Tektites in Cretaceous-Tertiary boundary rocks on Haiti

By

G.A. Izett[1], F.J-M.R. Maurrasse[2], F.E. Lichte[3], G.P. Meeker[4], and Robin Bates[5]

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[1] U.S. Geological Survey, MS 913, Denver, CO 80225
[2] Florida International University, Miami, FL 33199
[3] U.S. Geological Survey, MS 973, Denver, CO 80225
[4] U.S. Geological Survey, MS 905, Denver, CO 80225
[5] WHYY TV, 150 North 6th Street, Philadelphia, PA 19106

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ABSTRACT

Cretaceous-Tertiary (K-T) boundary rocks on Haiti contain corroded glassy objects (up to 4.0 mm) in cores of clay spherules that have shapes identical to tektites. Because the glassy objects occur only in tektite-like clay spherules strongly implies that the glassy objects are tektites. The glass lacks microlites and crystallites, and this petrographic feature distinguishes tektites from other natural glasses such as obsidian. The refractive index (RI) of K-T tektites (n=1.518-1.542) is higher than most other classes of tektites; however, their RI is similar to that of Ivory Coast microtektites. The silica content of analyzed K-T tektites ranges from 60% to 68%, which in terms of igneous rocks, corresponds to andesite and dacite, respectively. The major-element content of K-T tektites is, in general, similar to other tektite groups, except that K-T tektites have lower Si and higher Fe, Ca, and Na. Their overall trace-element content is also similar to other types of tektites, except K-T tektites have more Sc, V, Cu, Zn, Ga, Sr, Sn, and Ba and less B, Mn, and Hf. Furthermore, the Cr, Ni, and Co content of K-T tektites is lower than most other tektite groups.

The rare-earth element (REE) content of K-T tektites is similar to other tektite groups. Light REE elements La and Ce are about 60-90 times chondrites and heavy REE are about 20 times chondrites. The REE content of the K-T tektites suggests that the target rock melted during the K-T impact was moderately siliceous, not mafic or ultramafic as has been widely speculated.

Transformation of tektite glass to clay spherules in the K-T bed apparently began by solution of the outer surface of a tektite by pore fluids. Smectite was precipitated from the pore fluids and formed a smectite shell that encased the tektite. This process carried to completion produced, in some cases hollow clay spherules and in other cases solid clay spherules. Si, Al, and Ti are roughly similar in the K-T tektites and the clay spherules. However, Mg is higher in the clay by a factor of three, Fe is slightly higher, and Ca, Na, and K are significantly lower in the clay spherules as compared to the tektites. Comparison of the amounts of REE and other elements thought to be relatively immobile during alteration of glass to clay showed that the REE are severely depleted in the clay spherules relative to K-T tektites. Thus, chondrite-normalized REE patterns of K-T boundary clay do not reflect the chemical composition of its progenitor material.

Shock-metamorphosed quartz grains in our sample of the Haiti K-T boundary claystone are about the same size as those at boundary sites in western North America. The percentage amount of shocked quartz in the K-T bed is far less than that in the K-T boundary impact layer in western North America.

Mineralogic observations indicate that the K-T bed is not a primary air-fall bed composed entirely of impact ejecta. Rather, it contains a small volcanogenic component of locally derived material admixed with impact ejecta during deposition on the sea floor. Thus, the thickness of the Haitian K-T bed may not accurately reflect the original air-fall thickness of impact ejecta.

The presence of tektites, which most earth scientists agree are of terrestrial impact origin, in the same bed with a Pt-group abundance anomaly and shocked quartz provides convincing proof of an asteroid or comet impact at the precise K-T boundary. The tektite evidence confirms the Alvarez K-T impact hypothesis and delivers a crippling blow to the Officer and Drake volcanic hypothesis for the explanation of Ir anomalies, shocked quartz, and boundary phenomena.

INTRODUCTION

Several lines of evidence indicate that a large asteroid or comet struck the Earth 66 Ma, and many earth scientists believe that the ensuing environmental disaster triggered one of the largest mass-extinction events in the geologic record. Geochemical evidence provided the first clue that an impact had occurred at the close of the Cretaceous Period. Alvarez and others (1980) measured trace amounts of Ir and other Pt-group metals in a thin marine claystone bed at the Cretaceous-Tertiary (K-T) boundary in Italy, Denmark, and New Zealand. Because the Pt-group element anomaly coincides stratigraphically with the classic mass extinction of animals and plants that happened at the close of the Cretaceous, the Alvarez team speculated that a 10 ± 4-km asteroid of chondritic composition (relatively rich in Pt-group elements) struck Earth and formed a crater 200 km in diameter. Since 1980, Pt-group metal abundance anomalies have been recorded worldwide at about 95 K-T boundary sites (Alvarez and Asaro, 1990).

Mineralogic evidence, discovered by Bohor and others (1984), provided important support for the Alvarez impact-extinction hypothesis. They found grains of quartz containing multiple intersecting sets of planar lamellae (shock lamellae) in K-T boundary sedimentary rocks in the Hell Creek area of Montana. Such microstructures can be formed in quartz during laboratory experiments at high pressure (>60 kb) and strain rate (10^6/s). In nature, shock lamellae in quartz have been seen only in rocks at known meteorite impact sites and at surface and subsurface nuclear explosion sites. Izett and Pillmore (1985) also found grains of shocked quartz, quartzite, metaquartzite, and feldspar at about 20 K-T boundary sites in the Raton basin of Colorado and New Mexico. To date, shocked quartz grains have been identified at numerous K-T boundary sites in western North America, Europe, Asia, Haiti, and the Pacific Ocean (Izett, 1987b, 1990).

A few earth scientists have offered alternative ideas to explain the origin of the Ir anomaly and shocked quartz in K-T boundary rocks. Officer and Drake (1985), McLean (1985), and Officer and others (1987) proposed that the Ir is of terrestrial volcanic rather than of extraterrestrial impact origin. According to them, the Ir and shocked quartz were generated during an intense period of volcanic activity such as the enormous volume of basalt, the Deccan Traps, which were extruded in India during the Late Cretaceous and early Cenozoic. Quartz and plagioclase with alleged shock features were found (Carter and Officer, 1986, 1989) in the Toba Tuff, and if their evidence were valid, it would provide an alternative mechanism for the formation of shocked minerals in K-T boundary rocks. However, the alleged shock features in the plagioclase and quartz of the Toba are unlike the shock features in K-T quartz grains (multiple sets of planar lamellae) that all agree are of shock origin. Moreover, Izett and Pillmore (1985) and Izett (1987b, 1990) demonstrated that a large percentage of the shocked minerals in the K-T boundary are quartzite and metaquartzite whose source was sedimentary, metasedimentary, and metamorphic rocks and certainly could not have been silicic pyroclastic rocks (Izett, 1990).

Other more controversial evidence frequently used to support the Alvarez impact-extinction hypothesis includes the presence of microtektite-like authigenic spherules (Smit and Klaver, 1981), soot (Wolbach and others, 1985), stishovite (McHone and others, 1989) and abiotic amino acids (Zhao and Bada, 1989) in K-T boundary rocks. Soot (five sites), stishovite (one site), and abiotic amino acids (one site) occur only at a few K-T boundary sites, but authigenic spherules of sanidine, clay, aluminum phosphate (gorceixite or goyazite), and pyrite have been reported at numerous sites in K-T boundary rocks (Izett, 1990). The term "spherule" is used herein for all authigenic pellets regardless of their exact shape. Some are forms of revolution ("splash forms" of some authors); others are irregular in shape (Izett, 1987a). The term "tektite" is used for convenience only at some places in this paper for both tektites and microtektites, although the term "microtektite" should be applied to glassy silicate objects of impact origin less than 1.0 mm in diameter.

The origin of authigenic spherules in K-T boundary sedimentary rocks has been a controversial subject. The spherules occur at numerous sites, and the shapes of many are identical to tektites and microtektites, especially at sites in western North America. Smit and Klaver (1981), Montanari and others (1984), Kyte and Smit (1986), and Smit (1990) argued that sanidine and clay spherules in K-T boundary rocks in Spain and Italy are of impact origin while Hansen and others (1986) proposed that pyrite spherules in Danish K-T interval rocks are infilling of prasinophyte algae. Izett (1987b, 1990) emphasized observational data inconsistent with an impact origin for sanidine and aluminum phosphate spherules at Spanish and North American sites, respectively. Schmitz (1988) concluded that pyrite spherules at Danish sites are not of impact origin.

Discovery of the K-T boundary site on Haiti by Maurrasse (1982) and subsequent detection by Hildebrand and Boynton (1990a, 1990b) of clay spherules in these rocks provided important new insight relative to the origin of the spherules. Maurrasse studied uppermost Cretaceous and lowermost Tertiary rocks near Beloc in the 1970's, and in the early 1980's, he made collections of rocks that yielded Ir abundance anomalies (peak amount 2.3 ppb) at the paleontologic K-T boundary (Alvarez and others, 1982). Maurrasse's section on Haiti is, and will be, one of the most important sections in the world for unraveling the complicated K-T boundary impact event.

PURPOSE OF THE REPORT

Critical new observations relative to the K-T boundary impact-extinction hypothesis were made during study of a Haitian K-T boundary rock sample collected by two of us in September 1990. During filming of a TV series on the extinction of the dinosaurs, being produced by WHYY (Philadelphia), Florentin Maurrasse of Florida International University and Robin Bates of WHYY collected a 11x11x16-cm block of the K-T boundary bed. In this sample, Izett found relic tektites in cores of clay spherules that have shapes identical to tektites and microtektites. Tektites are unusual silicate glassy objects, which most earth scientists agree, are of terrestrial impact origin (Koeberl, 1986). Obviously, the discovery of the tektites and the writing of this paper would not have been possible without the full cooperation of Maurrasse and Bates. F.E. Lichte and the senior author analyzed the tektites and their clay alteration as part of Lichte's development of a relatively new chemical analytical system, laser ablation inductively coupled plasma mass spectrometry. G.P. Meeker guided the senior author in analyzing the tektites and clay using the electron microprobe. All other aspects of the preparation of this paper were the responsibility of the senior author.

The tektites, which are the subject of this paper, are in the same bed that contains an Ir abundance anomaly (Alvarez and others, 1982) and shocked quartz grains (Hildebrand and Boynton, 1990b, p. 844, fig. 2). The triple coincidence of three different types of impact-produced material in the calcareous claystone bed that marks the K-T boundary enormously strengthens the Alvarez team impact-extinction hypothesis. Moreover, the discovery of tektites opens many new avenues of research and makes it possible to (1) identify some of the rock types in the K-T impact area by geochemical and isotopic-tracer studies (Nd-Sm; Rb-Sr; U-Pb), (2) determine potassium-argon (^{40}Ar/^{39}Ar method) radiometric ages of glass produced by the K-T impact, (3) understand the relative mobility of elements during geochemical transformation of tektite glass to clay, and (4) unravel the origin of spherules at K-T boundary sites elsewhere in the world. Therefore, it is the purpose of this paper to show that relic tektites occur in K-T boundary rocks and to present preliminary information summarizing some of the new observational and geochemical data for the tektites and their clay spherule hosts.

K-T CLAY SPHERULES

The clay spherules, which contain the tektites, occur in a 0.55 m thick bed composed chiefly of clay and calcium carbonate. Spherules in this bed are exceptionally well preserved (not deformed), abundant, and distributed throughout the bed. They are more common in the lower 2.0 cm of the bed where they constitute about 60% of the rock (based on point count of polished surface). In the upper part of the sample studied, they form about 30% of the sample. Their shapes are identical to those of small tektites and microtektites pictured by Beyer (1961) and Baker (1963), and there is little doubt that they are indeed altered microtektites and tektites. The most common form is a sphere, but other forms of revolution are conspicuous in the rock, including dumbbells (figs. 1, 2C), teardrops or spindles, buttons, discs, oblate or prolate spheroids, and irregular-shaped objects. Some spherules, chiefly teardrops and spindles, must have been broken during aerial transportation or marine depositional processes, inasmuch as matrix clay wraps around broken ends of the objects (figs. 2A, 2B). The exterior surface of many of the clay spherules are amazingly smooth as seen with an optical microscope and an SEM. However, rare clay spheres have wart-like knobs (fig. 3) on their surface similar to silica-rich protrusions on microtektites illustrated by Glass (1984a, p. 272, fig. 4A). Peculiar patterns were seen on the surfaces of some spherules. One possibility is that these patterns reflect compositional flow lines in the original glass of the tektites.

The clay of the spherule shells or walls is generally light brown, brittle, and breaks with conchoidal fracture (fig. 4A). Nevertheless, some of clay is soft and porous (figs. 4B, 4C). Broken surfaces of the clay shells have a porcellaneous aspect. Structurally the clay is dioctahedral smectite (X-ray diffraction by R.A. Sheppard of the U.S. Geological Survey). The approximate chemical composition of the clay shells, as determined by J.M. Nishi of the U.S. Geological Survey and the senior author using the energy dispersive X-ray spectrometer (EDS) of a scanning electron microscope (SEM), consists mainly of 60%-70% SiO_2 and 13%-20% Al_2O_3. The Fe (7%-10% as Fe_2O_3) and Mg (2%-6% as MgO) content of the clay is high, and the alkali metals K and Na are low, much less than 1.0%.

Spheres range in size from a few tenths of a millimeter up to as much as 3.5 mm; on the other hand, oblate spheroids, dumbbells, and teardrops are typically larger than 1.0 mm. The mean diameter of 110 complete spheres extracted from the claystone was determined to be 1.2 ± 0.49 mm (1 sigma). Dumbbells, teardrops, and prolate or oblate spheroids generally range in size from 1.5 to 4.0 mm. Irregular chunks of smectite, as large 7.5 mm, in our sample are probably altered tektites. Hildebrand and Boynton (1990b) reported complete spherules as large as 7.0 mm and chunks of smectite as large as 1.0 cm in their samples of Haiti K-T rocks.

Many of the large clay spherules are hollow, and in this respect they resemble hollow gorceixite or goyazite spherules in K-T boundary sections in Wyoming (Izett, 1990, fig. 21A). Some Haiti spherules were filled or partially filled with calcite. The shells of the spherules vary in thickness from paper thin to a few tenths of a millimeter thick. Some of the spherules, however, are solid. One of the chief characteristics of the hollow spherules is that the inner surface of their shells is mammillary, and this inner surface is frequently coated with a white lacy material (fig. 5A). EDS-SEM study of this material showed that its crystal habit and composition are similar to smectite (fig. 5B).

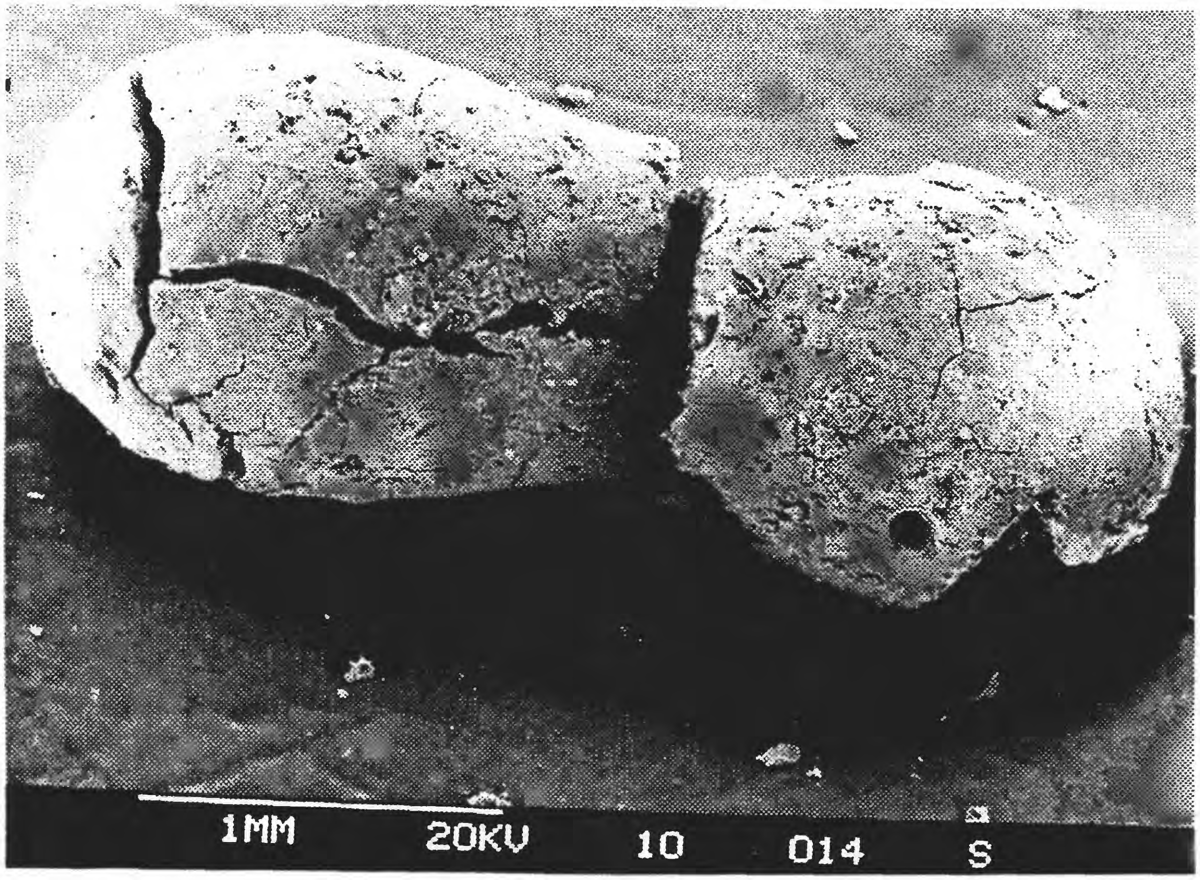

Figure 1.--Scanning electron microscope image of a hollow dumbbell-shaped clay-altered tektite about 3.0 mm long from the Haiti K-T boundary site. Dumbbell broken during extraction from matrix.

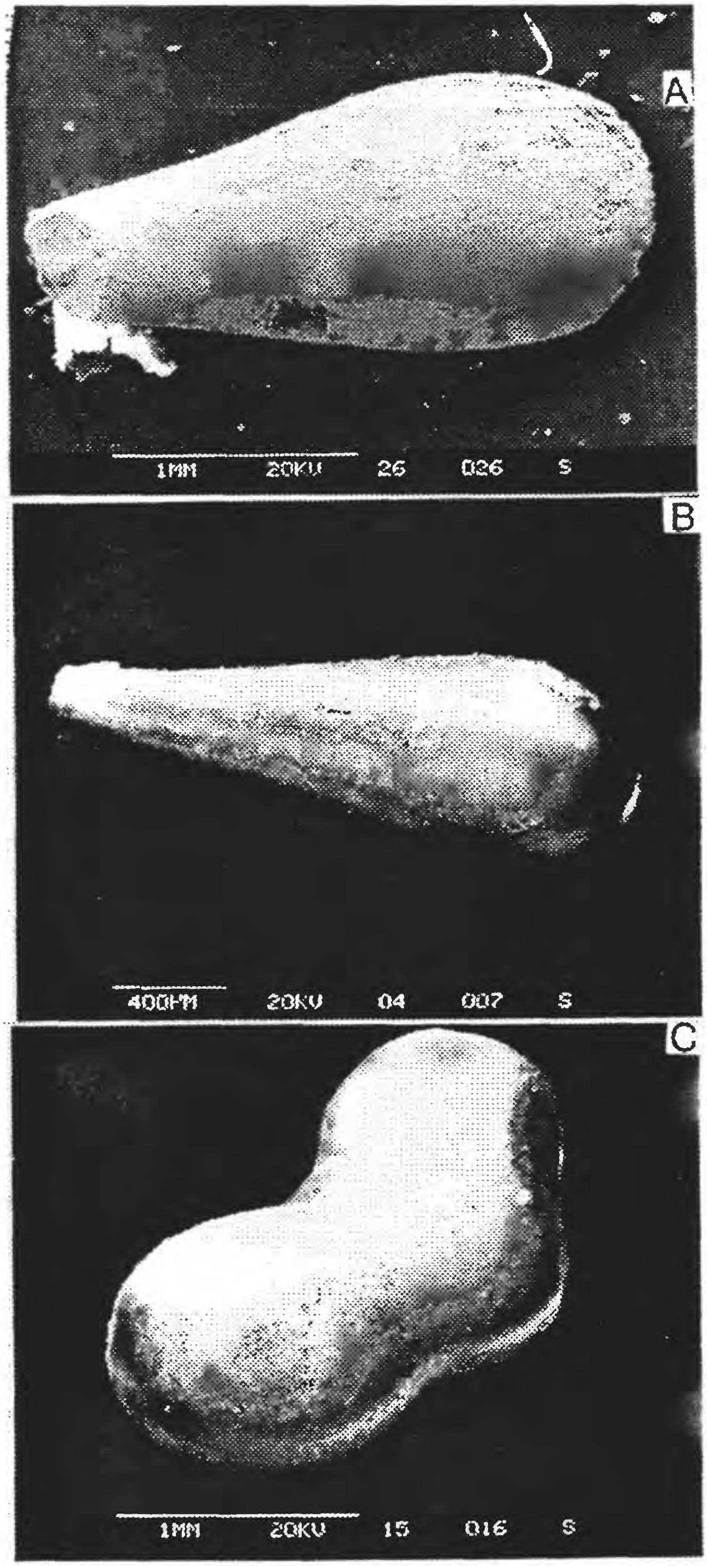

Figure 2.--Scanning electron microscope images of two teardrop-shaped and one triple dumbbell-shaped clay-altered tektites from the Haiti K-T boundary site. 2A, Teardrop-shaped altered tektite. End of tektite broken during deposition. 2B, Teardrop-shaped altered tektite showing narrowly tapered end. 2C, Dumbbell-shaped clay-altered tektite showing three sections.

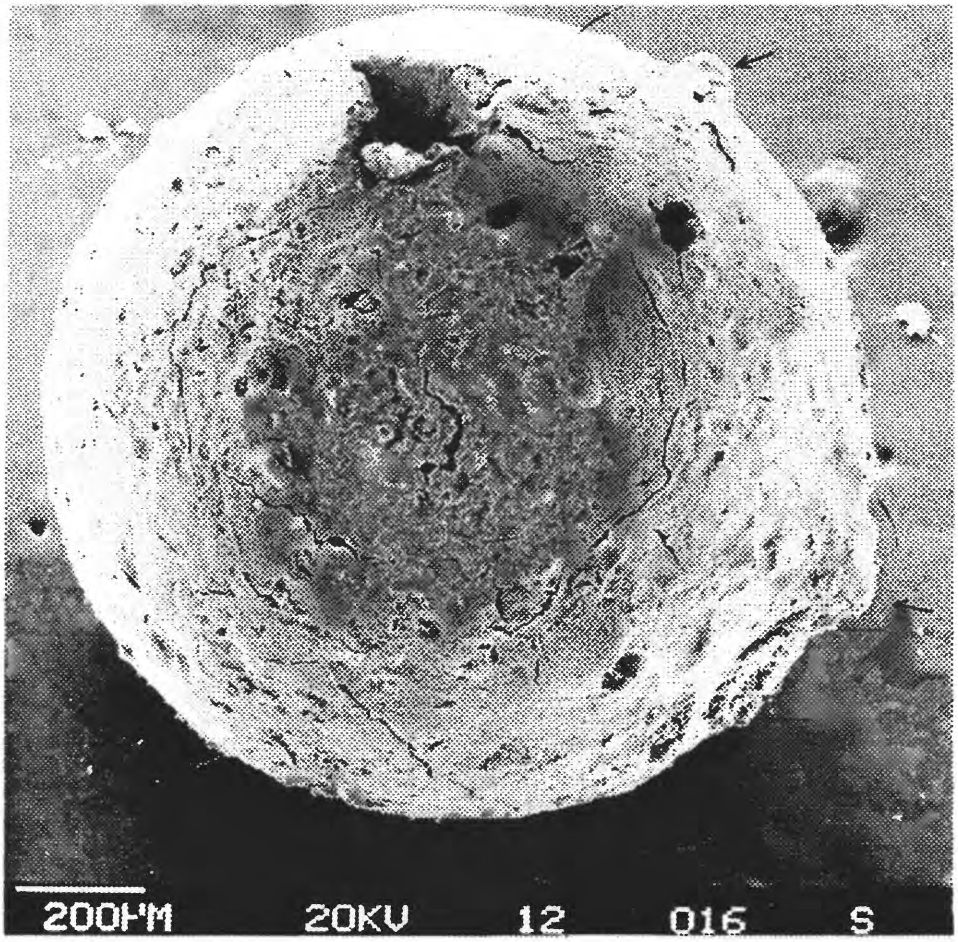

Figure 3. Scanning electron microscope image of a hollow clay-altered spherical tektite about 1.3 mm in diameter. The exterior surface of the spherule has wart-like knobs (shown at arrows) on its surface similar to silica-rich protrusions on microtektites illustrated by Glass (1984a, p. 272, fig. 3A).

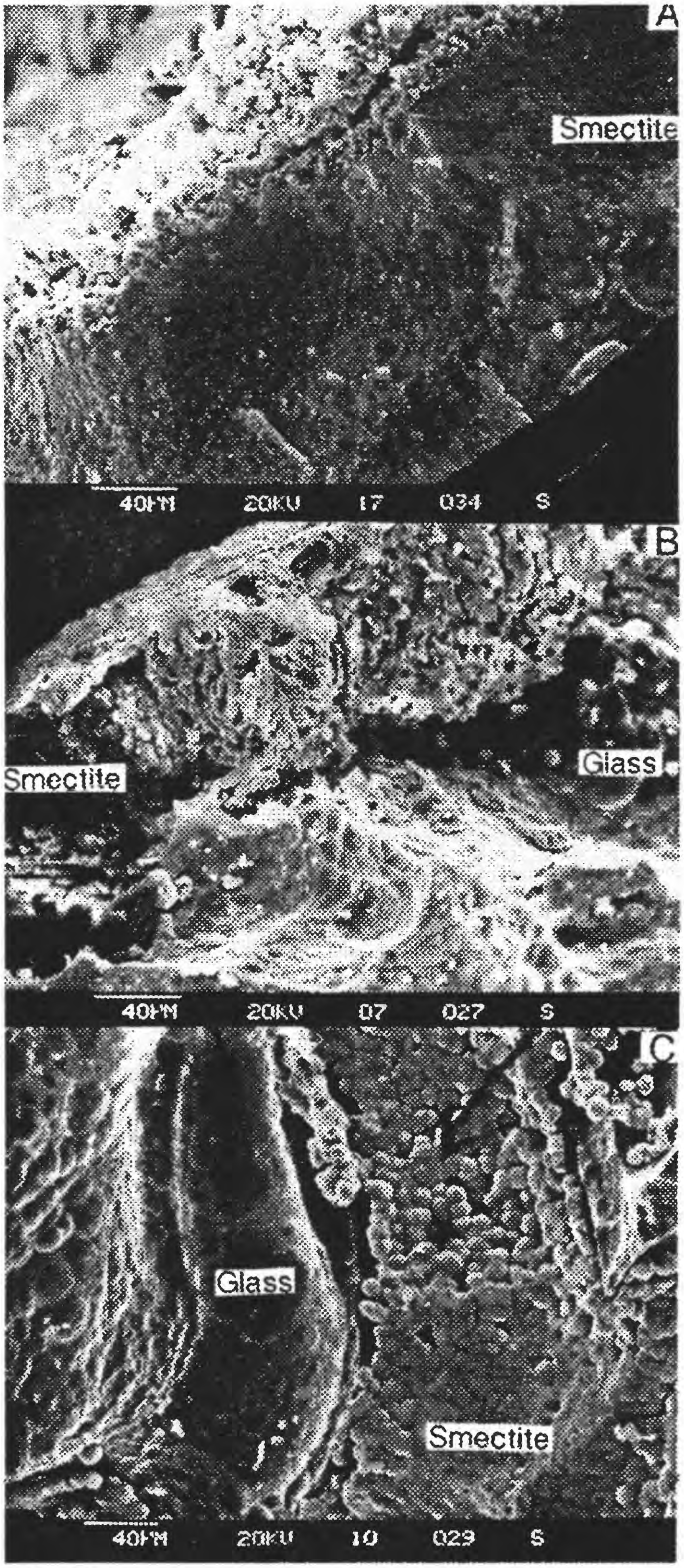

Figure 4. Scanning electron microscope images of three spherical clay-altered tektites from the Haiti K-T boundary site. 4A, Thick-walled shell of spherule formed by transformation of tektite to clay. Shell composed of dense porcellaneous smectite formed by solution of glass and precipitation of smectite. 4B, Shell of spherule formed by transformation of tektite to clay. Porous smectite shell produced by solution of glass and precipitation of smectite. 4C, Same as 4B. Note sharp contact between glass of tektite and spherical smectite.

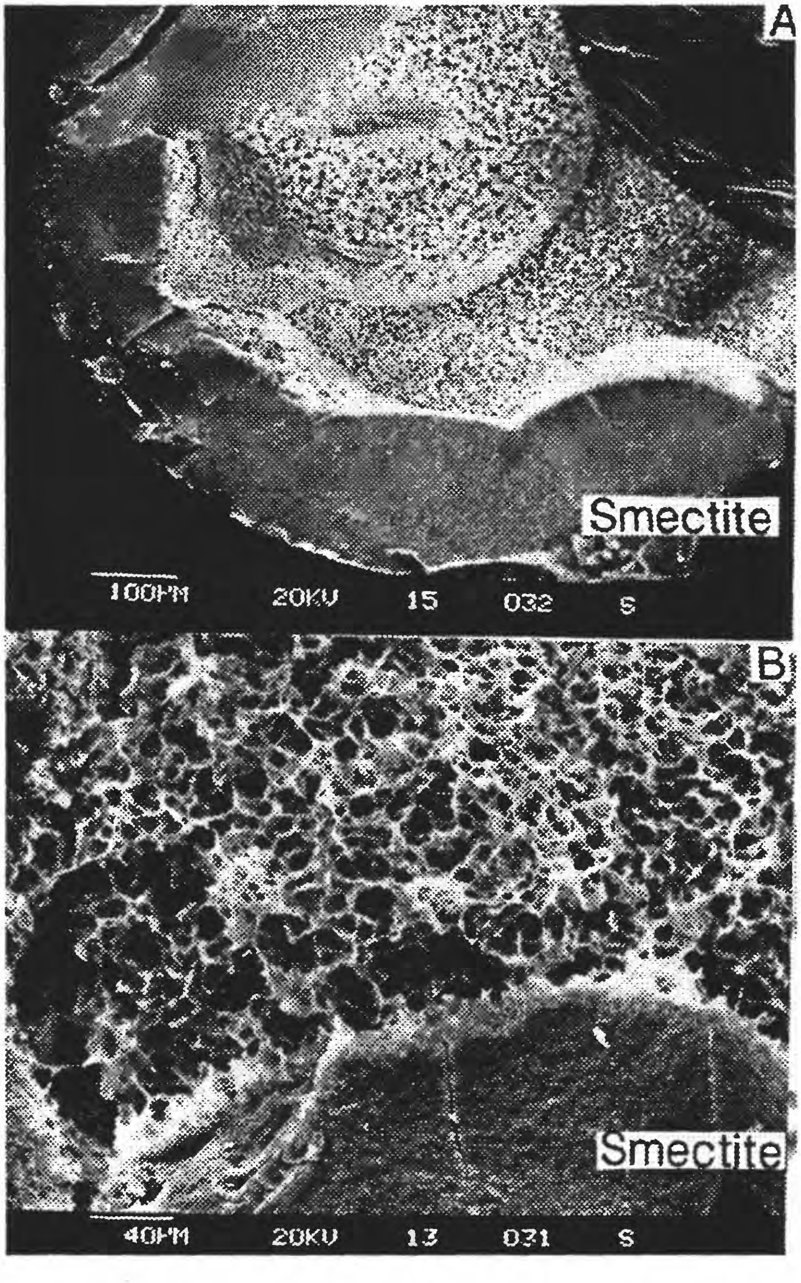

Figure 5. Scanning electron microscope images of clay-altered tektites from the Haiti K-T boundary site. 5A, Hollow spherical shell of altered microtektite showing mammillary inner surface coated with lacy smectite. 5B, Magnified view of 5A showing delicate lacy structure of smectite coating inner surface of spherule.

K-T TEKTITES

During the study of polished surfaces of the large sample of K-T boundary rock collected by Maurrasse and Bates, small corroded glass objects were seen in the cores of some clay spherules (figs. 6A, 6B). The spherules that contain the glass objects occur in a 2-cm-thick zone at the base of the K-T bed. These glass objects are tektites as shown in a subsequent paragraph. Less than 2% of the spherules in the tektite-bearing zone contain glass, and they are found in all types of spherules. The estimate of the abundance of tektites in the clay spherules was made by point counting polished surfaces of slabs of the K-T boundary bed. The tektites occur only in a 1- to 2-cm-thick zone that is at the base of the 0.55-m-thick calcareous claystone that marks the K-T boundary.

Macroscopically, the glass of the tektites (1-4 mm) appears black (fig. 7), but under low magnification of a biologic-type microscope, crushed thin fragments of the tektites are transparent and have a much lighter color, characteristically pale brown. Some tektite fragments are very pale brownish yellow. Exceptionally thin chips may be almost clear as window glass. Study of the glass in the immersion cell of a Wilcox spindle stage (Wilcox, 1959) using a polarizing light microscope showed that the glass is perfectly isotropic and generally featureless.

Several lines of evidence indicate that the glass is of impact rather than volcanic origin. The principal evidence is that the glass lies within clay spherules whose shapes are identical to those of small tektites. In addition, the glass is devoid of microlites and crystallites, and this observation essentially excludes the possibility that it is of volcanic origin. Typically, glasses of volcanic origin (obsidian) are charged with microlites. The occasional presence in the glass of large (0.5 mm) spherical and almond-shape bubble cavities of a type generally not found in obsidian suggests that the glass is not of volcanic origin. The glass surely has a low water content because electron microprobe analyses of the major elements (as oxides) in the glass (given in a subsequent section of this report) total nearly near 99%. Glass of tektites is essentially anhydrous, typically only a few ppm (Friedman, 1958, table 1, p. 318; Adams, 1984, p. 205), and this fact makes it especially chemically stable as compared to volcanic glasses. Only rarely has volcanic glass survived for 60-70 million years, and where it has survived it is superhydrated and is known to contain at least 5% water (Forsman, 1984, p. 459).

Most of the tektites within the clay spherules are heavily corroded, and their present irregular shape does not reflect their original shape, as inferred by the geometry of the host clay spherule. Rare tektites are almost completely preserved; that is they make up more than 95% of a clay spherule. In contrast, a nearby clay spherule may only contain a tiny shred of a tektite. The entire surface of the tektites is rough and covered with overlapping shallow pits separated by sharp cusps similar to those shown by Glass (1984a, p. 270, figs. 1B, 1C; Glass, 1984b, p. 338, fig. 5B). Some tektites have deep planar

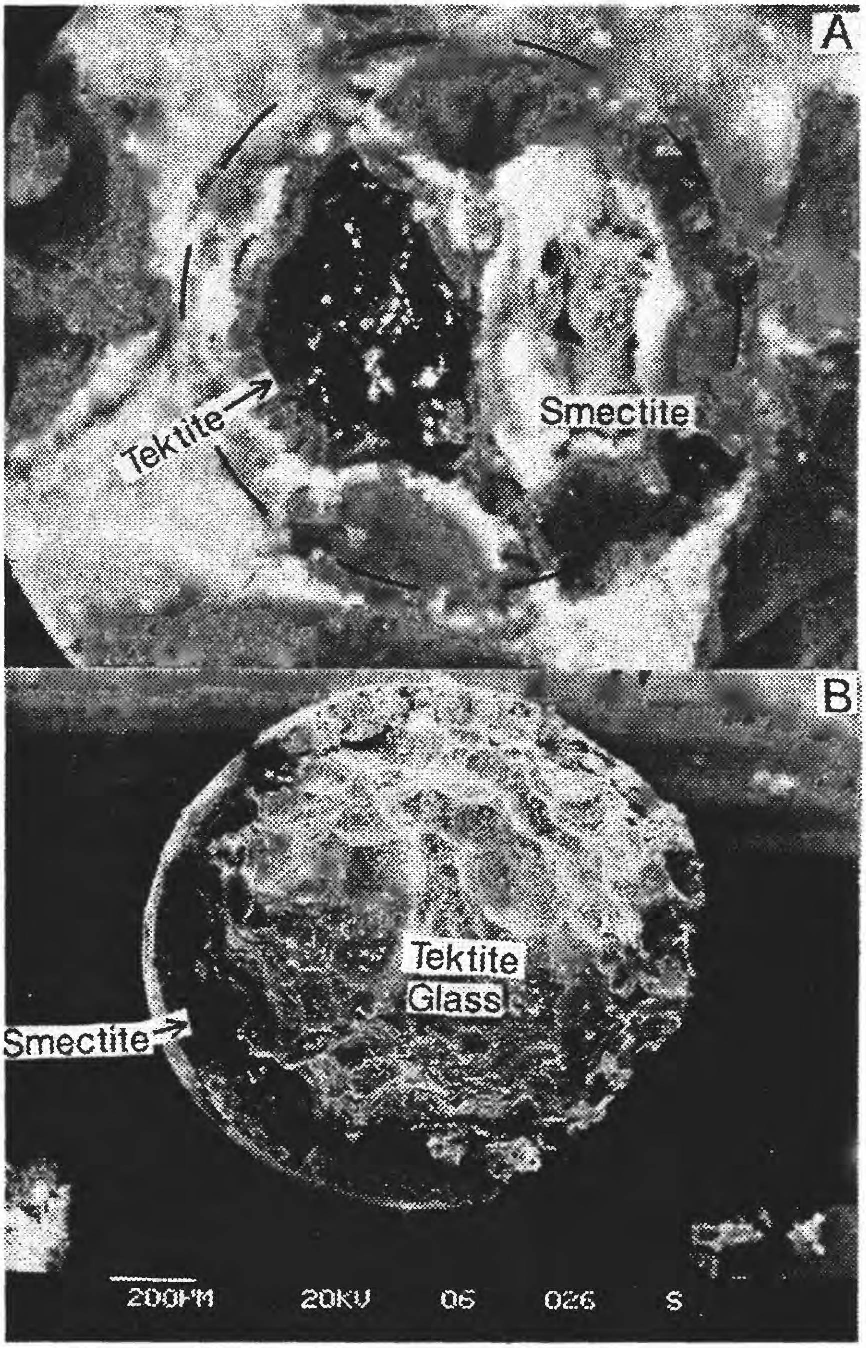

Figure 6. Photographs of tektites from the Haiti K-T boundary site. 6A, Cross section of clay spherule imbedded in host calcareous claystone. Spherule contains a corroded tektite. Spherule is about 0.9 mm in diameter. Dashed circle shows outline of clay spherule. 6B, Scanning electron microscope image of clay spherule containing a tektite. Solution of the glass formed a surface of shallow bowl-shaped pits separated by cusps.

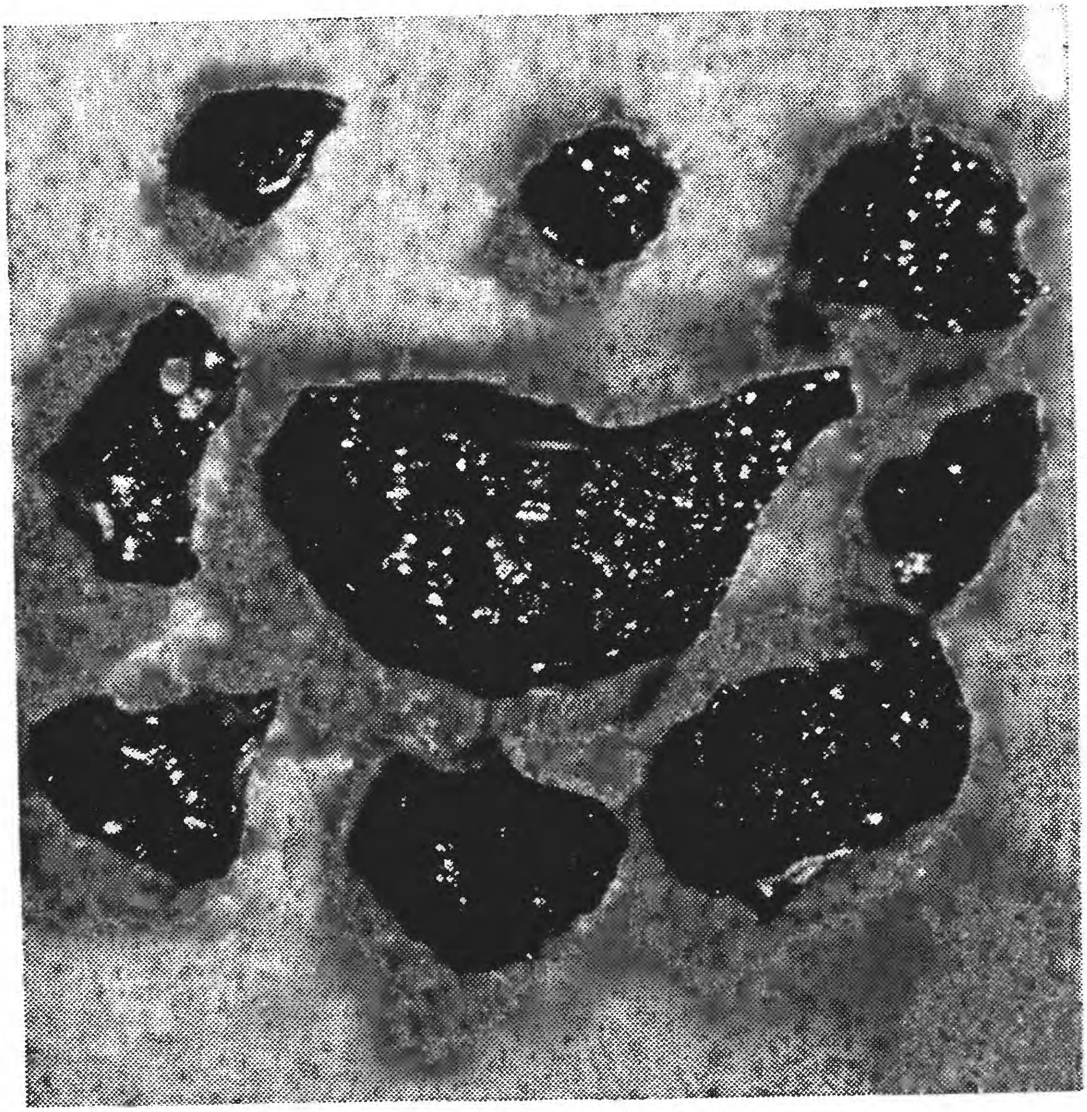

Figure 7. Photograph of several corroded K-T tektites removed from the center of clay spherules. Largest tektite is about 2.3 mm long.

cracks akin to those in some North American and other tektites pictured by Glass (1984a, p. 270, fig. 1C).

The index of refraction of tektites provides a major clue as to their chemical composition, and it varies inversely with the silica content (Chao, 1963, p. 57). Forty randomly selected small (~100 µm) chips of tektite glass were mounted on steel spindles, and their indices of refraction were measured using a spindle stage and the focal masking technique (Wilcox, 1983). Use of the focal masking method allowed the detection of compositional zoning, as much as n=0.004, within the small glass chips. The index of refraction of the K-T tektite chips measured average n=1.529 ± 0.006 and vary from n=1.518 to n=1.542 (fig. 8). They are similar in this respect to a class of microtektites called "Ivory Coast tektites and microtektites" found in oceanic deposits off the west coast of Africa (n=1.521 to n=1.540, Glass, 1969, table 1). The Ivory Coast tektites and microtektites (about 1.0 Ma) are much younger than the K-T tektites. The silica content of the above cited Ivory Coast microtektites ranges from 62.4% to 67.3%. A wider perspective of the variability of the index of refraction was made in oil-immersion mounts of several score of glass fragments. The range of refractive index measured in this way matched that measured on individual tektite chips using a spindle stage.

CHEMICAL COMPOSITION OF K-T TEKTITES

The chemical composition of K-T boundary tektites was determined using two different analytical techniques. An electron microprobe and a quadrupole mass spectrometer were used to determine the major- and trace-element content of the tektites, respectively. Eleven different tektites were analyzed, and the results are tabulated on table 1.

The electron-microprobe analyses show that the K-T tektites are, in terms of volcanic rocks, intermediate in composition--that is between rhyolite (70%-77% SiO_2) and basalt (45%-52% SiO_2). Silica in the K-T tektites varies from about 60% to 68%, and alumina ranges within narrow limits between 14% and 15%. The silica content of the K-T tektites is in the lower part of the compositional range of most other tektite groups (compare Chao, 1963; Schnetzler and Pinson, 1963; Glass, 1984b; Koeberl, 1986). The silica content is much lower than in bediasites, georgiaites, moldavites, normal australites, indochinites, and philippinites, which generally contain over 70% SiO_2. But the silica content in K-T tektites is comparable to the lower part of the silica content range of Ivory Coast microtektites (Glass, 1969, table 1). Amounts of Mg, K, and Ti are similar to amounts within other tektite groups. The Fe and Na are slightly higher and Ca significantly higher in K-T tektites as opposed to most other tektites groups. The oxide totals (table 1) are near 99%, which indicates that the glass has a low volatile content.

Table 1.--Chemical analyses of K-T boundary tektites and their clay alteration product smectite spherules. [Major-element analyses by electron microprobe by G.A. Izett and G.P. Meeker. Instrument conditions: accelerating voltage 15 KV, beam current 15 nannoamps on brass, 20 second count time. Data reduction based on program CITZAF (Armstrong, 1988) Trace elements by laser ablation inductively coupled mass spectrometry by F.E. Lichte and G. A. Izett; ND, below detection limit]

SAMPLE	MATERIAL	SiO2	Al2O3	FeO	MgO	CaO	K2O	Na2O	TiO2	MnO		SUM		
90G15-1	TEKTITE	60.3	13.7	5.7	3.8	10.9	1.0	2.4	0.8	0.2		98.8		
90G15-B	TEKTITE	61.6	14.9	5.4	2.8	7.9	1.7	3.5	0.8	0.2		98.7		
90G15-2	TEKTITE	61.7	14.9	5.4	2.7	7.7	1.6	3.6	0.8	0.2		98.6		
90G15-4	TEKTITE	61.9	14.9	5.4	2.8	7.7	1.6	3.6	0.8	0.2		98.8		
90G15-5	TEKTITE	62.0	15.0	5.3	2.7	7.4	1.6	3.5	0.8	0.2		98.5		
90G15-A	TEKTITE	62.3	15.0	5.5	2.7	7.4	1.6	3.5	0.8	0.2		99.1		
90G15-C	TEKTITE	62.3	15.1	5.3	2.7	7.5	1.7	3.6	0.8	0.2		99.1		
90G15-E	TEKTITE	64.7	15.3	5.0	2.4	5.5	1.7	3.4	0.7	0.1		98.8		
90G15-D	TEKTITE	65.3	14.1	5.3	2.7	6.0	1.5	3.0	0.7	0.1		98.7		
90G15-3	TEKTITE	66.1	14.3	5.0	2.5	5.0	1.8	3.5	0.7	0.1		99.0		
90G15-6	TEKTITE	67.6	14.4	4.7	2.5	4.7	1.3	2.9	0.7	0.1		98.8		
MEAN		63.2	14.7	5.3	2.8	7.1	1.5	3.3	0.8	0.2		98.8		
90G15-7	CLAY SPHERULE	59.1	14.2	6.1	7.4	3.4	0.2	<.01	0.7	<.01		91.0		
90G15-8	CLAY SPHERULE	58.9	14.6	5.5	7.0	3.6	0.1	<.01	0.8	<.01		90.7		
		Li	Be	B	Cl	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Ga
90G15-A	TEKTITE	16	1.8	3.7	0.01	64	160	33	0.10	15	15	41	32	18
90G15-B	TEKTITE	15	2.4	3.3	0.01	66	150	29	0.08	14	16	30	30	18
912H4A	CLAY SPHERULE	55	0.22	1.7	<.01	9	45	4.8	0.03	2.4	53	21	37	ND
912H4B	CLAY SPHERULE	67	0.23	2.0	<.01	15	49	4.6	0.02	3.2	59	29	51	ND
912HS24A	CLAY SPHERULE	120	0.33	4.0	0.03	10	31	22	<.01	2.4	36	13	22	ND
912HS4C	CLAY SPHERULE	130	0.31	3.3	0.01	10	29	20	<.01	1.5	30	11	18	ND
		Ge	As	Rb	Sr	Y	Zr	Nb	Mo	Pd	Ag	Cd	In	Sn
90G15-A	TEKTITE	0.26	0.38	55	790	37	200	7.2	<.01	0.01	0.01	0.04	<.01	7.1
90G15-B	TEKTITE	0.36	0.24	55	910	53	300	8.9	<.01	0.03	0.03	0.04	<.01	8.6
912H4A	CLAY SPHERULE	0.73	0.20	0.64	25	0.27	27	0.40	<.01	ND	<.01	0.03	0.01	1.2
912H4B	CLAY SPHERULE	1.1	0.21	0.69	41	0.41	37	0.47	<.01	ND	0.01	0.07	0.02	1.7
912HS24A	CLAY SPHERULE	1.4	0.32	1.8	20	0.14	26	0.15	<.01	ND	0.01	0.05	0.02	2.3
912HS4C	CLAY SPHERULE	1.3	0.07	1.2	19	0.17	23	0.23	<.01	ND	0.01	0.01	0.02	2.4
		Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
90G15-A	TEKTITE	0.09	0.00	1.2	1000	22	52	5.8	23	5.1	1.5	4.8	0.8	4.2
90G15-B	TEKTITE	0.08	0.00	1.2	1300	29	70	8.2	32	7.5	2.0	7.5	1.1	6.1
90G15-C	TEKTITE	ND	ND	ND	ND	28	61	7.3	30	7.1	1.7	7.4	1.1	7.0
912H4A	CLAY SPHERULE	0.15	ND	0.05	52	0.05	0.01	ND	ND	ND	0.01	ND	ND	ND
912H4B	CLAY SPHERULE	0.10	ND	0.08	68	0.07	0.01	ND	ND	ND	0.00	ND	ND	ND
912HS24A	CLAY SPHERULE	0.14	ND	0.07	29	0.06	0.18	ND	ND	ND	ND	ND	ND	ND
912HS4C	CLAY SPHERULE	0.04	ND	0.07	28	0.05	0.26	ND	ND	ND	ND	ND	ND	ND
90G15X	AVG. 2 CLAY SPHERULES					0.039	0.127	0.015	0.059	0.011	0.008	0.011	0.002	0.008
		Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb	Bi	U	
90G15-A	TEKTITE	0.9	2.3	0.28	2.7	0.63	4.0	0.29	0.43	<.01	5.0	<.01	0.90	
90G15-B	TEKTITE	1.3	3.5	0.47	3.7	1.2	8.2	0.66	0.48	0.01	5.8	0.06	1.6	
90G15-C	TEKTITE	1.4	4.0	0.58	4.1	0.70	ND	ND	ND	ND	ND	ND	ND	
912H4A	CLAY SPHERULE	ND	ND	ND	ND	ND	0.67	0.04	<.01	ND	2.7	0.03	ND	
912H4B	CLAY SPHERULE	ND	ND	ND	ND	ND	0.80	0.09	<.01	ND	4.1	0.01	ND	
912HS24A	CLAY SPHERULE	ND	ND	ND	ND	ND	0.88	0.06	<.01	ND	2.4	0.03	ND	
912HS4C	CLAY SPHERULE	ND	ND	ND	ND	ND	0.96	0.03	<.01	ND	1.5	0.02	ND	
90G15X	AVG. 2 CLAY SPHERULES	0.001	0.004	0.001	0.007	0.001								

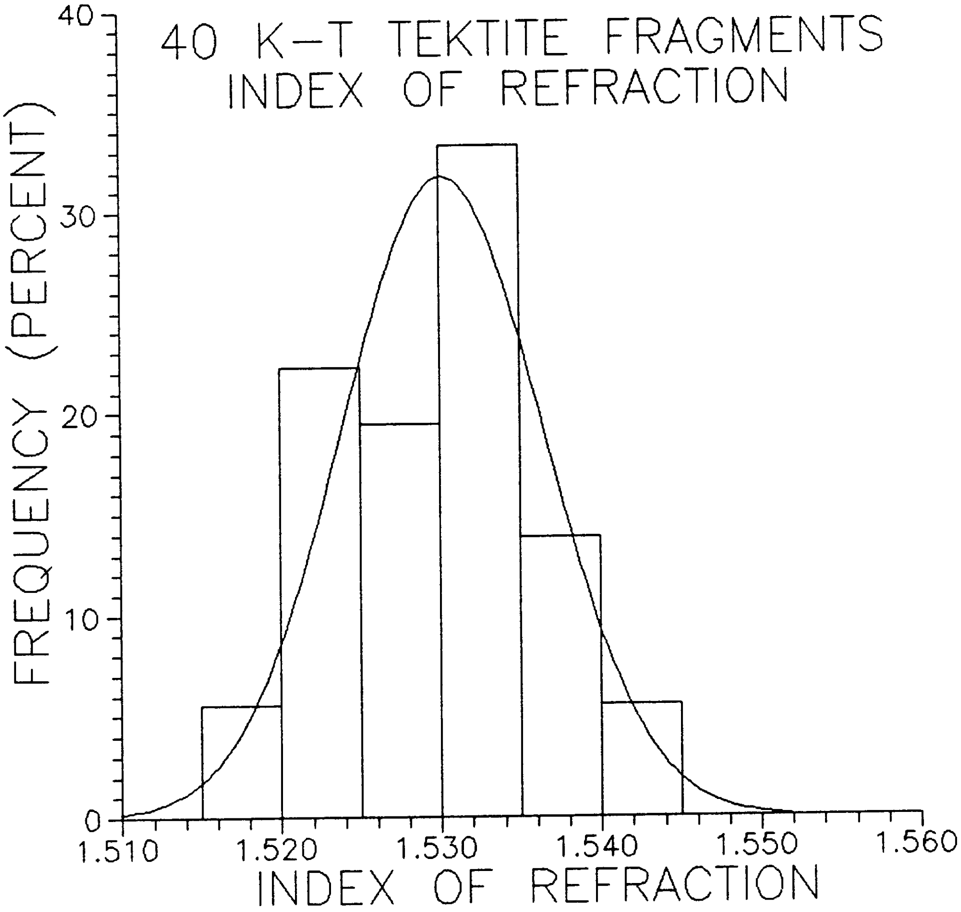

Figure 8. Frequency diagram showing the range of index of refraction of 40 tektite chips from the Haiti K-T boundary site. Superposed chi-square distribution curve also shown.

The composition of the K-T tektites differs only slightly, if at all, from average volcanic rocks with silica contents of 60%-70%. In terms of volcanic rocks, K-T tektites having the lowest silica content (60%-62%) are close to average andesite, and tektites having the highest silica content (66%-68%) are close to average dacite. CIPW normative minerals of the K-T tektites are not unusual in any way. However, the amount of Ca in the tektites seems slightly high for most high silica dacites.

Trace elements were measured using a relatively new analytical system (Lichte and Ridley, 1990; Lichte and Izett, 1990), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Advantages of the LA-ICP-MS system over conventional analytical tools are: (1) speed, 1-2 minutes per analysis, (2) broad chemical coverage, typically 75 elements per analysis, (3) minimal sample preparation, (4) continuous profiles possible, (5) precise geometric traverses, and (6) permanent record of sampled material for future studies.

Laser profiles were made across the surface of small polished wafers that contained tektites and clay spherules mounted in epoxy. Using this analytical device, we were able to search for and measure all the major and minor elements in common silicate rocks and, more importantly, search for and measure in some cases about 50 trace elements including Pt-group elements. This analytical system offers a new, powerful approach for the nearly complete chemical analysis of trace, minor, and major elements in geologic materials.

The analytical system (LA-ICP-MS) used consisted of a pulsed Nd/YAG laser that ablated material from the surface of samples. The laser could be controlled allowing discreet in situ sampling of nearly any surface. Laser crater diameters were 100-300 μm; crater depths were typically as much as 500 μm. A stream of argon carried the submicron-size ablated material into an inductively-coupled argon plasma where it was ionized. The ions were further carried into a quadrupole mass spectrometer. The argon plasma, which was operated at atmospheric pressure, provided an ideal ionization source for the mass spectrometer and allowed nearly complete ionization of 60-75 elements. The quadrupole mass spectrometer has high sensitivity for trace metals and moderate precision and dynamic range for major and minor elements. In this study, 51 trace elements were profiled and estimated concentrations were determined. The detection limit for the Pt-group elements was only a few ppb.

The trace-element content of the K-T tektites is similar to that in other types of tektites (table 1) for many elements. The K-T tektites are unusual in their somewhat higher content of Sc, V, Cu, Zn, Ga, Sr, Sn, and Ba; they are also unusual in their low content of B, Mn, and Hf (compare Koeberl, 1986, table 5). The Cr, Ni, and Co content are perhaps lower than other tektite groups. All of the platinum-group elements were searched for but not detected (detection limit about 5 ppb) in the tektites and clay spherules.

The rare-earth element (REE) content of the K-T tektites is about normal for reported values (Koeberl, 1986, table 5) of other tektite groups. Figure 9 shows a chondrite-normalized plot

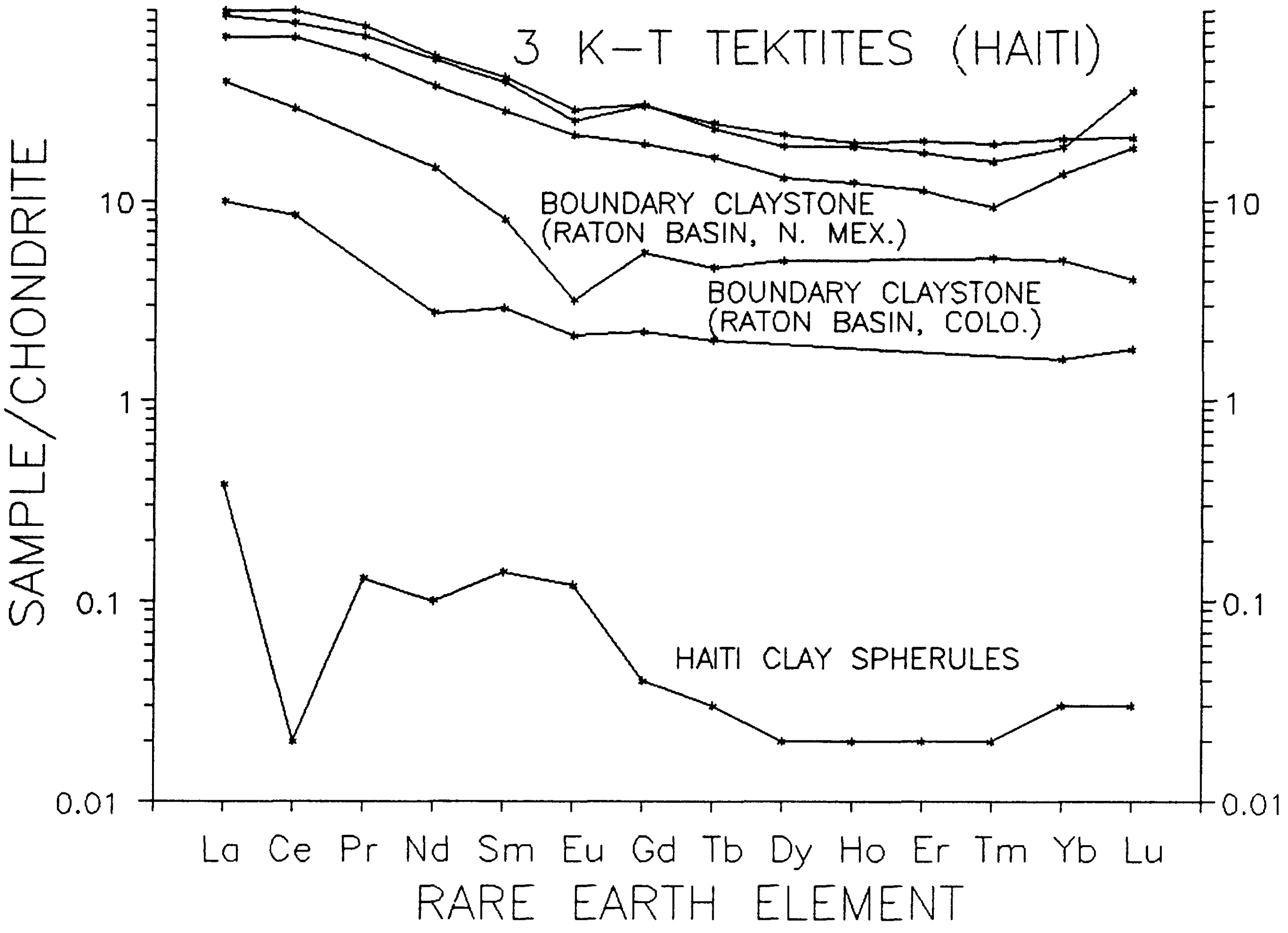

Figure 9. Chondrite normalized rare-earth element (REE) diagram of three K-T tektites from the Haiti K-T boundary site, K-T clay spherules, and two K-T boundary claystone beds from the Raton basin of Colorado and New Mexico. REE pattern of K-T tektites similar to other tektite groups. REE content of tektites and clay determined by LA-ICP-MS by F.E. Lichte and G.A. Izett of the U.S. Geological Survey.

of the rare-earth elements in three K-T tektite fragments. As can be seen, the light REE elements La and Ce are about 60-90times, and the heavy REE are about 20 times chondrites. The REE pattern of the K-T tektites is similar to the pattern of bediasites and georgiaites illustrated by Koeberl and Glass (1988, fig. 2). The REE content of the tektites suggests that the target rock melted during the K-T impact was moderately siliceous, not mafic or ultramafic as has been widely speculated (Shaw and Wasserburg, 1982; DePaolo and others, 1983; Montanari and others, 1984; Smit, 1990; and Hildebrand and Boynton, 1990b).

ALTERATION OF K-T TEKTITES

The discovery of tektite glass in cores of clay spherules affords an ideal situation for determining how tektites are transformed into clay. Optical microscopic and SEM study of polished surfaces of K-T boundary rock established geometric and chemical relationships between the tektites and their host spherules.

Individual clay spherules were pried out of the matrix and mounted on SEM stubs for photography or potted in epoxy for electron microprobe and LA-ICP-MS analysis. Our study of the spherules showed that a shell composed of smectite of variable thickness surrounds the tektites. In some spherules, a film or rind of alteration products, generally clay but sometimes calcium carbonate, coats the tektites in the spherules. This coating can occur between the glass and the smectite shell of a spherule. The contact between the alteration product and the glass is sharp (fig. 4).

Transformation of glass to clay apparently began by solution of the outer surface of a tektite by pore fluids. Smectite was precipitated from the pore fluids and formed a smectite shell encasing the tektite. Thus, this process preserved the exact external morphology of the tektites. In some cases this clay shell may have protected the tektite from further solution. Continued solution of the tektite and precipitation increased the thickness of the clay shell encompassing a shrinking corroded tektite. This process when carried to completion produced, in some instances hollow clay spherules and in other instances solid clay spherules. The hollow smectite spherules resemble hollow gorceixite (or goyazite) spherules in K-T boundary sections in Wyoming (Izett, 1990, fig. 21A). Bohor and Triplehorn (1987) and Bohor and others (1987, p. 899) speculated that the gorceixite spherules formed during the K-T boundary impact as hollow glass spherules. They imagined that the spherules were derived from the depressurized rocks exposed at the K-T impact-crater floor. Clearly, this fanciful interpretation can no longer be sustained considering the fact that some Haitian hollow clay spherules contain tektites in their cores.

The relative mobility of elements during the transformation of glass to clay was established by analyzing tektite glass and clay spherules by both EDS-SEM and LA-ICP-MS. The data of table 1 for the major elements (recalculated volatile free) shows that the content of Si, Al, and Ti in the tektite and its alteration product smectite are roughly similar. However, significant changes in chemistry accompanied the transformation of glass to clay. Mg is higher in the clay spherules by a factor of three, Fe is slightly higher, and Ca, Na, and K are significantly lower in the clay as compared to the tektite.

The REE and some other elements such as Ti, Ga, Zr, Nb, Hf, Ta, and Th are thought by some geologists (Hildebrand and Boynton, 1990b, p. 844) to be relatively immobile during alteration of impact or volcanic glass to clay (compare Zielinski, 1982, 1985). Comparison of the amounts of the REE elements and other elements thought to be relatively immobile shows that the REE and others are severely depleted in the clay relative to the tektite (table 1). Thus, the chondrite-normalized REE patterns for the Haiti K-T clay spherules do not reflect the chemistry of their progenitor material. Table 1 and figure 9 show that the REE content of Haiti clay spherules are two orders of magnitude less than in K-T tektites. The average REE content of two spherule fragments (sample no. 90G15X of table 1) is far less than 1 ppm. The especially low content of REE and the small sample size (two small chips) present a difficult analytical challenge. The data are shown to three decimal places, but analytically only two significant decimal places are warranted. Accordingly, the amounts of the REE in sample 90G15X are somewhat uncertain; however, their concentration is certainly less than 0.1 ppm. In addition to the Haiti clay spherules, the chondrite-normalized data (INAA data) for two samples of the K-T boundary claystone from continental sites in the Raton basin of Colorado and New Mexico (Izett, 1990) are plotted on figure 9 for comparison. Clearly, the REE patterns of the K-T tektites and Raton boundary claystone beds are significantly different. The fact that REE are so mobile during diagenesis of K-T boundary rocks precludes their use as a geochemical tool for predicting the composition of the progenitor of the clay.

SHOCK-METAMORPHOSED QUARTZ

Several large fragments of the sample collected by Maurrasse and Bates were digested in acids to determine if the sample contains shock-metamorphosed quartz grains. Previously, Izett had identified shocked quartz grains (reported by Hildebrand and Boynton, 1990b) in samples from Haiti sent to him by A.R. Hildebrand, a graduate student at the University of Arizona. The amount and size of the shocked quartz grains in the Haiti samples are of vital importance in delineating the size distribution of shocked quartz on a global scale (Izett and Pillmore, 1985; Izett, 1987a, 1987b, 1990).

A 335 g (corrected to 302 g for 10% H_2O in the smectite) sample of the K-T bed from above the tektite-bearing 2 cm layer was prepared by dissolving it in HCl and HF following the procedure outlined by Izett (1987b). The insoluble residue weighed 0.0192 g, or 0.006% of the rock. Optical microscopic study of the insoluble residue showed that it was composed of shocked quartz grains (45%), opaque grains (22%), unshocked quartz (16%), green-brown volcanic hornblende (10%), unshocked quartzite and metaquartzite (3%), shocked quartzite and metaquartzite (2%), and trace amounts of chalcedony, chert,

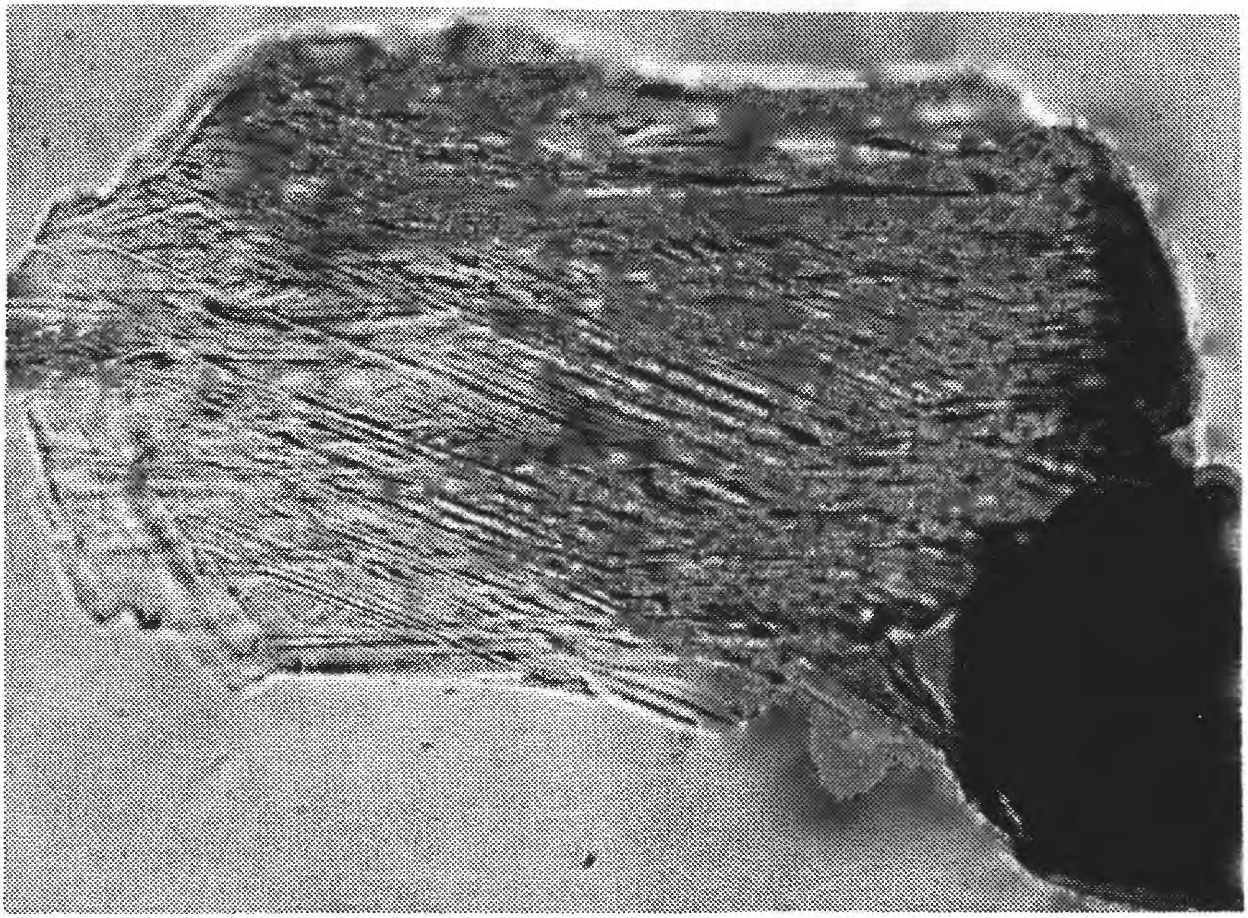

Figure 10. Shock-metamorphosed quartz grain 0.48 mm long from the Haiti K-T boundary bed. Grain shows three prominent sets of shock lamellae in this orientation.

epidote, garnet, and oxyhornblende. Shocked quartz grains contain multiple intersecting sets of planar lamellae similar to those in other K-T boundary sites (fig. 10). Shocked quartzite and metaquartzite are not as abundant in the Haiti K-T rocks as they are in western North American K-T sites.

The amount of shocked quartz in the insoluble residue is about 0.003%, far less than in the K-T boundary impact layer in the western United States (see Izett, 1990). The low content of insoluble residue in the K-T bed is not surprising because at least 30%-60% of the bed is composed of altered tektites that do not contain quartz and other detrital minerals. In addition calcium carbonate also forms a significant part of the sample.

Other than the shocked quartz grains, the assemblage of grains is dominated by fresh-appearing volcanic minerals. Within the assemblage of unshocked quartz grains are numerous crystals of volcanic quartz that have the high temperature morphology of beta quartz. The uniform-appearing hornblende grains, as much as 0.5 mm in length, are surely of volcanic origin. The opaque grains include many perfectly formed crystals of magnetite and ilmenite probably of volcanic origin. The presence of these volcanic minerals in the Haiti K-T bed is unusual for K-T boundary sites. It is also unusual for magnetite and hornblende to survive essentially unaltered in marine beds of Cretaceous age. For example, these minerals are not commonly preserved in Cretaceous bentonites of the western United States. Furthermore, the Ir- and shocked quartz-bearing K-T boundary bed is unusual for boundary interval rocks because of its lack of pyrite and commonly associated reddish brown iron-oxide staining.

The above cited mineralogic observations indicate that the K-T bed on Haiti is not a primary air-fall unit composed entirely of impact ejecta. Rather, it contains a small volcanogenic component of locally derived material admixed with impact ejecta during deposition on the sea floor. This idea is further demonstrated by the presence of (1) sponge spicules in the insoluble residues of the bed and (2) centimeter-size ripup clasts of soft limestone in the Haiti K-T bed. On the basis of bedding structures, Maurrasse (1986) suggested that the K-T bed is a turbidite. For the reasons given above, the thickness of the bed (0.55 m) may not accurately reflect the original thickness of air-fall impact ejecta at the Haiti K-T site we studied.

The size distribution of shocked quartz grains at the Haiti K-T sites was determined by measuring their longest dimension in oil-immersion mounts of the insoluble residue, and a frequency diagram showing a graphical summary of the measurements is given in figure 11. The method used was described by Izett (1990). The mean of 342 grains was determined to be 0.15 mm ±0.06 mm, and the largest grain encountered was 0.53 mm. Comparison of the mean value for shocked quartz in our sample from Haiti with similar data on a global basis shows that the Haiti data are similar to those from sites in western North America (Izett, 1990) but larger than those from sites elsewhere in the world.

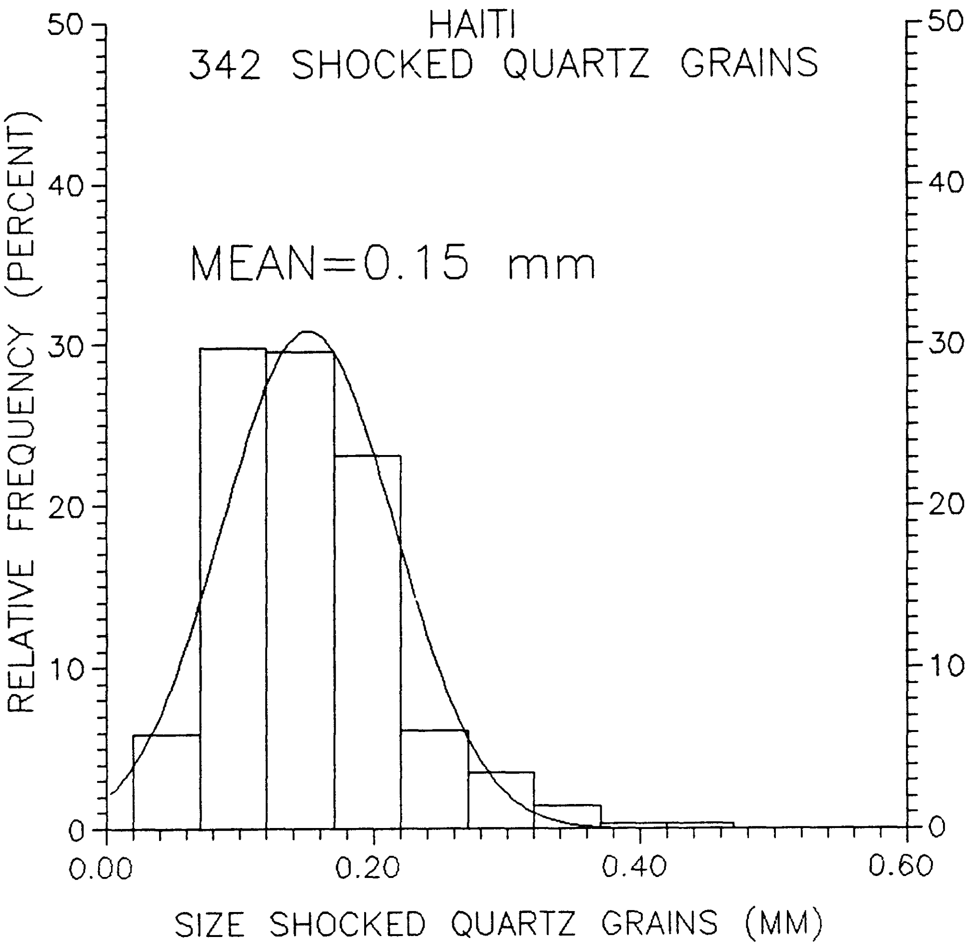

Figure 11. Frequency diagram showing size distribution of shock-metamorphic quartz grains from Haiti K-T boundary site. Superposed chi-square distribution curve also shown.

CONCLUSIONS

1.) Clay spherules in the K-T boundary bed at the Beloc site on Haiti contain relic tektites. The presence of tektites, which most earth scientists agree are of terrestrial impact origin, in the same bed with a Pt-group abundance anomaly and shocked quartz provides unambiguous proof of an asteroid or comet impact at the precise K-T boundary. The tektite evidence confirms the Alvarez K-T impact hypothesis and delivers a devastating blow to the Officer and Drake volcanic hypothesis for the explanation of Ir anomalies, shocked quartz, and other boundary phenomena.
2.) The major- and trace-element composition of the K-T tektites, in particular the REE, suggest that the target rock melted during the K-T impact was moderately siliceous, not mafic or ultramafic as has been widely speculated.
3.) Analysis of the K-T tektites and their altered counterparts, the clay spherules, shows that wholesale chemical changes accompanied the transformation of glass to clay. In particular, the REE were severely depleted during the transformation. The widely held view that the REE are immobile during alteration of glass in K-T boundary rocks can no longer be sustained, and use of REE diagrams to infer the progenitor of the K-T boundary claystone is inappropriate.
4.) Shock-metamorphosed quartz grains in our sample of the Haiti K-T boundary claystone are about the same size as those at boundary sites in western North America. The amount of insoluble residue and shocked quartz in the K-T bed is far less than in the K-T boundary impact layer in western North America. However, this is not surprising because at least 30% of the bed is composed of altered tektites that could not contain quartz and other detrital minerals.
5.) Mineralogic observations indicate that the K-T bed on Haiti is not a primary air-fall unit composed entirely of impact ejecta. Rather it contains a small volcanogenic component of locally derived material admixed with the impact ejecta during deposition on the sea floor. Thus, the thickness of the bed may not accurately reflect the original thickness of air-fall impact ejecta at the Haiti sites.
6.) Finally, the discovery of relic K-T boundary tektites opens many new avenues of K-T boundary research and confirms the widely held view that tektites form during asteroid or comet impacts with the Earth.

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