Meteoritics & Planetary Science 41, Nr 5, 705–714 (2006)
Abstract available online at http://meteoritics.org

Sr and Nd analyses of upper Eocene spherules and their implications for target rocks

Shaobin LIU[1]†*, D. A. PAPANASTASSIOU[2, 3], H. H. NGO[3], and B. P. GLASS[1]

[1]Department of Geology, University of Delaware, Newark, Delaware 19716, USA
[2]Lunatic Asylum, Division Geological Planetary Sciences, Caltech 170-25, Pasadena, California 91125, USA
[3]Science Division, JPL 183-335, Caltech, 4800 Oak Grove Drive, Pasadena, California 91109–8099, USA
†Present address: Division of Machine Research, Caterpillar Incorporated, Mossville, Illinois 61552, USA
*Corresponding author. E-mail: Liu_Shaobin@cat.com

(Received 20 April 2005; revision accepted 21 December 2005)

Abstract–Upper Eocene impact ejecta has been discovered all over the world. The number of upper Eocene impact layers and the geographic distribution of each layer, based on major chemical composition and biostratigraphic data, are not agreed upon. We have performed four Sr-Nd isotopic analyses of clinopyroxene-bearing spherules (cpx spherules) and three Sr-Nd analyses of microtektites from five Deep Sea Drilling Project/Ocean Drilling Program (DSDP/ODP) sites in the South Atlantic and Indian Oceans. Our data support the hypothesis that there is only one cpx spherule layer in upper Eocene sediments. We also find that the microtektites associated with the cpx spherule layer in the South Atlantic and Indian Oceans are not part of the North American tektite strewn field, but belong to the same event that produced the cpx spherules. The microtektites, together with cpx spherules, are more heterogeneous than microtektites/tektites from other strewn fields. No direct link has been established between the microtektites from this study and possible target rock at the Popigai crater.

INTRODUCTION

Upper Eocene distal impact ejecta, including microtektites, clinopyroxene-bearing spherules (cpx spherules), and shock-metamorphosed rock and mineral grains, has been recovered from marine sediments from the Caribbean Sea, Gulf of Mexico, equatorial Pacific, equatorial Indian Ocean, western equatorial Atlantic Ocean, Barbados, northwest Atlantic Ocean, southern South Atlantic Ocean, and from Massignano, Italy (e.g., Donnelly and Chao 1973; Glass et al. 1985; Sanfilippo et al. 1985; Thein 1987; Keller et al. 1987; Clymer et al. 1996; McHugh et al. 1996; Glass et al. 1998; Vonhof and Smit 1999; Liu and Glass 2001 [Table 1; Fig. 1]). Upper Eocene microtektites, found in piston core RC9-58 from the Caribbean Sea, are believed to belong to the North American tektite (NAT) strewn field, based on their geographical location, stratigraphic age, fission-track age, and major element compositions (Glass et al. 1973). Ar-Ar dating of tektite fragments from Barbados indicates an age of 35.4 ± 0.6 Ma (Glass et al. 1986), which is the same as the age of North American tektites (Storzer and Wagner 1971; Bottomley et al. 1979). Other locations that contain upper Eocene microtektites, such as Deep Sea Drilling Project (DSDP) sites 94, 149, 612, and Ocean Drilling Program (ODP) site 904, are also regarded as part of the NAT strewn field (Donnelly and Chao 1973; Sanfilippo et al. 1985; Glass et al. 1985; Thein 1987; Glass et al. 1998). At sites where both the cpx spherules and North American microtektites are found, they often occur in the same sediment layer and were originally thought to belong to the same impact event (e.g., John and Glass 1974). The cpx spherule layer is now recognized as belonging to an older event (Glass et al. 1985). The cpx spherule layer was also reported to be associated with a positive iridium anomaly (Ganapathy 1982; Alvarez et al. 1982). The term microkrystite was coined to describe impact-produced microspherules containing primary crystal phases (Glass and Burns 1988), and some authors (e.g., Wei 1995; Vonhof and Smit 1999) refer to the cpx spherules as microkrystites.

The number of upper Eocene spherule layers has been a matter of debate. Up to six different layers have been proposed, based primarily on biostratigraphic and compositional data (Keller et al. 1983; Keller et al. 1987; Hazel 1989; Miller et al. 1991). However, Glass and colleagues concluded that there are probably only two layers: the North American microtektite layer and the slightly older

Table 1. Sites where upper Eocene spherules and/or impact ejecta have been found.

Site	Latitude	Longitude	Location	Types of ejecta	Reference[e]
RC9-58	14°33.4′N	70° 48.6′W	Caribbean Sea	NAMT[a], CPX[b], UM[c]	1, 2, 3
E67-128	28°14′N	86°56′W	Gulf of Mexico	NAMT	3, 4
DSDP 65	4°21.210′N	176°59.142′E	Equatorial Pacific	CPX	3
DSDP 69A	6°0.000′N	152°51.930' W	Equatorial Pacific	CPX	3, 4
DSDP 70A	6°20.082′N	140°21.720′W	Equatorial Pacific	CPX	3, 4
DSDP 94	24°31.638′N	88° 28.158′W	Gulf of Mexico	NAMT	3, 4, 5
DSDP 149	15°06.252′N	69°21.852′W	Caribbean Sea	NAMT	3, 4, 5, 6
DSDP 166	3°45.702′N	175°04.800′W	Equatorial Pacific	CPX	3
DSDP 167	7°04.098′N	176°49.500′W	Equatorial Pacific	CPX	3, 4
DSDP 216	1°27.732′N	90°12.480′E	Eastern Indian Ocean	CPX, MT[d], UM	3, 4
DSDP 291	12°48.432′N	127°49.848′E	Philippine Sea	CPX	4
DSDP 292	15°49.110′N	124°39.048′E	Philippine Sea	CPX	3, 4
DSDP 315A	4°10.260′N	158°31.542′W	Equatorial Pacific	CPX	4
DSDP 462	7°14.250′N	165°01.830′E	Equatorial Pacific	CPX	4
DSDP 543	15°42.738′N	58°39.222′W	Equatorial Atlantic	NAMT, UM	19
DSDP 612	38°49.212′N	72°46.428′W	Northwest Atlantic	NAMT, UM, CPX	4, 7, 8
DSDP 689B	64°31.020′S	3°05.994′E	Weddell Sea, Southern Ocean	CPX, MT	9, 10
DSDP 689D	64°31.020′S	3°06.024′E	Weddell Sea, Southern Ocean	CPX, MT	15
ODP 699A	51°32.520′S	30°40.620′W	Southern Atlantic	MT	16
ODP 709C	3°54.900′S	60°33.102′E	Western Indian Ocean	CPX, MT, UM	16
ODP 786A	31°52.500′N	141°13.560′E	Western Pacific	CPX	16
ODP 903C	38°56.304′N	72°49.026′W	Northwest Atlantic	UM	12
ODP 904A	38°51.804′N	72°46.086′W	Northwest Atlantic	MT, UM	11, 12
ODP 1073A	39°13.522′N	72°16.546′W	Northwest Atlantic	UM	16
ODP 1090B	42°54.822′S	8°53.982′E	Southern Atlantic	CPX, MT	17, 18
Bath Cliff	13°11.712′N	59°29.490′N	Barbados, West Indies	MT, UM	3, 4, 13
Gay’s Cove	13°11.712′N	59°29.490′N	Barbados, West Indies	MT, UM	3, 13
Massigano	43°32.4′N	13°35.4′N	Ancona, Italy	UM	14

[a] NAMT: North American microtektite.

[b] CPX: cpx spherules.

[c] UM: unmelted ejecta.

[d] MT: microtektite.

[e] 1 = Glass et al. (1973); 2 = John and Glass (1974); 3 = Glass et al. (1985); 4 = Keller et al. (1987); 5 = Glass and Zwart (1979); 6 = Donnelly and Chao (1973); 7 = Thein (1987); 8 = Glass (1989); 9 = Vonhof and Smit (1999); 10 = Glass and Koeberl (1999a); 11 = McHugh et al. (1996); 12 = Glass et al. (1998); 13 = Sanfilippo et al. (1985); 14 = Clymer et al. (1996); 15 = Liu and Glass (1999); 16 = Liu and Glass (2001); 17 = Liu et al. (2000); 18 = Kyte (2001); 19 = Liu (unpublished data).

cpx spherule layer (Glass et al. 1985; Glass and Burns 1987). Wei (1995) and Whitehead et al. (2000) agreed with the two-layer hypothesis, based on nannofossil biochronology and Sr-Nd isotopic data, respectively.

Shaw and Wasserburg (1982) provided new insight into tektite origin and provenance and concluded that each tektite group has rather distinctive pairs of ^{143}Nd/^{144}Nd and ^{87}Sr/^{86}Sr values. The isotopic association of microtektites and tektite fragments from Barbados to North American tektites was demonstrated by Ngo et al. (1985) using Sr and Nd systematics. The Sr and Nd analyses of tektite material from an 8 cm thick impact layer at DSDP 612, off the coast of New Jersey, USA, show a much wider range than the previous, tightly constrained group of North American tektites and microtektites (Stecher et al. 1989). The Sr and Nd isotopic data analyzed by Whitehead et al. (2000) and in a comprehensive paper by Kettrup et al. (2003) support the hypothesis that the Popigai crater is the source crater of the globally distributed cpx spherules.

Both microtektites and cpx spherules were found in sediments at DSDP hole 689B (Vonhof and Smit 1999). Since the elemental composition of microtektites from DSDP hole 689B is comparable to tektites of the NAT strewn field, Vonhof and Smit (1999) suggested that these microtektites might be associated with NAT. Glass and Koeberl (1999a) agreed with their suggestion, based on the major and minor element analyses of the microtektites and the vertical relationship between the peak abundance of the cpx spherules and the peak abundance of the microtektites at ODP hole 689B. If confirmed, this would mean that the NAT strewn field stretches to the southern South Atlantic Ocean, and is at least four times larger than previously mapped. However, the possibility of a third event was also discussed, based on differences in the ^{87}Sr/^{86}Sr ratios between the hole 689B microtektites and the North American tektites/microtektites (Vonhof and Smit 1999). A preliminary study shows that both major oxide and trace element contents of the DSDP site 216 microtektites are similar to those of DSDP hole 689B (Glass

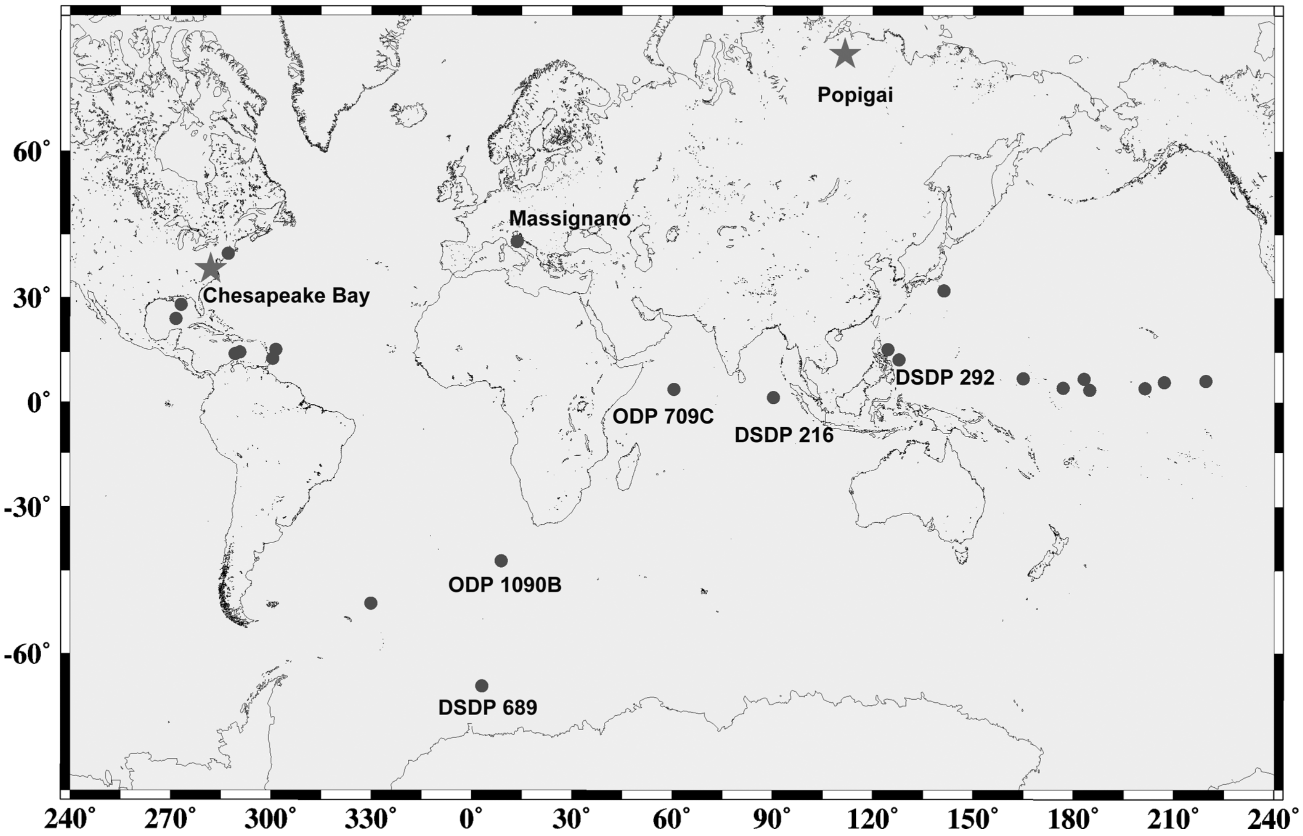

Fig. 1. Sites where upper Eocene impact ejecta has been found. The samples used in this study are from four of the labeled sites. The stars indicate the locations of large impact structures of late Eocene age.

and Koeberl 1999b), suggesting that the NAT strewn field may extend into the Indian Ocean.

Shocked quartz and feldspar with multiple sets of planar deformation features, coesite, stishovite, and reidite (a high-pressure $ZrSiO_4$ polymorph) were discovered in the North American microtektite layer (Thein 1987; Glass and Wu 1993; Glass and Liu 2001). However, prior to 1996, no unmelted impact ejecta had been reported to be associated with the cpx spherule layer. Montanari et al. (1993) reported multiple Ir anomalies in an upper Eocene section at Massignano, Italy. Shocked quartz was discovered within the lower Ir anomaly peak by Clymer et al. (1996). Langenhorst (1996) studied the shocked quartz associated with the Ir anomaly at Massignano and concluded that they were probably from the Popigai crater. Pancake-shaped spherules, containing and sometimes coated with Ni-rich spinel crystallites, were reported from this well-defined layer (Pierrard et al. 1998). The pancake-shaped spherules are thought to be diagenetically altered cpx spherules (Glass et al. 2004). Whitehead et al. (2000) determined Nr and Sr isotopic data for cpx spherules from four sites and microtektites from the cpx spherule layer at site 216, which provided support for the hypothesis that the cpx spherules were derived from the Popigai impact structure. Since their study, cpx spherules and associated microtektites have recently been found at ODP hole 1090B located in the southern South Atlantic Ocean and ODP hole 709C in the western Indian Ocean (Fig. 1).

The objectives of this study were to test the linkage between cpx spherules and the Popigai impact crater, determine whether or not microtektites associated with the cpx spherule layer in the Indian Ocean and southern South Atlantic Ocean are part of the North American tektite strewn field, and determine the possible target rocks of cpx spherules and associated microtektites. In order to address these problems, we determined the Sr and Nd systematics for cpx spherules from three sites and microtektites associated with the cpx spherules from two sites (Table 2). This is the first time that Sr and Nd isotopic data have been determined for cpx spherules from the southern South Atlantic and western equatorial Indian Ocean.

METHODS

Cpx spherules were recovered from DSDP site 216 and ODP site 709 in the Indian Ocean and ODP site 1090 in the South Atlantic, and microtektites were recovered from cores taken at ODP site 689 in the South Atlantic and ODP site 709 in the Indian Ocean. The sediment samples from these sites were disaggregated in water using ultrasonication and sieved into 63–125 µm and >125 µm size fractions. Heavy liquid

Table 2. Major oxide compositions of microtektites from ODP holes 1090B and 709C (determined by EDX).

Sample	Description	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	Cr_2O_3	NiO	Total
ODP hole 1090B												
829s1	Light green sph.[a]	59.5	13.2	9.57	8.33	4.29	1.58	2.44	0.40	0.09	0.03	99.39
829s2	Dark green sph.	73.3	10.0	5.20	5.21	2.01	0.97	2.13	0.39	0.04	0.06	99.33
829s3	Brownish sph.	77.6	11.7	6.01	0.60	0.54	0.00	2.51	0.41	0.01	0.03	99.43
830A1	Transparent sph.	86.6	11.0	0.25	0.41	0.27	0.00	0.39	0.41	0.06	0.03	99.48
830B1	Transparent sph.	78.3	13.4	3.59	0.44	0.55	0.00	2.61	0.44	0.05	0.02	99.42
830B2	Transparent sph.	83.8	12.2	0.41	0.31	0.25	0.00	1.86	0.47	0.04	0.02	99.45
830B3	Reddish sph.	70.5	11.5	5.72	3.59	2.48	1.63	2.92	0.53	0.21	0.36	99.50
830B4	Reddish sph.	71.2	5.96	9.89	4.10	1.87	2.01	3.78	0.33	0.10	0.25	99.51
8331b	Ttransparent sph.	76.9	15.3	3.25	0.76	0.20	0.00	2.34	0.68	0.01	0.00	99.38
8331c	Transparent sph.	76.5	17.0	2.08	0.88	0.44	0.00	2.00	0.68	0.01	0.00	99.57
Average		75.4	12.1	4.60	2.46	1.29	0.62	2.30	0.47	0.06	0.08	99.44
Standard deviation		7.2	2.83	3.19	2.60	1.28	0.79	0.82	0.12	0.06	0.12	0.07
ODP hole 709C												
838-01	Transparent oval	78.4	13.5	1.99	0.57	0.23	0.00	2.76	0.61	0.00	0.01	98.08
84301A	Brownish TK frag.[b]	76.1	12.6	5.73	0.38	0.54	0.51	3.15	0.41	0.03	0.00	99.39
843C2	Brownish TK frag.	76.1	12.8	5.61	0.39	0.49	0.40	3.20	0.42	0.00	0.02	99.38
85411	Brownish cylinder	68.4	17.3	7.83	1.22	0.25	0.91	2.80	0.71	0.00	0.00	99.43
85432	Greenish cylinder	55.6	9.56	7.58	12.4	12.3	0.98	0.44	0.37	0.12	0.08	99.46
85433	Brownish teardrop	76.7	11.7	4.38	1.03	1.25	0.79	3.16	0.39	0.00	0.00	99.37
Average		71.9	12.9	5.52	2.67	2.51	0.60	2.58	0.49	0.03	0.02	99.19
Standard deviation		8.7	2.54	2.16	4.79	4.80	0.37	1.07	0.14	0.05	0.03	0.54
DSDP site 216[c] (analysis of 3 MTs)												
Average		74.6	13.7	3.91	1.21	1.78	0.71	3.14	0.64	n.a.	n.a.	99.7
Standard deviation		3.1	2.25	0.99	0.40	1.25	0.18	0.21	0.12	n.a.	n.a.	0.22
ODP hole 689B[d] (analysis of 32 MTs)												
Average		78.8	14.2	2.79	0.63	0.31	0.08	2.09	0.54	n.a.	n.a.	99.4
Standard deviation		3.2	2.7	2.38	0.17	0.25	0.13	0.71	0.12	n.a.	n.a.	0.06
NAT/MT[e] (analysis of 147 NAT/MTs)												
Average		73.5	14.0	4.12	1.55	1.37	1.16	3.14	0.72	n.a.	n.a.	99.49
Standard deviation		5.3	2.3	1.52	1.63	0.86	0.48	0.73	0.24	n.a.	n.a.	0.20

[a] sph. = spherule.

[b] TK frag. = tektite fragment.

[c] Data from Glass et al. 1985 (Sample 122-4) and D'Hondt et al. 1987 (Samples M5S42 and M5S44).

[d] Data from Glass and Koeberl 1999a.

[e] NAT/MT: from RC9-58, E67-128, Barbados, sites 94, 149, 612, and 904 (see Fig. 2 for reference).

separations were used to concentrate the spherules in the 63–125 µm size fractions and make recovery easier. Spherules were then handpicked using a binocular microscope with up to 50× magnification. Several microtektites from hole 709C and hole 1090B were mounted on glass slides, ground down to expose an interior surface, polished, coated with carbon, then analyzed by scanning electron microscopy (SEM) with EDX for major element contents (see Glass and Koeberl 1999a for a detailed discussion of the major oxide analyses). Microtektites and cpx spherules that were selected for Sr and Nd isotopic studies were leached in dilute acids to remove potential localized, secondary ferromanganese, and iron sulfide coatings following the method described by Stecher et al. (1989). The sample weights ranged from 0.4 to 4 mg. Except for one clase, the Sr-Nd isotopic values were derived for composite samples of two or more spherule/microtektites. The Nd was measured with high sensitivity, as NdO^+, on the Lunatic I mass spectrometer at Caltech (e.g., see the standard paper on Sm/Nd ratios and Sm and Nd isotope compositions by Wasserburg et al. 1981). Typical amounts per mass spectrometer analysis were ~10 ng Nd, yielding ion beam currents of 0.7×10^{-11} A, for several hours. Sr was measured on the same instrument.

RESULTS

Most of the microtektites associated with the cpx spherules from the South Atlantic and the Indian Oceans are transparent colorless to pale brown. These microtektites have similar average SiO_2 contents (~75 wt% at site 1090; ~72 wt% at site 709, ~75 wt% at site 216; ~79 wt% at site 689; see Table 2 for reference), compared to North American microtektites (Table 2; Fig. 2). Some rare greenish and reddish microtektites have very high magnesium, especially sample 85432 from site 709 whose MgO is about 12.4%, compared to the average value (1.55%) of North American microtektites. The microtektites from sites 216, 689, 709, and 1090 have very much lower sodium (Fig. 2), than the North American microtektites. The major oxide composition of microtektites, associated with the cpx spherule layer, overlap with the major oxide compositions of North America tektites and microtektites.

The $\varepsilon(^{87}Sr/^{86}Sr)$ present-day values of the dark cpx spherules from sites 216, 709C, and 1090B are between 218.7 and 298.5, and the $\varepsilon(^{143}Nd/^{144}Nd)$ present-day values are between −26.0 and −29.7 (Table 3; Fig. 3a). The T(UR)Sr model ages are very close to each other and range only from 1110 to 1160 Ma. T(CHUR)Nd model ages have a wider range, from 1130 to 1950 Ma (Table 3; Fig. 3b).

The $\varepsilon(^{87}Sr/^{86}Sr)$ present-day values of the microtektites from sites 689B and 709C range from 130.2 to 213.8, and the $\varepsilon(^{143}Nd/^{144}Nd)$ present-day values are from −16.6 to −25.4. The T(UR)Sr model ages are from 918.42 to 3628.41 Ma, and the T(CHUR)Nd model ages range from 1360 to 2050 Ma. The T(UR)Sr model ages (following Shaw and Wasserburg 1982; Stecher et al. 1989; Whitehead et al. 2000) for microtektites MT-9a and MT-9d are probably not meaningful since there is no significant Rb/Sr fractionation as indicated by their low f(Rb/Sr) values (~2 and ~4, respectively). That is why the two samples give much older T(UR)Sr model ages.

DISCUSSION

The major oxide contents of microtektites associated with the cpx spherules in ODP holes 709C and 1090B are similar to the major oxide contents of the microtektites associated with the cpx spherules from DSDP site 216 and ODP hole 689B (Table 2; Fig. 2). The microtektites from all four of these sites have major oxide contents similar to the major oxide contents of the North American microtektites. However, the microtektites (excluding greenish and reddish ones) associated with the cpx spherules generally have lower Na_2O contents and lower average CaO contents and a somewhat wider range in Al_2O_3 and FeO contents for a given SiO_2 content compared with the North American microtektites (Fig. 2). If only based on the major oxide contents, these microtektites appear to belong to the North American microtektite layer.

The $\varepsilon^{143}Nd/^{144}Nd$ values of both microtektites (MT-4, MT-9a, M9b, and MT9d) (−16.62 to −25.4) and cpx spherules (MT-1, MT-2, and MT-3) (−26.0 to −29.7) from the South Atlantic and Indian Oceans are distinctive from the range defined by North American tektites (−5 to −10), but overlap with the much wider range of Popigai target rocks and impactites (−7.6 to −33.7) (Fig. 3a) (Kettrup et al. 2003) . This suggests that the microtektites from these locations are not part of the NAT strewn field and that the NAT strewn field may not extend into the Southern Atlantic and Indian Oceans, as previously suggested (e.g., Glass and Koeberl 1999a and 1999b). The $\varepsilon^{143}Nd/^{144}Nd$ values (MT-1 and MT-3) of dark-colored cpx spherules from DSDP site 216 and ODP site 709C are about −26, which is less than the values (−21.8 to −23.2) of dark-colored cpx spherules at site 216, but larger than the values (~ −27) of light-colored cpx spherules at site 292 and dark-colored cpx spherules at site 315, as previously reported by Whitehead et al. (2000). The $\varepsilon^{143}Nd/^{144}Nd$ value (MT-2) of dark-colored cpx spherules at ODP site 1090B is −29.7, which is lower than the reported $\varepsilon^{143}Nd/^{144}Nd$ values for other cpx spherules. The $\varepsilon^{143}Nd/^{144}Nd$ values of cpx spherules (MT-1, MT-2, and MT-3), in this study, overlap with the $\varepsilon^{143}Nd/^{144}Nd$ values of cpx spherules from other sites. This indicates that the spherules may be produced by a single event and that the upper Eocene cpx spherule strewn field is global. However, the wide range of $\varepsilon^{143}Nd/^{144}Nd$ values shows that the globally distributed cpx spherules are heterogeneous in terms of $\varepsilon^{143}Nd/^{144}Nd$, which may be due to incomplete mixing of the heterogeneous target rocks during the impact (Kettrup et al. 2003).

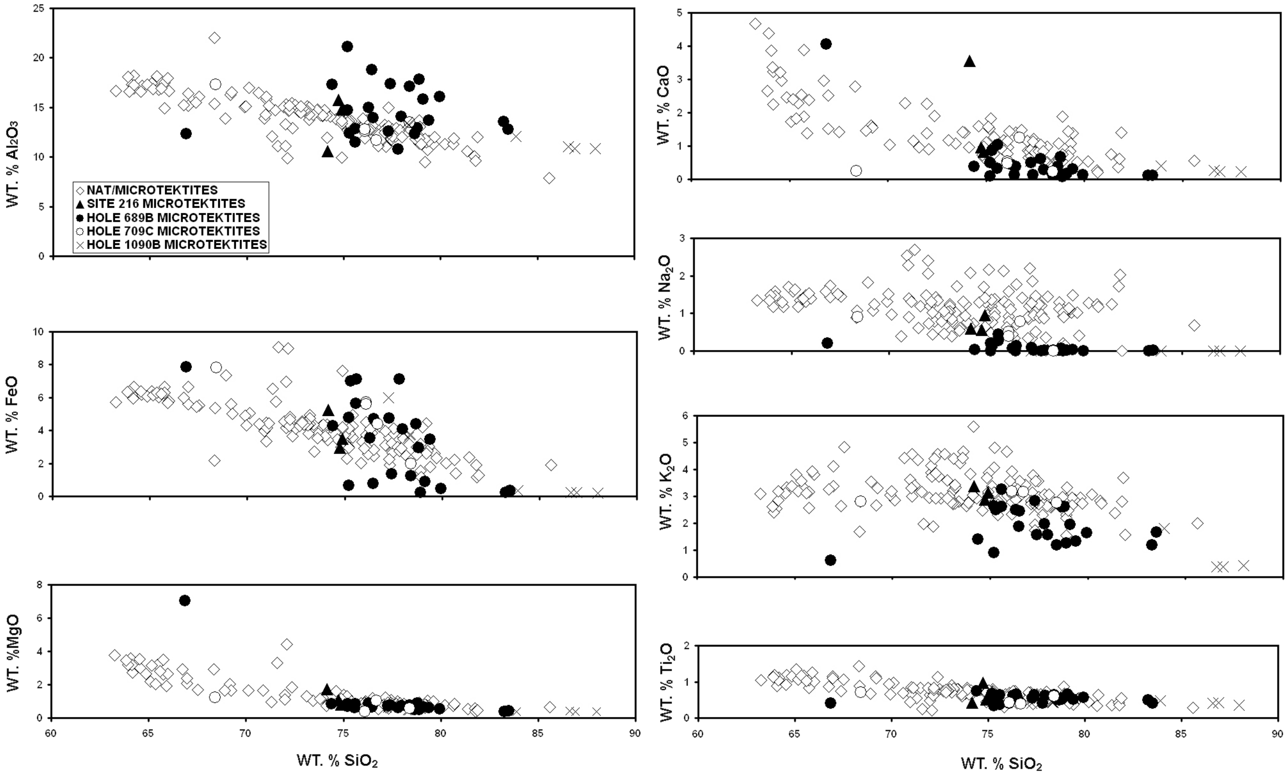

Fig. 2. A comparison of the major oxide compositions between NAT (North American tektites)/microtektites and microtektites associated with cpx spherules layer. Data for the NAT/microtektites are from Glass et al. (1973), Glass and Zwart (1979), Glass et al. (1985), Glass (1989), and Glass et al. (1998). Data for microtektites from hole 689B are from Glass and Koeberl (1999a). Data for microtektites from site 216 are from Glass et al. (1985) (Sample 122-4) and D'Hondt et al. (1987) (Samples M5S42 and M5S44).

The ε^{143}Nd/^{144}Nd and ε^{87}Sr/^{86}Sr values of a clear microtektite (216C) from DSDP site 216 were reported by Whitehead et al. (2000) as −16 and 187.2, respectively. But the significance of these results was not further discussed in that paper. We determined isotopic values for one microtektite and three microtektites composites: three of them are from ODP 709C, and one is from DSDP site 689D. The greenish microtektite (MT9a, from ODP 709C) has a ε^{143}Nd/^{144}Nd value of −16.6 (Table 3), which is similar to that of the clear microtektite from DSDP site 216 (Whitehead et al. 2000). However, the green microtektite has a ε^{87}Sr/^{86}Sr value of 130.2, which is less the 187.2 value obtained by Whitehead et al. (2000) for the clear microtektites from this site. The green microtektite must have had an open Rb-Sr system as indicated by the unrealistic T(UR) model age. A composite of two brownish microtektites (MT9b) have a ε^{143}Nd/^{144}Nd value of −21.25 (Table 3), close to that of the light-colored cpx spherules at DSDP site 216. The ε^{143}Nd/^{144}Nd values of the clear transparent microtektites from holes 709C and 689D are close to each other, around −25, which is between the values of cpx spherules. Our data indicate that the range of microtektites in terms of ε^{143}Nd/^{144}Nd is as wide as that of cpx spherules, which may reflect the heterogeneity of target rocks that produced these microtektites and cpx spherules. The ε^{143}Nd/^{144}Nd values of microtektites from the cpx spherule layer have a wider range (~−17 to ~−27) than that of the North American tektites, which is from ~−5 to ~−10; however, their ε^{87}Sr/^{86}Sr values seem to be less variable, ranging between 150 and 220, compared to a range of 100 to 650 for the North American tektites and microtektites, which are linked to the Chesapeake Bay impact structure according to the Sr-Nd data (Deutsch 2005; Deutsch and Koeberl 2005). Since the Nd and Sr isotopic values of microtektites associated with the cpx spherules in the southern South Atlantic and Indian Oceans overlap those of cpx spherules, we believe that they were probably produced by the same event which, according to the current data set, is probably Popigai.

The close Sr and Nd isotopic relationship of dark-colored cpx spherules with the Popigai tagamite melt has been demonstrated by Whitehead et al. (2000) and Kettrup et al. (2003). However, among the Sr-Nd isotopic values of about 15 impact melt glass samples, 11 tagamite samples, 8 gneiss samples, and 8 other samples (Kettrup et al. 2003), the Sr-Nd isotopic values of microtektites from the South Atlantic Ocean and the Indian Ocean are only close to that of one gneiss sample, one tagamite sample and one quartzite sample (Fig. 3a). The Nd model age is interpreted to reflect the mean crustal age of the source of a sample, while the Sr model ages are interpreted to reflect the time of sedimentation associated

Table 3. Sm-Nd and Rb-Sr isotopic data for upper Eocene cpx spherules and microtektites from DSDP site 216 and ODP sites 689, 709, and 1090.

Sample	MT-1	MT-2	MT-3	MT-4	MT-9a	MT-9b	MT-9d
Site	DSDP 216	ODP 1090B	ODP 709C	ODP 689D	ODP 709C	ODP 709C	ODP 709C
Type	Dark color cpx	Dark color cpx	Dark color cpx	Colorless to pale brown microtektites	One greenish microtektite	Two brownish microtektites	Two colorless microtektites
Weight (mg)	4.0	0.4	0.5	3.5	0.30	1.94	0.52
^{87}Rb (nM/g)	80.08	280.50	263.40	104.20	61.93	257.55	170.06
Rb (ppm)	24.58	86.09	80.84	31.98	19.01	79.05	52.20
^{88}Sr (nM/g)	477.9	2224.1	1780.7	819.1	1989.8	2146.1	3300.3
Sr (ppm)	50.84	236.45	189.38	87.08	211.41	228.09	350.71
^{87}Sr/^{86}Sr	0.72553	0.71991	0.72347	0.71956	0.71367	0.71653	0.71525
±	0.00010	0.00008	0.00007	0.00006	0.00013	0.00007	0.00009
Epsilon Sr	298.5	218.7	269.3	213.8	130.2	170.8	152.6
^{87}Rb/^{86}Sr	1.4032	1.0563	1.2389	1.0655	0.2607	1.0051	0.4316
f(Rb/Sr)	15.97	11.77	13.98	11.88	2.15	11.15	4.22
T(UR) Ga	1.12	1.11	1.16	1.08	3.63	0.92	2.17
^{147}Sm (nM/g)	0.602	27.498	9.788	3.774	2.605	5.434	11.072
Sm (ppm)	0.6036	27.572	9.815	3.785	2.610	5.430	11.100
^{144}Nd (nM/g)	35.75	354.47	167.27	40.74	25.70	62.09	171.31
Nd (ppm)	21.68	214.97	101.44	24.71	15.59	37.65	103.87
^{143}Nd/^{144}Nd	0.51051	0.51033	0.51051	0.51045	0.51100	0.51076	0.51055
±	0.00003	0.00004	0.00003	0.00003	0.00006	0.00003	0.00002
Epsilon ^{143}Nd	–26.0	–29.7	–26.1	–27.3	–16.6	–21.3	–25.4
±	0.6	0.8	0.5	0.6	1.3	0.6	0.4
^{147}Sm/^{144}Nd	0.01684	0.07757	0.05852	0.09263	0.10135	0.08751	0.06463
f(Sm/Nd)	–0.9144	–0.6056	–0.7025	–0.5291	–0.4847	–0.5551	–0.6714
T (CHUR) Ga	1.13	1.95	1.48	2.05	1.36	1.52	1.51

with significant Rb/Sr enrichment (Shaw and Wasserburg 1982). We note that we calculate TNdCHUR model ages (relative to the chondritic evolution). By comparison Kettrup et al. (2003) report TNdDM model ages (relative to a terrestrial depleted mantle). For these very fractionated Sm/Nd samples, the difference between TNdCHUR and TNdDM is of the order of 100 to 200 Ma and does not change significantly the attempt to characterize parent materials for our impact samples. From our data, tabulated in Table 3, given as the present day, measured ε^{143}Nd value and f(Sm/Nd) any other model age can be calculated. The T(CHUR)Nd model ages of microtektites from ODP site 709C range from 1360 to 1520. The only target rock with a similar age (TNdDM) (Kettrup et al. 2003) is a Cambrian carbonate (1350 Ma). Since the calcium oxide contents of the microtektites from the cpx spherule layer are very low (most are less than one percent), it is unlikely that the Cambrian carbonate is the major source rock. The T(CHUR)Nd model ages of microtektites from ODP site 689D is 2050 Ma, which is close to the T(CHUR)Nd model ages of four cpx spherules; this implies that some microtektites have a similar source rock as cpx spherules, but the Sr-Nd isotopic values do not support this idea. In summary, our data suggest that the source rocks for the microtektites from the cpx spherule layer may not be one of the above rock types. So the linkage between microtektites and a specific rock type has not been established.

One of the anomalous ages is associated with green microtektites and one with what appear to be a normal or common microtektite; but two other samples of the common microtektites give ages that we expect from sedimentary deposits (i.e., T(UR)Sr ages are less than T(CHUR)Nd ages). The green microtektites may have been contaminated with meteoritic material and/or vapor fractionated, but neither meteoritic contamination nor vapor fractionation can explain the anomalous results. Based on geochemical data and equation of state-based estimates, Artemieva (2002) concluded that the target region no deeper than 50 m and compressed up to 100–300 Gpa during the impact should be considered as the main source of tektites. Thus, more Sr and Nd isotopic data for Popigai surface and near surface deposits is needed to address the source rocks for the microtektites associated with the cpx spherule layer, although some of target lithologies may no longer be present due to impact-induced ejection and/or subsequent erosion.

Shaw and Wasserburg (1982) concluded that each tektite group has a rather distinctive ε^{Nd} value; however, this is not the case for the microtektites associated with cpx spherules layer. The ε^{143}Nd/^{144}Nd values of these microtektites from ODP site 689 and DSDP site 709 have a wider range, than all the other known tektite groups (Fig. 4), which suggests that distal impact melts from large impact structures can be fairly heterogeneous in terms of Nd-Sr isotopic compositions, as well as major oxide compositions.

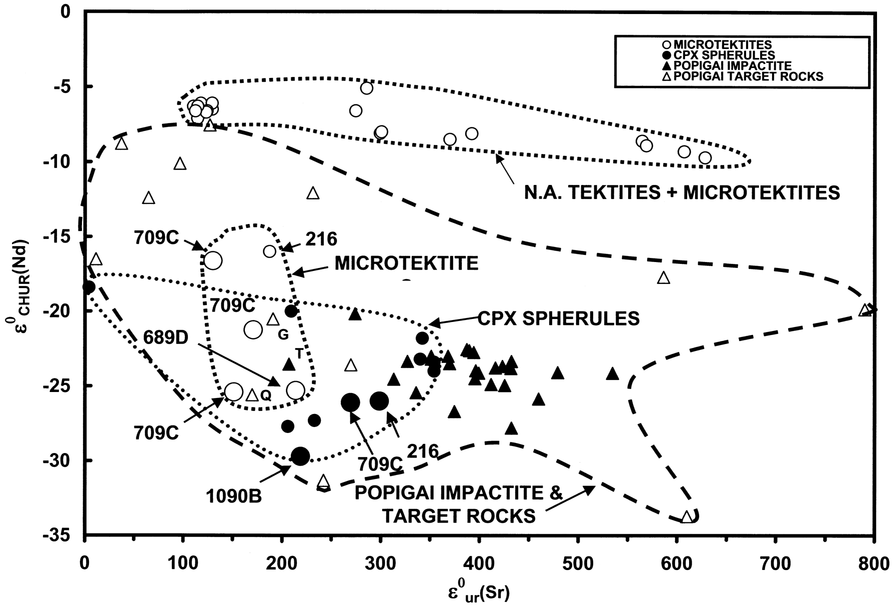

Fig. 3. a) The Nd and Sr isotopic compositions of upper Eocene microtektites and cpx spherules. Bigger circles are from this study; smaller circles and triangles are from Shaw and Wasserburg (1982), Ngo et al. (1985), Stecher et al. (1989), Glass et al. (1998), Whitehead et al. (2000), and Kettrup et al. (2003). G, T, and Q stand for gneiss, tagamite, and quartzite, respectively.

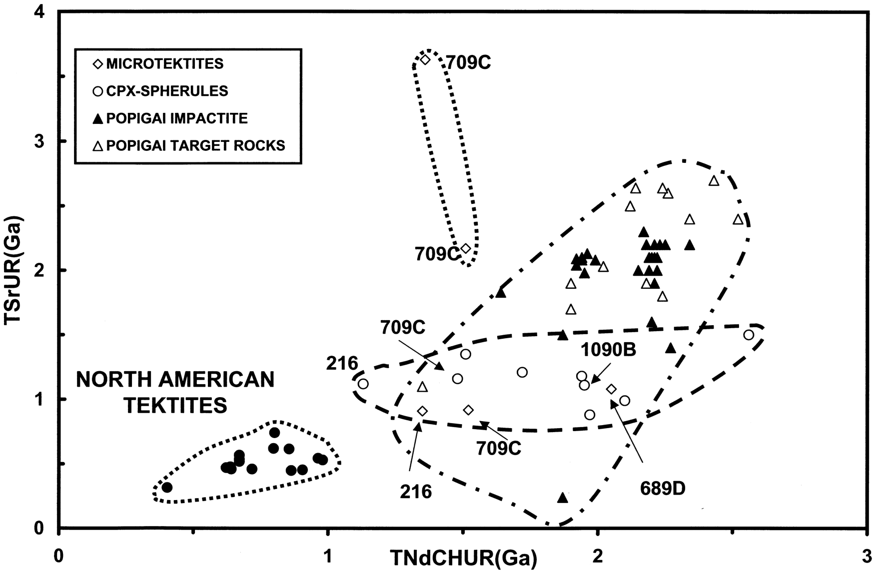

Fig. 3. *Continued.* b) The Sr and Nd model ages of upper Eocene microtektites and cpx spherules. The bigger circles are from this study; the smaller circles are from Shaw and Wasserburg (1982), Ngo et al. (1985), Stecher et al. (1989), Whitehead et al. (2000), and Kettrup et al. (2003) (TNdDM). The range of Nd ages (microtektites from the cpx spherule layer and cpx spherules) is wider than the range of Popigai impactites and target rocks.

CONCLUSIONS

1. The Nd isotopic compositions of upper Eocene impact ejecta are more heterogeneous than the other known tektites/microtektites groups.
2. Our data support the conclusion that there is only one cpx spherule layer, which appears to be global in geographic extent.
3. We agree with Whitehead et al. (2000) and Kettrup et al. (2003) that the Sr and Nd isotopic data support the hypothesis that the Popigai crater is the source crater for the cpx spherules. However, there is currently no proven link between the microtektites from this study and those target rocks so far analyzed from Popigai. More sampling of surface and near surface deposits is needed to address this problem.

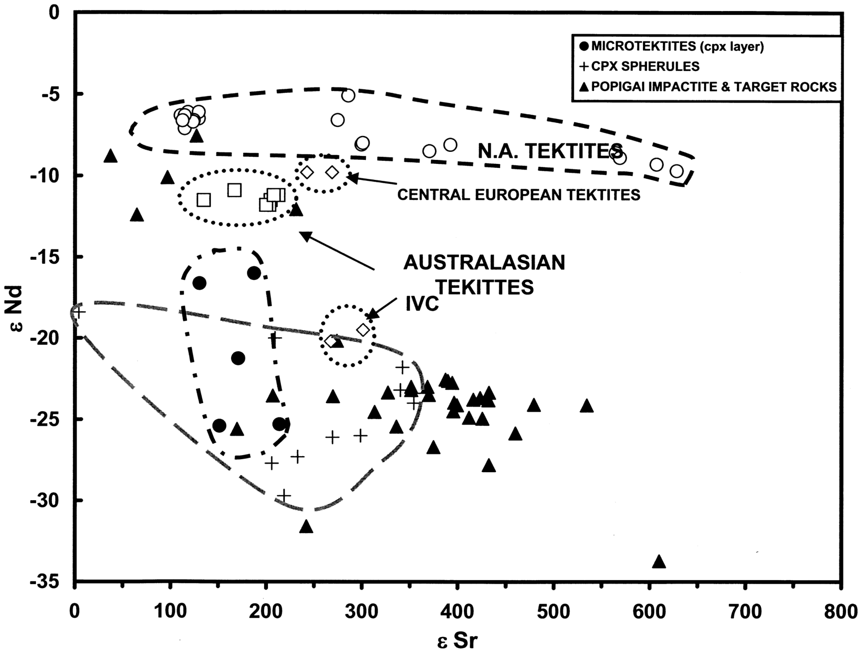

Fig. 4. A comparison of Sr-Nd isotopic data among different tektites/microtektites group. While the ε^{Nd} values of tektites from four different tektite strewn fields are distinctive from each other and show small variations, the ε^{Nd} values of cpx spherules and microtektites associated with cpx spherules show a much wider range, which may indicate the heterogeneity of the target rocks. The data is from Shaw and Wasserburg (1982), Ngo et al. (1985), Stecher et al. (1989), Whitehead et al. (2000), and Kettrup et al. (2003).

4. Our Sr and Nd isotopic data do not support the hypothesis that microtektites found in the cpx spherule layer at sites at in the South Atlantic and Indian Oceans belong to the North American tektite strewn field. Rather, the data suggest that these microtektites have the same source as the cpx spherules (i.e., the Popigai crater).

Acknowledgments–We thank the Ocean Drilling Program (ODP) for the samples used in this study. Paul Steineck and Detlef Warnke forwarded a bulk ODP sample from hole 689D and five samples from hole 1090B, respectively, for use in this study. We benefited from perceptive reviews by Alex Deutsch, Lucy Thompson, and John Spray. This work was supported by NASA NAG5-8251 (Caltech) and NSF EAR-9903811 (University of Delaware). This is part of Shaobin Liu's Ph.D work. Caltech Contribution number 8737 (1068).

Editorial Handling—Dr. John Spray

REFERENCES

Alvarez W., Asaro F., Michel H. V., and Alvarez L. W. 1982. Iridium anomaly approximately synchronous with terminal Eocene extinction. *Science* 216:886–888.

Artemieva N. 2002. Tektite origin in oblique impacts: Numerical modeling of the initial stage. In *Impacts in Precambrian shields,* edited by Plado J. and Pesonen L. J. Heidelberg: Springer. pp. 257–276.

Bottomley R. J., York D., and Grieve R. A. F. 1979. Possible source craters for the North American tektites: A geochronological investigation (abstract). *Eos* 60:309.

Clymer A. K., Bice D. M., and Montanari A. 1996. Shocked quartz from the late Eocene: Impact evidence from Massignano, Italy. *Geology* 24:483–486.

D'Hondt S. L., Keller G., and Stallard R. F. 1987. Major element compositional variation within and between different late Eocene microtektite strewnfields. *Meteoritics* 22:61–79.

Donnelly T. W. and Chao E. C. T. 1973. Microtektites of late Eocene age from the eastern Caribbean Sea. *Initial reports of the Deep Sea Drilling Project,* vol. 15. pp. 1031–1037.

Deutsch A. 2005. Sr-Nd isotope systematics as final evidence for the link between the North American tektite strewn field and the Chesapeake impact structure (abstract #EGU05-A-06686).2005 EGU General Assembly.

Deutsch A. and Koeberl C. 2006. Establishing the link between the Chesapeake Bay impact structure and the North American tektite strewn field: The Sr-Nd isotopic evidence. *Meteoritics & Planetary Science*. This issue.

Ganapathy R. 1982. Evidence for a major meteorite impact on the Earth 34 million years ago. *Science* 215:885–886.

Glass B. P. 1989. North American tektite debris and impact ejecta from DSDP Site 612. *Meteoritics* 24:209–218.

Glass B. P. and Burns C. A. 1987. Late Eocene crystal-bearing spherules: Two layers or one? *Meteoritics* 22:265–279.

Glass B. P. and Burns C. A. 1988. Microkrystites: A new term for impact-produced glassy spherules containing primary crystallites. Proceedings, 18th Lunar and Planetary Science Conference. pp. 455–458.

Glass B. P. and Koeberl C. 1999a. Ocean Drilling Project Hole 689B spherules and upper Eocene microtektite and clinopyroxene-bearing spherule strewn fields. *Meteoritics & Planetary Science* 34:197–208.

Glass B. P. and Koeberl C. 1999b. North American microtektites in the Indian Ocean? *Meteoritics & Planetary Science* 34:43–44.

Glass B. P. and Liu S. 2001. Discovery of high-pressure $ZrSiO_4$ polymorph in naturally occurring shock-metamorphosed zircons. *Geology* 29:371–373.

Glass B. P. and Wu J. 1993. Coesite and shocked quartz discovered in the Australasian and North American microtektite layers. *Geology* 21:435–438.

Glass B. P. and Zwart M. J. 1979. North American microtektites in Deep Sea Drilling Project cores from the Caribbean Sea and Gulf of Mexico. *Geological Society of America Bulletin* 90:595–602.

Glass B. P., Baker R. N., Storzer D., and Wagner G. A. 1973. North American microtektites from the Caribbean Sea and their fission track age. *Earth and Planetary Science Letters* 19:184–192.

Glass B. P., Burns C. A., Crosbie J. R., and DuBois D. L. 1985. Late Eocene North American microtektites and clinopyroxene-bearing spherules. Proceedings, 16th Lunar and Planetary Science Conference. D175–D196.

Glass B. P., Hall C. M., and York D. 1986. $^{40}Ar/^{39}Ar$ laser-probe dating of North American tektite fragments from Barbados and the age of the Eocene-Oligocene boundary. *Chemical Geology* 59:181–186.

Glass B. P., Koeberl C., Blum J. D., and McHugh C. M. G. 1998. Upper Eocene tektite and impact ejecta layer on the continental slope off New Jersey. *Meteoritics & Planetary Science* 33:229–241.

Glass B. P., Liu S., and Montanari A. 2004. Impact ejecta in upper Eocene deposits at Massignano, Italy. *Meteoritics & Planetary Science* 39:589–597.

Hazel J. E. 1989. Chronostratigraphy of upper Eocene microspherules. *Palaios* 4:318–329.

John C. and Glass B. P. 1974. Clinopyroxene-bearing spherules associated with North American microtektites. *Geology* 2:599–602.

Keller G., D'Hondt S., and Vallier T. L. 1983. Multiple microtektite horizons in upper Eocene marine sediments: No evidence for mass extinctions. *Science* 221:150–152.

Keller G., D'Hondt S. L., Orth C. J., Gilmore J. S., Oliver P. Q., Shoemaker E. M., and Molina E. 1987. Late Eocene impact microspherules: Stratigraphy, age, and geochemistry. *Meteoritics* 22:25–60.

Kettrup B., Deutsch A., and Masaitis V. L. 2003. Homogeneous impact melts produced by a heterogeneous target? Sr-Nd isotopic evidence from the Popigai crater, Russia. *Geochimica et Cosmochimica Acta* 67:733–750.

Kyte F. T. 2001. Identification of late Eocene impact deposits at ODP Site 1090. *Proceedings of the Ocean Drilling Program, scientific results*, vol. 177, edited by Gersonde R., Hodell D. A., and Blum P. College Station, Texas: Ocean Drilling Program.

Langenhorst F. 1996. Characteristics of shocked quartz in late Eocene impact ejecta from Massignano (Ancona, Italy): Clues to shock conditions and source crater. *Geology* 24:487–490.

Liu S. and Glass B. P. 1999. Comparison of the stratigraphic relationship of the upper Eocene couplet of microtektites-microkrystites between Holes 689D and 689B (abstract #1847). 31st Lunar and Planetary Science Conference. CD-ROM.

Liu S. and Glass B. P. 2001. Upper Eocene impact ejecta/spherule layers in marine sediments: New sites (abstract #2027). 32nd Lunar and Planetary Science Conference. CD-ROM.

Liu S., Kyte F. T., Glass B. P., and Gersonde R. 2000. Upper Eocene spherules at Ocean Drilling Project Site 1090B. *Meteoritics & Planetary Science* 35:98–99.

McHugh C. M. G., Snyder S. W., Deconinck J. F., Saito Y., Katz M. E., and Aubry M. P. 1996. Upper Eocene tektite of the New Jersey continental margin, Site 904. In *Proceedings of the Ocean Drilling Program, scientific results*, vol. 150. College Station, Texas: Ocean Drilling Program. pp. 241–265.

Miller K. G., Berggren W. A., Zhang J., and Palmer-Julson A. A. 1991. Biostratigraphy and isotope stratigraphy of upper Eocene microtektites at Site 612; how many impacts? *Palaios* 6:17–38.

Montanari A., Asaro F., Michel H. V., and Kennett J. P. 1993. Iridium anomalies of late Eocene age at Massignano (Italy), and ODP Site 689B (Maud Rise, Antarctic). *Palaios* 8:420–437.

Ngo H. H., Wasserburg G. J., and Glass B. P. 1985. Nd and Sr isotopic compositions of tektite materials from Barbados and their relationship to North American tektites. *Geochimica et Cosmochimica Acta* 49:1479–1485.

Pierrard O., Robin E., Rocchia R., and Montanari A. 1998. Extraterrestrial Ni-rich spinel in upper Eocene sediments from Massignano, Italy. *Geology* 26:307–310.

Sanfilippo A., Riedel W. R., Glass B. P., and Kyte F. T. 1985. Late Eocene microtektites and radiolarian extinctions on Barbados. *Nature* 314:613–615.

Shaw H. F. and Wasserburg G. J. 1982. Age and provenance of the target materials for tektites and possible impactites as inferred from Sm-Nd and Rb-Sr systematics. *Earth and Planetary Science Letters* 60:155–177.

Stecher O., Ngo H. H., Papanastassiou D. A., and Wasserburg G. J. 1989. Nd and Sr isotopic evidence for the origin of tektite material from DSDP Site 612 off the New Jersey coast. *Meteoritics* 24:89–98.

Storzer D. and Wagner G. A. 1971. Fission track ages of North American tektites. *Earth and Planetary Science Letters* 10:435–440.

Thein J. E. 1987. A tektite layer in upper Eocene sediments of the New Jersey continental slope (Site 612, Leg 95). *Initial reports of the Deep Sea Drilling Project*, vol. 95. pp. 565–579.

Vonhof H. B. and Smit J. 1999. Late Eocene microkrystites and microtektites at Maud Rise (Ocean Drilling Project Hole 689B; Southern Ocean) suggest a global extension of the approximately 35.5 Ma Pacific impact ejecta strewn field. *Meteoritics & Planetary Science* 34:747–755.

Waserburg G. J., Jacobsen S. B., DePaolo D. J., McCulloch M. T., and Wen T. 1981. Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica et Cosmochimica Acta* 45:2311–2323.

Wei W. 1995. How many impact-generated microspherule layers in the upper Eocene? *Palaeogeography, Palaeoclimatology, Palaeoecology* 114:101–110.

Whitehead J., Papanastassiou D. A., Spray J. G., Grieve R. A. F., and Wasserburg G. J. 2000. Late Eocene impact ejecta: Geochemical and isotopic connections with the Popigai impact structure. *Earth and Planetary Science Letters*181:473–487.