceous reworking in Danian sediments. As discussed above, results of analysis of single Lenticulina spp tests show that specimens across the K/T boundary are not reworked. Moreover, if specimens of the Cretaceous species Heterohelix globulosa, which is abundant in Danian sediments from Brazos River (Figure 2) are reworked, they must have Cretaceous $^{13}C/^{12}C$ ratios, but if this species lived after the K/T boundary event, it must have lower ¹³C/¹²C ratios relative to their Cretaceous relatives. Figures 2 and 3 illustrate the large difference in both δ^{13} C and δ^{16} O values of the Cretaceous <u>H.</u> globulosa from Maastrichtian and Danian sediments. We have also presented evidence in a previous section supporting the argument that these foraminiferal isotopic patterns are not the result of postdepositional alteration of foraminiferal signatures. Therefore, these data exclude the possibility that this species has been upwardly reworked into younger sediments and demonstrate the survival of this taxon after the K/T boundary event. The isotopic data of Lenticulina spp. (from analyses of samples of single and multiple specimens, Figures 2 and 3) also show that Maastrichtian values are consistently higher than those from Tertiary sediments, further indicating that reworking of older foraminiferal specimens is not significant in the Brazos core section and that probably many other species commonly present in Danian sediments are also survivors.

<u>Brazos River δ¹⁸O Record</u>

We interpret the gradual decrease of both the Brazos core benthonic and planktonic δ^{18} O values of about 2.5 permil paralleling the ¹³C depletion as reflecting regional conditions in the Brazos River area because this δ^{18} O patterns has not been observed at any other locality (Figure 2 and Table 2). This decrease beginning at

the K/T boundary and the lower Tertiary δ^{18} O values imply that early Paleocene waters became increasingly warmer and/or fresher than Late Maastrichtian waters. As discussed above, we reject the hypothesis that the isotopic decrease reflects entirely a change in salinity, although small salinity changes cannot be ruled out. A temperature increase of approximately 8°C could account for the ¹⁸0 depletion, and we favor a temperature change of this magnitude or less, and only small salinity variation as the most likely mechanism to explain these Tertiary values. A shallowing in the environment of deposition could have produced the desired effect. However, we found no sedimentological evidence just after the boundary or higher up in the section to suggest modification of the environment from a low-energy middle to outer shelf setting and recent studies have suggested a transgressive episode during deposition of sediments in Foraminiferal Zone PO and Pla based on patterns of sediment accumulation in continental margins and deep sea sections [MacLeod and Keller, 1990]. Nevertheless, if temperature was the primary factor contributing to the foraminiferal δ^{18} O change, the climate of the Brazos area in the early Danian was relatively unstable.

Planktonic Foraminiferal Extinctions

There is no extinction of foraminiferal species at the level of the first appearance of Tertiary planktonic species or the onset of the gradual carbon and oxygen isotope shifts, where we place the K/T boundary in the Brazos Core (Figure 2). Cretaceous species disappear in two major phases: (1) just below and at the tsunami bed where a hiatus spans about 195,000 years, and consequently, the species disappearance may have been more gradual than it appears; and (2) in the early Tertiary near the foraminiferal Zone PO/Pla boundary (Figures 2 and 3). The pattern of foraminiferal disappearance from the record in the Brazos core is not the fortuitous result of reworking or an isolated occurrence because it is also observed in the two nearby sections Brazos-Cm and Brazos 1 [Keller, 1989a] and in the section at El Kef [Keller, 1988, 1989b]. In the pre-K/T boundary extinction phase the Cretaceous species disappearing in Maastrichtian sediments are large, complex, and relatively rare forms which constituted less than 8% of the total number of

individuals in the population, but affected 46% of the total species population [Keller, 1989a,b]. In contrast, the dominant fauna is composed of primitive small species such as <u>H. globulosa</u> and Guembelitria cretacea whose relative abundance in late Maastrichtian sediments does not vary significantly. Thus, relatively minor environmental perturbations including a possible late Maastrichtian sea level regression could have led to the demise or disappearance from the record of these large and relatively rare Cretaceous forms without major effect on the remaining population. The δ^{18} O values of <u>H. globulosa</u> and Lenticulina spp. suggest that late Maastrichtian surface waters experienced greater temperature variability than bottom shelf waters, but there appear not to have been significant change in oceanographic conditions associated with this extinction event, although the presence of the hiatus makes this uncertain. Also, there are no significant faunal or isotopic changes associated with the tsunami deposit although there is a single point negative excursion in the δ^{18} O record of <u>H.</u> globulosa at the top of the tsunami bed (Figure 2), which may imply a warming of surface waters.

The second extinction phase near the Zone PO/Pla boundary caused the demise of about half (9) of the surviving Cretaceous species. This phase coincides with the minimum in δ^{18} and δ^{13} C values (Figures 2 and 3), suggesting that severely stressed environmental conditions led to the demise of these Cretaceous survivors. The effect of adverse environmental conditions is also apparent in <u>H. globulosa</u> the most dominant Cretaceous survivor species. Figure 2 illustrates that <u>H. globulosa</u> began to decline in abundance shortly after the K/T boundary mimicking the gradual decrease in isotopic ratios. In fact, the major drop in the abundance of <u>H.</u> globulosa coincides with its ¹³C depletion relative to values of <u>Lenticulina</u> spp. An increase in the $\delta^{13}C$ surface-to-bottom shelf water gradient, which became inverted, reflecting the decrease in surface water productivity occurred at this time (Figures 3 and 6). Moreover, post-K/T boundary foraminiferal tests appear generally smaller implying stunted growth or juveniles [Keller, 1989a]. After this extinction event the remaining Cretaceous survivors disappear gradually in sediments deposited between 100,000 and 250,000 years after the K/T

boundary (Zones Pla ('<u>G. eugubina</u>') and Plb (<u>G. pseudobulloides</u>)). Both oxygen and carbon isotopic ratios of <u>Lenticulina</u> spp. in this interval exhibit increased variability suggesting that the disappearance of the last Cretaceous species was caused by unstable climatic and oceanographic conditions.

CONCLUSION

The foraminiferal isotopic data from Brazos River indicate that different climatic conditions and circulation patterns from those of late Maastrichtian time developed in this area during the early Tertiary. The late Maastrichtian is generally interpreted as a time of gradually falling sea level which may have reached a local maximum about 300,000 years prior to the K/T boundary [Haq et al., 1987], or about the time of the tsunami deposit or hiatus. Keller [1989a] interpreted the species disappearance below the tsunami deposit as the result of a shallowing sea and destruction of deep water habitats; other species ranges are truncated by the hiatus. Sea level transgressed gradually in the earliest Tertiary [Haq et al., 1987] and may have reached a local maximum at the end of the '<u>G.</u>' <u>eugubina</u> Zone (Pla) resulting in starvation of sediments, glauconite deposition, and a short hiatus in the Brazos River sections, which is also observed in sections from the Negev, Israel [Keller et al., 1990; MacLeod and Keller, 1990]. By this scenario, the K/T boundary event is superimposed on a gradually changing environment and resulted in large scale changes in climate and productivity over at least a 200,000-year interval when most planktonic foraminifera which survived the K/T boundary event became extinct. The adverse effect of the K/T boundary event was not instantaneous as commonly thought but resulted in a gradual environmental deterioration that reached a maximum about 40,000 years later as indicated by the stable isotope data (Figures 2 and 3). The change involved a decrease in the $\delta^{13}{\rm C}$ of surface water TDC, a pronounced long-term reduction in the productivity of surface waters beginning about 20,000 years after the K/T boundary event and perhaps higher seawater temperatures. These conditions negatively affected the relative abundance and test size of Cretaceous survivor species which exhibit stunted growth in

this interval [Keller, 1989b]. It appears that some unknown phenomena, perhaps initiated by a bolide impact or volcanism but lasting for tens of thousand of years, brought about the gradual change in the marine carbon distribution and caused prolonged unstable environmental conditions. It is also apparent that these conditions persisted for several hundred thousand years, either because the perturbations were so severe that a long time was required for the recovery of the oceanic ecosystem or because the initial conditions that provoked them were still present. Although foraminiferal isotopic data for the K/T boundary transition in other stratigraphically complete sections are needed to clarify the input of local factors in the isotopic record of the Brazos core, these data question the sudden catastrophic effects on marine plankton or the environment proposed by the bolide impact hypothesis.

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