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Stable isotopic response to late Eocene extraterrestrial impacts

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ABSTRACT

We evaluated the age of two Upper Eocene impact ejecta layers (North American microtektites linked to the Chesapeake Bay impact structure and clinopyroxene [cpx] spherules from the Popigai crater) and the global effects of the associated impact events. The reported occurrence of cpx spherules from the Popigai impact structure at South Atlantic ODP Site 1090 within the middle of magnetochron C16n.1n yields a magnetochronologic age of 35.4 Ma. We generated high-resolution stable isotope records at Sites 1090, 612 (New Jersey slope), and Caribbean core RC9-58 that show: (1) a 0.5‰ δ^{13}C decrease in bulk-carbonate at Site 1090 coincident with the Popigai cpx spherule layer, and (2) a 0.4‰–0.5‰ decrease in deep-water benthic foraminiferal δ^{13}C values across the Popigai impact ejecta layer at Site 612 and core RC9-58. We conclude that the δ^{13}C excursion associated with Popigai was a global event throughout the marine realm that can be correlated to magnetochron C16n.1n. The amplitude of this excursion (~0.5‰) is within the limits of natural variability, suggesting it was caused by a decrease in carbon export productivity, potentially triggered by the impact event(s). North American microtektites associated with the Chesapeake Bay impact occur stratigraphically above the Popigai cpx spherules at Site 612 and core RC9-58. We found no definite evidence of a δ^{13}C anomaly associated with the North American microtektite layer, though further studies are warranted. High-resolution bulk-carbonate and benthic foraminiferal δ^{18}O records show no global temperature change associated with the cpx spherule or North American microtektite layers.

Keywords: impacts, climate, foraminifera, stable isotopes.

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INTRODUCTION

Two of the three largest impact craters found on Earth younger than 200 Ma (Popigai and the Chesapeake Bay) are well preserved, yet the environmental effects of these events are poorly understood. The 100-km-diameter Popigai crater, located in northern Siberia, generated clinopyroxene-bearing (cpx) spherules (Whitehead et al., 2000; Glass et al., 2004a; Liu et al., 2006) that are stratigraphically slightly older than the North American microtektite layer (Glass et al., 1998). The North American microtektite layer is thought to be associated with the 85-km-diameter Chesapeake Bay impact structure, located on the eastern shore of North America (Glass et al., 1985, 1998; Glass and Burns, 1987; Glass and Koeberl 1999; Poag et al., 1994; Koeberl et al., 1996; Deutsch and Koeberl, 2006). In situ fragments of tektites that belong to the North American microtektite layer have been radiometrically dated to ca. 35.4 ± 0.6 Ma (2σ) (Glass et al., 1986) and 35.5 ± 0.3 Ma (Obradovich et al., 1989). Recent radiometric dates on four North American tektites produced an age of ca. 35.3 ± 0.2 Ma (2σ) (Horton and Izett, 2005). Thus, the age of the Chesapeake Bay impact structure ranges from 35.3 Ma to 35.5 Ma, assuming the North American tektites/microtektites were formed by the Chesapeake Bay impact event. Cpx spherules have not been radiometrically dated; however, impact melt rocks occurring as irregular melt bodies and coherent sheets from the Popigai crater yielded an age of 35.7 ± 0.2 Ma (2σ) (Bottomley et al., 1997). Cpx spherules associated with the cpx spherule strewn field have been found in the western North Atlantic, South Atlantic, Gulf of Mexico, Caribbean Sea, equatorial Pacific, and eastern equatorial Indian Ocean (Fig. 1) (Glass, 2000, 2002; Glass and Burns, 1987; Glass et al., 1985, 1998; Keller et al., 1987; Glass and Koeberl, 1999; Liu et al., this volume). The Upper Eocene cpx spherule layer also contains clear microtektites, leucocratic and melanocratic microkrystites, and shocked minerals (Clymer et al., 1996; Langenhorst, 1996), as well as a positive iridium anomaly (200 parts per trillion) and Ni-rich spinel crystals (e.g., Pierrard et al., 1998; Glass et al., 2004b). North American microtektites found in sediments from the western North Atlantic, Barbados, Gulf of Mexico, and Caribbean Sea (Fig. 1) have been correlated to the North American tektite/microtektite strewn field based on geographic proximity, age, and geochemical evidence (Donnelly and Chao, 1973; Glass et al., 1982, 1985, 1998; Saunders et al., 1984; Sanfilippo et al., 1985; Keller, 1986; Thein, 1987; Glass and Burns, 1987; Glass and Koeberl, 1999; Deutsch and Koeberl, 2006). The North American microtektite layer also consists of tektite fragments, shocked mineral and rock fragments, and reidite, a high-pressure polymorph of zircon (e.g., Glass, 1989; Glass et al., 2002; Harris et al., 2004).

Both impact structures are well preserved, yet the global environmental response to these large and near-synchronous impacts remains poorly understood. No major extinctions are associated with the late Eocene impact events in benthic foraminifera (Miller et al., 1992), calcareous nannoplankton (Aubry, 1993), or planktonic foraminifera (Pearson et al., 2006), and late Eocene terrestrial biota was largely unaffected (Prothero, 1985). Evidence of a postimpact biological dead zone that is confined to a localized region at the Chesapeake Bay impact site has been reported in the Chickahominy Formation (Poag et al., 2004). One possible exception to the lack of global biotic effects is the reported abrupt decline in abundance of four (or five) low-latitude radiolarian species associated with the cpx spherule layer (Glass and Zwart, 1977; Glass et al., 1985; Sanfilippo et al., 1985; Glass and Burns, 1987; Glass, 2000). Detailed knowledge of environmental and paleoceanographic effects of these extraterrestrial impacts is lacking, in part, because most late Eocene stable isotopic studies have lacked sufficient resolution to decipher any response of Earth's climate system.

Previous studies noted that an extraterrestrial impact of an ice/volatile object could potentially cause a large (>0.5‰), rapid (<10 k.y.), negative excursion in global δ^{13}C records (Wilde and Quinby-Hunt, 1997). Such an explanation of a comet impact has been postulated for the carbon isotope excursion at the Paleocene-Eocene boundary (Kent et al., 2003; Cramer and Kent, 2005; see Schmitz et al. [2004] for an alternative view). If large comet impacts can cause large and rapid δ^{13}C excursions, then a large anomaly should be associated with the late Eocene impact events, if they were indeed part of a comet shower (Farley et al., 1998). However, published stable isotopic records lack the resolution to investigate this prediction adequately: (1) a closely sampled stable isotopic record from Ocean Drilling Program (ODP) Site 689 (Vonhof et al., 2000) lacks precise magnetochronologic age control; (2) isotopic records from Massignano, Italy, suffer from diagenesis (Bodiselitsch et al., 2004); and (3) other deep-sea records lack critical coverage of this time interval (Zachos et al., 2001) or precise calibration to the late Eocene impact record (e.g., ODP Site 1218; Coxall et al., 2005).

Previous studies (Vonhof et al., 2000) from Southern Ocean Site 689 found an ~0.5‰ δ^{13}C decrease in benthic foraminifera associated with an Ir anomaly (Montanari et al., 1993) and cpx spherule layer (Glass and Koeberl, 1999) at 128.7 m below seafloor (mbsf). Bodiselitsch et al. (2004) performed bulk-carbonate analyses on samples from Massignano, Italy, and reported that the lowest δ^{13}C and δ^{18}O values occur in the same stratigraphic interval as the upper Ir anomaly (6.17 m). However, foraminifera from Massignano are described as being altered considerably by diagenesis (Vonhof et al., 2000) and, therefore, may record postdepositional changes to the carbonate's isotopic composition.

We chose South Atlantic Site 1090 (Fig. 1) for this investigation because benthic foraminifera are well preserved, the identified cpx spherule layer is marked by an Ir anomaly (~950 pg/g) (Kyte and Liu, 2002), and the published magnetostratigraphic age control is excellent (Channell et al., 2003). The Upper Eocene impact ejecta layer at Site 1090 was first interpreted to consist of a cpx spherule layer containing microtektites (Kyte and Liu, 2002). Subsequent work at nearby Site 689 (Vonhof and Smit, 1999; Glass and Koeberl, 1999) concluded that microtektites from the cpx spherule layer belong to the North American microtektite

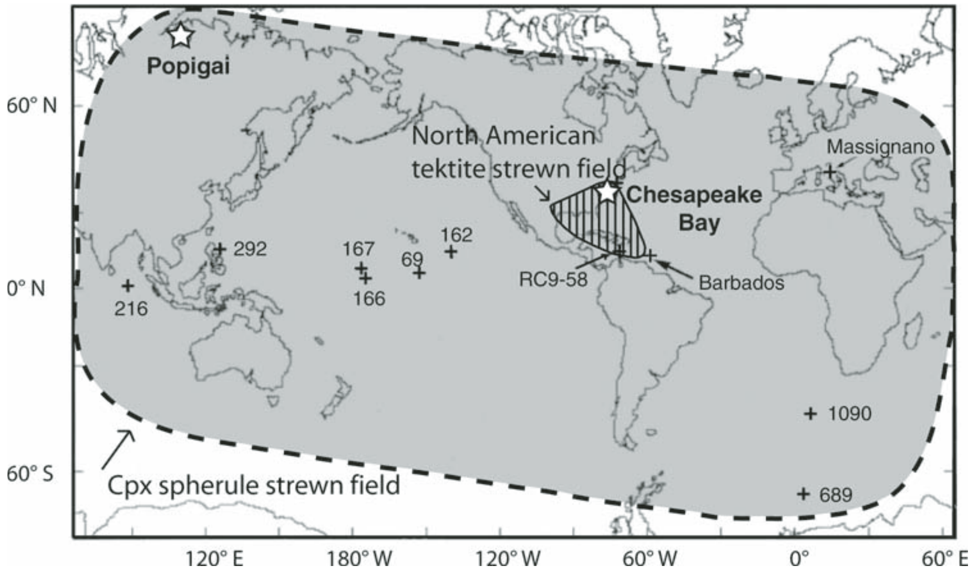

Figure 1. Map of the North American tektite/microtektite strewn field (black lines) and Popigai's clinopyroxene (cpx) spherule strewn field (gray shading). Popigai and Chesapeake Bay craters are shown by the white stars. Map also displays the geographic distribution of sites with identified Upper Eocene cpx spherules (+ signs) from Popigai event (modified from Glass et al., 2004a).

strewn field; this would be the first report of the North American strewn field outside of the North American region (Fig. 1). In contrast, Liu et al. (2006) used radiogenic isotopic studies to interpret the microtektites at Sites 1090 and 689 as exclusively related to the cpx spherule layer and the Popigai impact. We follow their interpretation, which is consistent with the mapped distributions of both the cpx spherule layer and the North American tektite/microtektite strewn field (Fig. 1).

We also analyzed New Jersey slope Deep Sea Drilling Project (DSDP) Site 612 and eastern Caribbean Sea core RC9-58 (Fig. 1) to generate benthic foraminiferal δ^{13}C records across Upper Eocene impact ejecta layers identified at these locations (Glass et al., 1982; Thein, 1987; Glass, 1989). Multiple high-resolution benthic foraminiferal δ^{13}C records from this study are compared with previous work (Vonhof et al., 2000) in order to evaluate the possibility of a δ^{13}C anomaly associated with the late Eocene extraterrestrial impact events.

MATERIALS AND METHODS

ODP Site 1090 (42°54′S, 08°53.98′E) is located in the South Atlantic on the southern flank of the Agulhas Ridge in 3702 m water depth (Shipboard Scientific Party ODP, 1999). Site 1090 paleowater depths of ~3200 m at 34 Ma were estimated using the equation paleodepth = initial depth + $300t^{1/2}$, with a crustal age of 83 Ma, and initial depth of 2700 m (i.e., average ocean crust), and accounting for the effects of sediment loading (Miller et al., 1986; using updated constant of Stein and Stein, 1992). The Upper Eocene cpx spherule layer (Fig. 2; 279 mbsf) is located in sediments described as radiolarian and nannofossil-diatom ooze (Shipboard Scientific Party ODP, 1999; Kyte, 2001). We generated a benthic foraminiferal δ^{13}C record at Site 1090 across the cpx spherule layer (279 mbsf) from 270 to 291 mbsf with a 20 cm (8 k.y.) sampling interval (Table 1). From 266 to 269 mbsf, we increased the sampling interval to every 40 cm (16 k.y.). A high-resolution bulk-carbonate isotopic record was constructed across the cpx spherule layer using a sampling interval every ~5 cm (2 k.y.) (Fig. 2; Table 2).

We produced two additional late Eocene benthic foraminiferal δ^{13}C records, DSDP Site 612 (Table 3) and Lamont-Doherty Earth Observatory (LDEO) piston core RC9-58 (Table 4), which we compare to published data from ODP Site 689 (Fig. 3). DSDP Site 612 (38°49.21′N, 72°46.43′W) is located in 1404 m water depth, with an Eocene paleowater depth of ~1000 m (Miller and Katz, 1987). Site 612 sediments are composed of chalk and biosiliceous calcareous ooze in core 21X section 5, between 110 and 119 cm (181.3 mbsf) (Fig. 3) (Thein, 1987; Glass, 1989). Site 612 shows 3–4 cm of separation between the highest abundance of North American microtektites and that of the cpx spherules (Glass, 1989), equivalent to 1.2–4 k.y., assuming continuous sedimentation (Fig. 3) (Miller et al., 1991). The peak concentration of North American microtektites occurs from 112 to 113 cm, and the highest occurrence of cpx spherules is positioned between 115 and 117 cm (Fig. 3) (Glass, 1989).

Caribbean Sea core RC9-58 (14°33.4′N, 70°48.6′W) is located in 3548 m water depth (Saito et al., 1974) with a late Eocene paleowater depth >1000 m (Baker and Glass, 1974). Core RC9-58 displays 25 cm of separation between the North American microtektite layer and the cpx spherule layer, with its coupled Ir anomaly (Fig. 3) (Ganapathy, 1982; Glass et al., 1982). The equivalent age separation equals ~25 k.y. (Maurrasse and Glass, 1976).

An average of four to five benthic foraminiferal specimens (of the epifaunal genus *Cibicidoides*) per sample were selected for stable isotopic analysis on a Micromass Optima mass spectrometer at the Stable Isotope Laboratory in the Department of Earth and Planetary Sciences at Rutgers University. Duplicate samples were intermittently run to ensure reproducibility of analyses. Samples were reacted with phosphoric acid for 15 min at 90 °C in a multiprep peripheral device and reported against

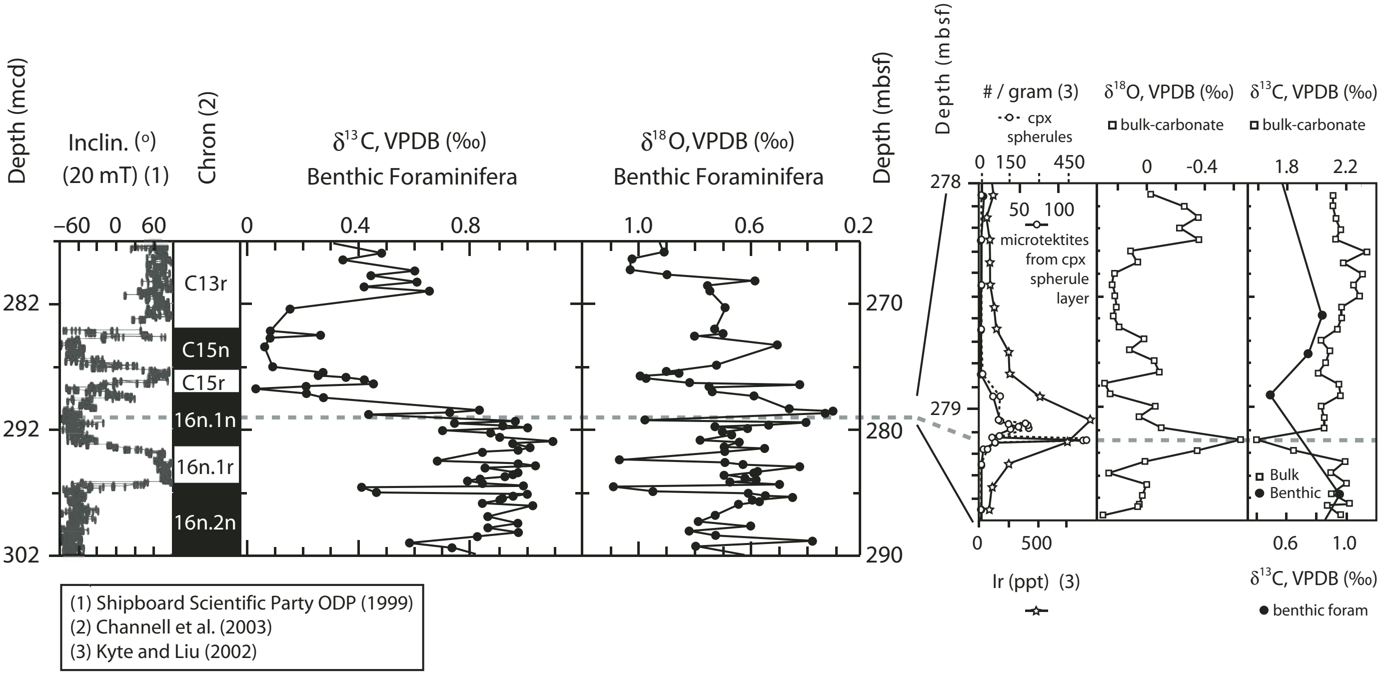

Figure 2. South Atlantic Ocean Drilling Program (ODP) Site 1090 shipboard magnetic inclination (Shipboard Scientific Party, 1999; Channell et al., 2003) plotted with benthic foraminiferal $\delta^{13}C$ and $\delta^{18}O$ data across the clinopyroxene (cpx) spherule layer at ~279 m below seafloor (mbsf) in chron C16n.1n, with a corresponding magnetochronologic age of ca. 35.4 Ma. Meters below seafloor (mbsf) and meters composite depth (mcd) are both displayed to match the work for the magnetic inclination (Channell et al., 2003) and cpx spherule layer (Kyte and Liu, 2002) references. Enlarged plots show Popigai cpx spherule layer, microtektites belonging to the cpx spherule layer, and iridium abundances at Site 1090 plotted next to high-resolution bulk-carbonate $\delta^{18}O$ and $\delta^{13}C$ data. VPDB—Vienna PeeDee belemnite.

the V-PDB (Vienna PeeDee belemnite) standard ($\delta^{18}O = -2.20$‰ and $\delta^{13}C = 1.95$‰; following Coplen et al., 1983). The laboratory standard was checked regularly against NBS-19, which has a $\delta^{18}O$ offset equal to 0.04‰ and a $\delta^{13}C$ offset of 0.10‰. The laboratory standard error (1σ) is equal to 0.08‰ for $\delta^{18}O$ and 0.05‰ for $\delta^{13}C$.

RESULTS

ODP Site 1090 provides a first-order correlation of the Upper Eocene cpx spherule layer to the geomagnetic polarity time scale (GPTS) (Cande and Kent, 1995; Berggren et al., 1995) in chron C16n.1n (279 mbsf; Fig. 2; Channell et al., 2003). Chron C16n.1n has an estimated magnetochronologic age of 35.526–35.343 Ma, and the cpx spherule layer occurs near the middle of the chronozone. Based on interpolations of sedimentation rates between the chron C16n.1n boundaries, the cpx spherule layer has a corresponding magnetochronologic age of 35.43 Ma, which is consistent with published radiometric ages for North American tektites/microtektites ranging from ca. 35.3 to 35.5 Ma (Glass et al., 1986; Obradovich et al., 1989; Horton and Izett, 2005), and slightly offset from Popigai crater melt rocks dated at 35.7 ± 0.2 Ma (2σ) (Bottomley et al., 1997).

Distinct $\delta^{13}C$ decreases are associated with the Upper Eocene cpx spherule layer at ODP Site 1090 (Fig. 2). An ~0.5‰ transient $\delta^{13}C$ anomaly in bulk carbonate occurs precisely at the cpx spherule layer (279.15 mbsf) at this site: the $\delta^{13}C$ decrease occurs within 5 cm (~2 k.y.) of the peak cpx spherule concentration and recovers to near pre-excursion values within 5 cm (~2 k.y.) (Fig. 2). Benthic foraminiferal $\delta^{13}C$ values decrease across the cpx spherule layer (Fig. 2) and return to pre-excursion values ~20 cm (~8 k.y.) above the cpx spherule layer, though our resolution is not sufficient to provide more detail. The transient $\delta^{13}C$ decrease is superimposed on a longer-term decrease (occurring within 1.5 m, equivalent to ~60 k.y.) and numerous 0.2‰–0.5‰ $\delta^{13}C$ changes that reflect variability on a scale of 10^4–10^5 yr (Fig. 2). Site 1090 bulk-carbonate $\delta^{18}O$ values show a distinct 0.5‰ decrease at the cpx spherule layer; however, there is no significant change in benthic foraminiferal $\delta^{18}O$ at the layer (Fig. 2).

DSDP Site 612 displays the cpx spherule layer and North American microtektite layer (Glass, 1989; Miller et al., 1991). We show the onset of a negative (~0.5‰) $\delta^{13}C$ anomaly in benthic foraminifera associated with the cpx spherule layer (Fig. 3). Site 612 benthic foraminiferal $\delta^{13}C$ values are ~0.7‰ just below the cpx spherule layer and drop to ~0.2‰ at 1 cm above the layer (Fig. 3). Insufficient carbonate content prevented us from obtaining benthic and bulk-carbonate data across the peak abundance of North American microtektites at Site 612 in core 21X, section 5, 110–112 cm (Fig. 3).

Core RC9-58 shows that minimum benthic foraminiferal δ^{13}C values occur at 2.9 m, immediately below the cpx spherule layer (2.8 m) (Fig. 3). The 10 cm offset between the δ^{13}C minimum and Ir/cpx spherule peak is within the range for biological mixing depths of deep-sea sediments (Guinasso and Schink, 1975) and is most likely the result of bioturbation of rare benthic foraminiferal specimens versus more common cpx spherules. RC9-58 benthic foraminiferal δ^{13}C values show no significant change across the stratigraphically higher North American microtektite layer (Fig. 3). Bulk-carbonate δ^{13}C values at RC9-58 show minima at 2.8 m, coincident with the cpx spherule layer, at 2.4 m, ~10 cm above the North American microtektite layer, and at 2.1 m (Fig. 3). Large variations in the bulk δ^{13}C at RC9-58 contrast with minimal to no variation in the bulk δ^{13}C record at Site 1090; the only communality is a minimum at the cpx spherule layer at both sites, which, in concert with benthic foraminiferal values, is interpreted as the only interval of whole-ocean δ^{13}C change associated with the cpx spherule layer.

ODP Site 1090 benthic foraminiferal δ^{18}O values show minimal variation across the cpx spherule layer (Figs. 2 and 4). A transient (~0.4‰) δ^{18}O increase in benthic foraminifera occurs ~25 cm below the cpx spherule layer, which is one of several 0.3‰–0.4‰ δ^{18}O changes that reflect variability on a scale of 10^4–10^5 yr (Fig. 2). However, no significant variation in benthic foraminiferal δ^{18}O values occurs across the cpx spherule layer at Site 1090 (Figs. 2 and 4). Site 1090 bulk-carbonate δ^{18}O values display a transient ~0.5‰ decrease at the cpx spherule layer (Figs. 2 and 4). Site 1090 bulk-carbonate δ^{18}O values equal ~0.11‰ just 10 cm below the cpx spherule layer and drop to ~–0.55‰ right at the layer (Figs. 2 and 4).

DSDP Site 612 benthic foraminiferal δ^{18}O values show an overall decrease of ~0.4‰ across the cpx spherule layer (Fig. 4). Site 612 benthic foraminiferal δ^{18}O ratios center on 0.35‰–0.4‰ at 2 cm below the cpx spherule layer and decrease to 0‰ at 1–2 cm above the layer (Fig. 4). Core RC9-58 benthic foraminiferal δ^{18}O values display no change across the cpx spherule layer, but they show a positive shift equal to ~0.4‰ occurring 20 cm above the layer (Fig. 4). RC9-58 benthic foraminiferal δ^{18}O ratios remain steady across the North American microtektite layer around ~0.8‰ (Fig. 4). Core RC9-58 bulk-carbonate δ^{18}O values show an increase of ~0.4‰ at 10 cm above the cpx spherule layer, but they decrease by ~0.3‰ just 10 cm above the North American microtektite layer (Fig. 4). RC9-58 bulk-carbonate δ^{18}O values remain steady around ~–0.6‰ throughout the youngest part of the core from 2.4 to 2.0 m (Fig. 4).

DISCUSSION

Timing and Correlation

The amount of offset in timing between the Popigai and Chesapeake impact events remains unclear. The duration between the two impact events is estimated at less than 25 k.y. from Caribbean core RC9-58, based on constant sedimentation rates across this interval (Fig. 3) (Maurrasse and Glass, 1976; Miller et al., 1991). Although the peak abundance of cpx spherules occurs ~4 cm below that of North American microtektites at DSDP Site 612 (Fig. 3), they occur within the North American microtektite/tektite layer (also consisting of tektite fragments from ~116–117 cm) (Glass, 1989) due to bioturbation. The peak abundance of cpx spherules and North American microtektites at Site 612 also occurs just above a hiatus, which may reflect unusually low sedimentation rates. As noted already, isotopic (Liu et al., 2006), vertical distributional, and global distributional data (Fig. 1) argue that Southern Ocean ODP Sites 1090 and 689 preserve only a single impact ejecta layer (cpx spherule layer associated with Popigai). At Barbados, the North American microtektite layer and a stratigraphically lower Ir anomaly (Sanfilippo et al.., 1985) are separated by 26 cm (~13 k.y.). The inference from stratigraphic constraints of <25 k.y. separation between the two impacts is significantly better than the constraint from radiometric dating (0–400 k.y.).

We show that the Popigai cpx spherule layer is associated with a carbon isotopic excursion (~0.5‰) in bulk carbonate (ODP Site 1090 and core RC9-58) and benthic foraminifera (DSDP Site 612, ODP Site 689, and core RC9-58) (Fig. 3). The timing of this anomaly (ca. 35.43 Ma) is coeval with an ~0.4‰ benthic foraminiferal δ^{13}C decrease at equatorial Pacific ODP Site 1218 (Fig. 3; Coxall et al., 2005; Lear et al., 2004). Of the sites with impact ejecta layer(s) (core RC9-58; Sites 612, 1090, and 689; Fig. 3), two have reasonably complete magnetostratigraphic records (Sites 1090 and 689). The most recent magnetostratigraphic interpretation at ODP Site 689 (Florindo and Roberts, 2005) suggests that chronozone C16n.1r is absent from Hole 689B, making it difficult to obtain a first-order correlation to the geomagnetic polarity time scale. However, the cpx spherule layer and Ir anomaly found at Hole 689B are also identified at nearby Hole 689D (Liu et al., this volume) in chronozone C16n.1n, which is consistent with the first-order correlation at ODP Site 1090 (Fig. 2). We show that the ~0.5‰ δ^{13}C excursion is associated with the Upper Eocene cpx spherule layer found at Sites 612, 689, 1090, and core RC9-58 (Figs. 2 and 3). The wide distribution of the carbon isotopic anomaly, both geographically (Atlantic and Pacific Oceans) and oceanographically (bulk-carbonates representing surface waters, Pacific and Southern Ocean deep water, and Atlantic intermediate water), suggests that this is a global marine event that should also be recognizable in the terrestrial realm. We predict that this global event can be correlated consistently to magnetochron C16n.1n.

Marine Oxygen Isotope Response to Popigai and Chesapeake Bay Impacts

Benthic foraminiferal δ^{18}O values show no consistent trend or variation at Sites 1090, 612, and core RC9-58 (Fig. 4). At low-latitude Site 612, a 0.4‰ decrease (Fig. 4) indicates a maximum warming of 2 °C in intermediate waters.

TABLE 1. BENTHIC FORAMINIFERA (*CIBICIDOIDES* SPP.) STABLE ISOTOPE DATA FOR OCEAN DRILLING PROGRAM SITE 1090

Sample (core-section-depth [in cm])	Depth (mbsf)*	Age (Ma)†	δ^{13}C (‰, VPDB)§	δ^{18}O (‰, VPDB)§
29X-3-84 (cm)	266.14	34.499	0.48	0.91
29X-3-136	266.66	34.513	0.34	1.03
29X-4-65	267.45	34.534	0.60	1.03
29X-4-107	267.87	34.545	0.44	0.90
29X-5-5	268.35	34.558	0.61	0.59
29X-5-43.5	268.73	34.568	0.42	0.76
29X-5-86	269.16	34.579	0.65	0.75
29X-6-64	270.44	34.613	0.15	0.69
29X-7-18.5	272.18	34.671	0.08	0.73
30X-1-58.5	272.58	34.709	0.26	0.70
30X-1-76	272.76	34.726	0.08	0.80
30X-1-142	273.42	34.788	0.06	0.51
30X-2-148.5	274.98	34.937	0.09	0.73
30X-3-58.5	275.58	35.055	0.27	0.90
30X-3-76	275.76	35.091	0.25	0.85
30X-3-96	275.96	35.131	0.35	0.99
30X-3-116	276.16	35.171	0.42	0.97
30X-3-137.5	276.37	35.214	0.45	0.82
30X-4-6	276.56	35.252	0.21	0.43
30X-4-26	276.76	35.292	0.03	0.75
30X-4-66	277.16	35.349	0.21	0.74
30X-4-104	277.54	35.364	0.27	0.59
30X-5-58.5	278.58	35.407	0.83	0.47
30X-5-75.5	278.75	35.414	0.72	0.31
30X-5-94	278.94	35.421	0.43	0.34
30X-5-105 (Ir peak)#	279.05	35.426	N.D.**	N.D.**
30X-5-114 (cpx spherule)††	279.14	35.430	N.D.**	N.D.**
30X-5-138	279.38	35.439	0.96	0.98
30X-6-12	279.62	35.449	0.74	0.40
30X-6-33	279.83	35.457	0.91	0.54
30X-6-48.5	279.98	35.464	1.00	0.73
30X-6-67	280.17	35.471	0.70	0.61
30X-6-87	280.37	35.479	0.87	0.70
30X-6-107.5	280.57	35.488	0.90	0.67
30X-7-5.5	281.05	35.507	1.09	0.78
30X-7-25.5	281.25	35.515	0.95	0.65
30X-7-44	281.44	35.523	1.01	0.70
31X-1-6.5	281.76	35.542	0.97	0.56

(*continued*)

Low-latitude core RC9-58 shows no significant variation in benthic foraminiferal δ^{18}O values across the cpx spherule layer, but an increase of ~0.4‰ occurs 20 cm above the layer (Fig. 4). This suggests a delayed (~20 k.y.) cooling with a maximum temperature change of 2 °C associated with the Popigai impact event. However, no significant change in benthic foraminiferal δ^{18}O values occurs across the North American microtektite layer in core RC9-58. Higher-latitude Site 1090 also displays no major change in benthic foraminiferal δ^{18}O values across the cpx spherule layer, indicating that no temperature variation is associated with the Popigai impact event at this site. Previous work (Vonhof et al., 2000) at Site 689 found an ~0.5‰ increase in benthic foraminiferal δ^{18}O values (Fig. 4), indicating a 2.5 °C cooling. Overall, benthic foraminiferal δ^{18}O values at Site 612 indicate a 2 °C warming across the cpx spherule layer, core RC9-58 shows a delayed (20 k.y.) 2 °C cooling, Site 1090 shows no significant temperature variation, and Site 689 displays a 2.5 °C cooling (Vonhof et al., 2000) associated with the Popigai impact event (Fig. 4). Benthic foraminiferal values from core RC9-58 show no temperature change associated with the North American microtektite layer, and consequently the Chesapeake Bay impact event.

Bulk-carbonate δ^{18}O values from Site 1090 indicate a 2.5 °C warming in surface waters associated with the Popigai impact event, but core RC9-58 shows a maximum 2 °C cooling of surface waters within 10 k.y. of the event (Fig. 4). Core RC9-58 displays a maximum warming of 1.5 °C in surface waters occurring within 10 k.y. of the Chesapeake Bay impact event (Fig. 4). Bulk-carbonate δ^{18}O data from ODP Site 738 (southern Kerguelan Plateau; Liu et al., this volume) show an increase of 0.3‰ across the cpx spherule layer, suggesting a 1.5 °C cooling of surface waters associated with Popigai. This increase is consistent with our core RC9-58 data, but it differs from our South Atlantic Site 1090 data. Coccioni et al. (this volume) found planktonic foraminiferal assemblages that indicate a cooling associated with the Popigai event and a warming linked to the Chesapeake Bay impact. A comparison of these records suggests that any cooling is regional in extent.

TABLE 1. BENTHIC FORAMINIFERA (*CIBICIDOIDES* SPP.) STABLE ISOTOPE DATA FOR OCEAN DRILLING PROGRAM SITE 1090 (*continued*)

Sample (core-section-depth [in cm])	Depth (mbsf)*	Age (Ma)†	$\delta^{13}C$ (‰, VPDB)§	$\delta^{18}O$ (‰, VPDB)§
31X-1-25.5	281.95	35.554	0.84	0.69
31X-1-85	282.55	35.592	0.68	1.07
31X-1-105	282.75	35.604	0.97	0.70
31X-1-125	282.95	35.617	1.03	0.63
31X-1-145.5	283.15	35.630	0.85	0.43
31X-2-18	283.38	35.645	0.97	0.57
31X-2-37	283.57	35.657	0.95	0.59
31X-2-57	283.77	35.669	0.92	0.69
31X-2-75.5	283.95	35.681	0.83	0.62
31X-2-95.5	284.15	35.691	0.79	0.58
31X-2-113.5	284.33	35.698	0.84	0.67
31X-2-135	284.55	35.708	0.99	0.50
31X-3-6	284.76	35.717	0.41	1.09
31X-3-25	284.95	35.725	0.46	0.95
31X-3-45	285.15	35.733	1.00	0.61
31X-3-63	285.33	35.741	0.95	0.55
31X-3-83	285.53	35.749	0.91	0.46
31X-3-105	285.75	35.759	0.90	0.60
31X-3-123	285.93	35.766	0.84	0.58
31X-3-144	286.14	35.775	1.02	0.64
31X-4-82.5	287.02	35.813	0.86	0.73
31X-4-122	287.42	35.830	0.97	0.79
31X-5-12	287.82	35.847	0.86	0.61
31X-5-48.5	288.18	35.863	0.97	0.82
31X-5-88	288.58	35.880	0.82	0.73
31X-5-134	289.04	35.899	0.58	0.39
31X-6-25	289.44	35.916	0.73	0.79
31X-6-104.5	290.24	35.951	0.88	0.59
31X-6-144	290.64	35.968	0.88	0.84
31X-7-30	291.00	35.983	0.50	0.56
31X-CC-18	291.41	36.000	0.81	1.12

*mbsf—meters below seafloor.

†Ages were calculated by interpolating sedimentation rates between the chron boundaries from Channell et al. (2003).

§VPDB—Vienna PeeDee belemnite standard.

#Ir peak—marks depth of the Ir peak abundance, not complete extent of layer.

**N.D.—no data.

††cpx spherule—marks depth of the cpx spherule layer's highest abundance, not complete extent of layer.

Marine Carbon Isotope Response to Popigai and Chesapeake Bay Impacts

Bulk-carbonate isotopic data coincident with the Popigai cpx spherule layer from ODP Site 1090 (Figs. 2 and 3) and previous work at Site 689 (Vonhof et al., 2000) suggest a rapid (<< 10 k.y.) and short-lived (<10 yr) $\delta^{13}C$ response in surface waters. The bulk-carbonate $\delta^{13}C$ anomaly records a negative excursion of ~0.5‰ that is similar to the benthic foraminiferal $\delta^{13}C$ change across the Popigai cpx spherule layer from Site 612, core RC9-58, and previous work at Site 689 (Vonhof et al., 2000) (Fig. 3). ODP Site 1090 benthic foraminiferal $\delta^{13}C$ data show a $\delta^{13}C$ decrease no larger than 0.5‰ (Fig. 2), comparable to the amplitude of background variability. Benthic foraminiferal $\delta^{13}C$ data from the sites with the Upper Eocene cpx spherule layer (Sites 1090, 612, and 689, and core RC9-58) and Site 1218 all show a maximum response of 0.5‰ throughout the ocean carbon system (Fig. 3). Additional $\delta^{13}C$ data are needed to demonstrate that this anomaly also occurred in the terrestrial carbon system in order to evaluate the global response of the carbon cycle system.

We also lack sufficient $\delta^{13}C$ data to fully evaluate the marine carbon isotope response to the Chesapeake Bay impact event. Only two locations examined (Site 612 and core RC9-58) definitely contain microtektites belonging to the North American tektite/microtektite strewn field (Glass, 1989; Glass et al., 1982). Initial benthic foraminiferal data from RC9-58 suggest that a $\delta^{13}C$ anomaly is not associated with the North American microtektite layer, but further analyses at a higher resolution are needed in core RC9-58 and at Site 612 to help separate the global effects between the Popigai and Chesapeake Bay impact events.

Causes and Implications of Marine Carbon Isotope Response

The $\delta^{13}C$ decrease (~0.5‰) we found in bulk-carbonate and benthic foraminiferal values correlates with the cpx spherule layer but not the North American microtektite layer. The ~0.5‰

TABLE 2. BULK-CARBONATE STABLE ISOTOPE DATA FOR OCEAN DRILLING PROGRAM SITE 1090, HOLE B, CORE 30X, SECTION 5

Depth (cm)	Depth (mbsf)*	Age (Ma)†	δ^{13}C (‰, VPDB)§	δ^{18}O (‰, VPDB)§
5	278.05	35.3853	2.12	0.07
10	278.10	35.3873	2.12	–0.16
15	278.15	35.3894	2.14	–0.26
20	278.20	35.3914	2.17	–0.13
25	278.25	35.3934	2.14	–0.26
30	278.30	35.3955	2.35	0.21
35	278.35	35.3975	2.19	0.16
40	278.40	35.3995	2.32	0.32
45	278.45	35.4016	2.26	0.34
50	278.50	35.4036	2.30	0.32
55	278.55	35.4056	2.18	0.31
60	278.60	35.4077	2.18	0.33
65	278.65	35.4097	2.15	0.29
70	278.70	35.4117	2.04	0.11
75	278.75	35.4138	2.10	0.22
80	278.80	35.4158	2.07	0.05
85	278.85	35.4178	2.02	0.01
90	278.90	35.4199	2.16	0.39
95	278.95	35.4219	2.17	0.35
100	279.00	35.4239	2.04	0.04
105 Ir peak#	279.05	35.4260	2.06	0.15
110	279.10	35.4280	2.06	0.00
115 cpx spherule**	279.15	35.4300	1.60	–0.55
120	279.20	35.4321	1.85	–0.25
125	279.25	35.4341	2.20	0.11
130	279.30	35.4361	2.11	0.36
135	279.35	35.4382	2.21	0.10
140	279.40	35.4402	2.11	0.13
144	279.44	35.4418	2.23	0.15
145	279.45	35.4422	2.08	0.17
149	279.49	35.4439	2.17	0.41

*mbsf—meters below seafloor.

†Ages were calculated by interpolating sedimentation rates between the chron boundaries from Channell et al. (2003).

§VPDB—Vienna PeeDee belemnite.

#Ir peak—marks depth of the Ir peak abundance, not complete extent of layer.

**cpx spherule—marks depth of the cpx spherule layer's highest abundance, not complete extent of layer.

TABLE 3. BENTHIC FORAMINIFERA (*CIBICIDOIDES* SPP.) STABLE ISOTOPE DATA FOR DEEP SEA DRILLING PROJECT SITE 612, CORE 21X, SECTION 5

Core	Section	Interval (cm)	δ^{13}C (‰, VPDB)*	δ^{18}O (‰, VPDB)*
21X	5	114	0.21	0.01
21X	5	115	0.16	0.20
21X	5	116	0.31	0.09
21X	5	117	0.64	0.31
21X	5	118	0.68	0.35

*VPDB—Vienna PeeDee belemnite.

δ^{13}C anomaly was an abrupt (<10 k.y.), short-lived (< 10 yr), and apparently a global event. We considered, and then rejected, the possibility that the ~0.5‰ δ^{13}C anomaly resulted from the injection of chondritic or cometary carbon associated with the impactors that formed the Popigai and perhaps Chesapeake Bay craters. Reports of a late Eocene comet shower were based in part on extraterrestrial ^{3}He concentrations from Massignano, Italy (Farley et al., 1998). Impact ejecta deposits associated with the Chesapeake Bay impact structure lack typical extraterrestrial concentrations of certain siderophile, platinum group elements (PGEs), such as Ir (Tagle and Claeys, 2005), and may in fact be due to a cometary impact. However, impactites from the Popigai crater contain PGEs that indicate the impactor was an L-type ordinary chondrite (Tagle and Claeys, 2005). Chromium isotope data from the cpx spherules indicate that the Popigai impactor was an ordinary chondrite (Kyte et al., 2004), in addition to Cr, Ni, and Co interelement ratios, which are also consistent with an L- or LL-type chondrite (Glass et al., 2004a). Chondritic asteroids typically contain very low amounts of carbon (median 0.1 wt% carbon; Makjanic et al., 1993), compared to ~25 wt% carbon in comets (Jessberger and Kissel, 1991). Thus, if Popigai were formed by the impact of an asteroid (Kyte et al., 2004; Glass et al., 2004a; Tagle and Claeys, 2005), then it could not possibly explain the observed δ^{13}C anomaly. The 0.5‰ magnitude of the ocean δ^{13}C excursion is also too large to be explained by the size of a cometary impactor that possibly formed the Chesapeake crater. Typical cometary δ^{13}C values range from –110‰ to –45‰ (Messenger, 2000; Wyckoff et al., 2000; Arpigny et al., 2003); generation of a negative δ^{13}C anomaly of 0.5‰ by a cometary

TABLE 4. BENTHIC FORAMINIFERA (*CIBICIDOIDES* SPP.) AND BULK-CARBONATE STABLE ISOTOPE DATA FOR LAMONT-DOHERTY EARTH OBSERVATORY CARIBBEAN CORE RC9-58

Depth (m)	$\delta^{13}C$ (‰, VPDB)* Benthic Foram	$\delta^{18}O$ (‰, VPDB)* Benthic Foram	$\delta^{13}C$ (‰, VPDB)* Bulk CO_3	$\delta^{18}O$ (‰, VPDB)* Bulk CO_3
2.00	1.09	0.76	2.54	–0.64
2.09	1.19	0.70	2.51	–0.68
2.20	1.16	0.74	2.81	–0.52
2.30	1.06	0.75	2.68	–0.57
2.35	1.23	0.80	2.57	–0.49
2.46	1.11	0.84	2.74	–0.65
2.61	1.04	0.81	2.93	–0.37
2.69	0.83	0.47	2.79	–0.37
2.80	0.62	0.49	2.59	–0.81
2.90	0.55	0.60	2.76	–0.70
3.01	0.92	0.49	2.83	–0.63

*VPDB—Vienna PeeDee belemnite.

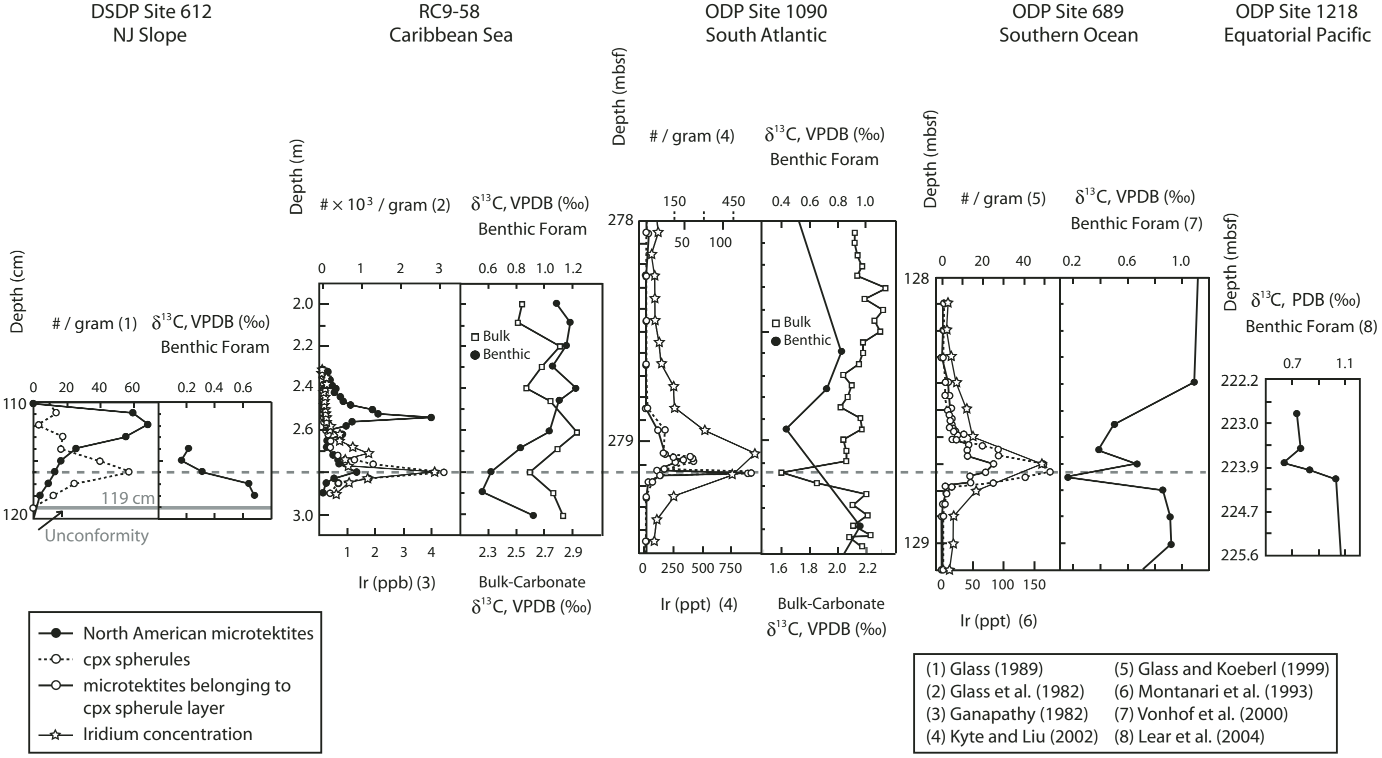

Figure 3. Synthesis of high-resolution late Eocene benthic foraminifera and bulk-carbonate $\delta^{13}C$ data from New Jersey (NJ) Slope Deep Sea Drilling Project (DSDP) Site 612, Caribbean core RC9-58, and South Atlantic Ocean Drilling Program (ODP) Site 1090 (all this study), and previous work at Southern Ocean ODP Site 689 (Vonhof et al., 2000), and equatorial Pacific ODP Site 1218 (Lear et al., 2004) across the identified Upper Eocene cpx spherule layer and the North American microtektite layer, except Site 1218. Data from Site 1218 are shown to illustrate that the carbon isotopic response was global according to our age model. VPDB—Vienna PeeDee belemnite; mbsf—m below seafloor.

impact requires 170 Gt (at –110‰) to 410 Gt (at –45‰) of extraterrestrial carbon (refer to Fig. 8 in Kent et al., 2003), which corresponds to 9.5- and 12.5-km-diameter comets, respectively. Modeling studies of the Chesapeake Bay impact structure (Collins and Wünnemann, 2005) indicate that the Chesapeake Bay impactor had a diameter of ~3.2 km. A 4-km-diameter comet (at –45‰) would only contribute ~13 Gt of carbon into the deep ocean reservoir, which can only explain 0.016‰ of the 0.5‰ observed $\delta^{13}C$ excursion. Even if Popigai was formed by the impact of a comet and not an L-type chondrite, the 100-km-diameter crater and associated 5-km-diameter impactor would only explain 25 Gt of carbon, well below the necessary 170–410 Gt.

We calculated the effects of other potential sources of low $\delta^{13}C$ carbon that may have contributed to the observed 0.5‰

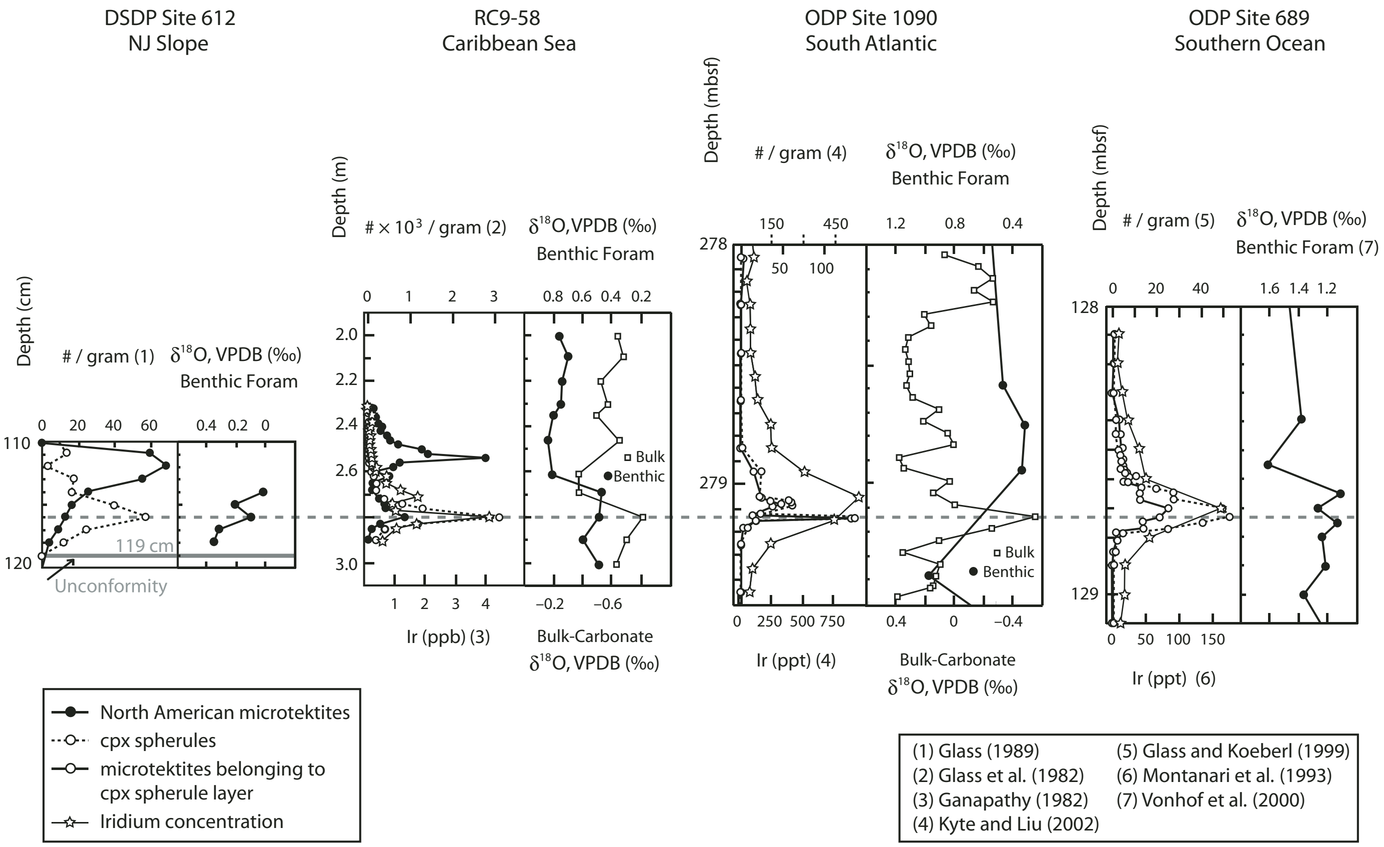

Figure 4. Compilation of high-resolution late Eocene benthic foraminifera and bulk-carbonate δ18O data from New Jersey (NJ) Slope Deep Sea Drilling Project (DSDP) Site 612, Caribbean core RC9-58, and South Atlantic Ocean Drilling Program (ODP) Site 1090 (all this study), and previous work at Southern Ocean ODP Site 689 (Vonhof et al., 2000) across the identified Upper Eocene cpx spherule layer and the North American microtektite layer. VPDB—Vienna PeeDee belemnite; mbsf—m below seafloor.

negative δ13C anomaly. One possible source is the dissociation of ~310 Gt of methane hydrates stored on continental margins, which are thought to be capable of abruptly releasing massive amounts of readily oxidized 12C-rich carbon (δ13C = –60‰) into the ocean-atmosphere system (e.g., Dickens et al., 1995, 1997; Katz et al., 1999, 2001), perhaps through slope failure triggered by an impact. We know of no data to support such a release, but we cannot exclude this hypothesis. Alternatively, a portion of the 0.5‰ oceanic δ13C decrease could be attributed to the rapid burning of terrestrial organic matter in the form of peat deposits, as has been invoked for the Paleocene-Eocene thermal maximum (Kurtz et al., 2003), perhaps triggered by intense heat from an incoming comet or L-type chondrite. However, terrestrial organic reservoirs cannot readily explain the rapid 0.5‰ δ13C decrease because this excursion requires 740 Gt of carbon from organic matter (–25‰), an amount comparable to the entire modern living terrestrial carbon reservoir (Falkowski, 2005). Furthermore, the lack of evidence for a mass extinction event argues against such a planetary holocaust. One final source that may have contributed to the observed δ13C anomaly could be a drop in export carbon productivity following an impact. For example, impact-induced mass mortality in surface waters is hypothesized for the cause of the negative δ13C anomaly (2‰) at the Cretaceous-Paleogene boundary (Hsu et al., 1982). Although a mass extinction in surface waters is apparently not associated with the late Eocene impact event(s), this hypothesis is readily testable because it predicts a carbonate preservational pulse versus the inverse prediction by the methane clathrate hypothesis.

From an empirical perspective, a δ13C excursion with 0.5‰ amplitude is not atypical for the ODP Site 1090 benthic foraminiferal δ13C record (Fig. 2). Eccentricity-controlled variability in Paleogene and Neogene deep-sea δ13C records has maximum amplitudes of 1‰, with average values of ~0.5‰ (Woodruff and Savin, 1991; Zachos et al., 1996, 1997; Cramer et al., 2003). Changes of this magnitude on eccentricity time scales are explainable by orbitally forced variations in the ratio of carbonate to organic carbon burial (Cramer et al., 2003; Pälike et al., 2006a, 2006b). The 0.5‰ δ13C decrease associated with the Popigai impact that we document here is apparently more rapid (<10 k.y.), but high-resolution (<4 k.y. sampling) benthic foraminiferal δ13C records from the late Paleogene–Neogene (e.g., Pälike et al., 2006a, 2006b) show variability of similar magnitude and abruptness.

As noted herein, it is difficult to explain a whole-ocean δ13C excursion of ~0.5‰ magnitude and <10 k.y. onset using standard carbon budgets. The observation that the $\delta^{13}C$ excursion coincident with the Popigai impact was a rapid (< 10 k.y.) whole-ocean event is therefore of interest for more general understanding of the carbon cycle. Variability of similar scale (~0.5‰ amplitude and <10 k.y.) is present in individual Oligocene to Miocene high-resolution benthic foraminiferal $\delta^{13}C$ records from the equatorial Atlantic and Pacific Oceans (Pälike et al., 2006a, 2006b), but, to our knowledge, it has not been demonstrated to be synchronous among geographically disparate sites. It is plausible that the Popigai impact triggered a carbon cycle response similar to that which occurs under the influence of natural climate variability. This hypothesis predicts that variability of similar scale in high-resolution $\delta^{13}C$ records is generally reflective of a global, rather than local, signal.

The large, rapid, and short-lived $\delta^{13}C$ change also implies either that the carbon cycle is less buffered than believed at present, or that our understanding of the modern to glacial carbon cycle is a poor framework for interpretation of past $\delta^{13}C$ variability. For example, the whole-ocean $\delta^{13}C$ change of 0.3‰ during the last glacial-interglacial cycle has perplexed paleoceanographers for decades (e.g., Shackleton, 1977; Broecker, 1982; Broecker and Peng, 1989), and we are reporting a larger, possibly more rapid change in whole-ocean $\delta^{13}C$. Reliance on the modern glacial change may lead to an exaggerated view of the severity of climate perturbations in the older geologic record, potentially implying a significantly smaller (~50%) ocean carbon reservoir, a larger (200%) terrestrial carbon reservoir, or the existence of some as-yet-unrecognized carbon reservoir.

CONCLUSIONS

ODP Site 1090 provides a first-order correlation of the identified Upper Eocene cpx spherule layer to the geomagnetic polarity time scale (Cande and Kent, 1995; Berggren et al., 1995) in chron C16n.1n (279 mbsf), with a corresponding magnetochronologic age of 35.43 Ma. Bulk-carbonate data from Site 1090 show large (~0.5‰), rapid, short-lived, and negative $\delta^{13}C$ anomalies at the Upper Eocene cpx spherule layer (279 mbsf) that are interpreted to reflect a transient response in surface waters. Three new benthic foraminiferal records from South Atlantic ODP Site 1090, New Jersey slope DSDP Site 612, and Caribbean core RC9-58 also show a coeval (~–0.5‰) $\delta^{13}C$ excursion associated with the cpx spherule layer and perhaps with the North American microtektite layer. The significant (~0.5‰), rapid (<<10 k.y.), short-lived (<10 yr), and negative $\delta^{13}C$ excursion found in benthic foraminifera associated with the cpx spherule layer in core RC9-58, at Sites 1090 and 612, and from previous work at Site 689 (Vonhof et al., 2000) is interpreted to be a global event. The $\delta^{13}C$ excursion may reflect a greater environmental perturbation associated with the impact(s) than has previously been recognized. Alternatively, it may imply a significantly different carbon budget than is generally assumed. We determined there was no global temperature change associated with the cpx spherule or North American microtektite layers, and consequently the Popigai and Chesapeake Bay impact events.

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