$^{40}Ar/^{39}Ar$ Age Spectra and Total-Fusion Ages of Tektites from Cretaceous-Tertiary Boundary Sedimentary Rocks in the Beloc Formation, Haiti

By G. Brent Dalrymple, Glen A. Izett, Lawrence W. Snee, *and* John D. Obradovich

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ABSTRACT

Fifty-two total-fusion ^{40}Ar/^{39}Ar ages, measured with a continuous laser system on single tektites from the Cretaceous-Tertiary (K-T) boundary layer within the Beloc Formation of southern Haiti, have a weighted mean of 64.42±0.06(σ_{best}) Ma. ^{40}Ar/^{39}Ar age spectra on four single Haitian tektites obtained with the same laser system are flat and each has a plateau over more than 95 percent of the ^{39}Ar released. The weighted mean of the four plateau ages is 64.38±0.18 Ma(σ_{best}). Two age spectra obtained using a resistance furnace system on bulk samples of about 50–70 of the tektites also have flat plateaus with a weighted mean age of 64.49±0.10 Ma. Our results indicate that the impact that formed the tektites occurred 64.43±0.05 Ma. Sanidine from two bentonites that lie 50–70 centimeters above the K-T boundary interval in continental sedimentary rocks in Montana was also dated with the laser system (28 measurements) and gives a weighted mean ^{40}Ar/^{39}Ar age of 64.77±0.07 Ma.

The Haitian tektites occur at the paleontological K-T boundary along with an Ir abundance anomaly and shocked quartz. They were the product of an impact on Earth of an extraterrestrial bolide (asteroid or comet) at the end of the Cretaceous Period. All available data, from our study and from those previously published, suggest that this event occurred 64.6±0.1 Ma.

INTRODUCTION

Slightly more than a decade ago, Alvarez and others (1980) proposed that a large (10±4 km diameter) asteroid of chondritic composition struck the Earth about 65 Ma and that the debris injected into the atmosphere by the impact caused the mass faunal extinctions that mark the end

of the Cretaceous Period. Their hypothesis was based on the presence of an unusually high content of Ir and other Pt-group metals, which are depleted in the Earth's crust relative to Solar System abundances, in a thin marine claystone bed at the Cretaceous-Tertiary (henceforth referred to as K-T for the sake of brevity) boundary in Italy, Denmark, and New Zealand. Since 1980, Ir abundance anomalies have been found in both marine and continental K-T boundary sedimentary rocks at nearly 100 sites worldwide (Alvarez and Asaro, 1990).

Some investigators proposed that the Ir anomaly is due to extensive volcanism (for example, Officer and Drake, 1985; McLean, 1985; Officer and others, 1987, 1992), possibly from the eruptions that emplaced the Deccan Traps of India. The general absence of significant concentrations of the Pt-group metals in terrestrial volcanic rocks, however, and the presence in the K-T boundary layer of shocked quartz, known to form only as the result of hypervelocity impact, makes the volcanism hypothesis, at least as an explanation of the K-T Ir anomaly, highly improbable and greatly strengthens the impact hypothesis. To date, shocked quartz grains have been identified in K-T boundary sediments that also contain Ir anomalies at sites in western North America, Europe, Asia, Haiti, and the Pacific Ocean (for example, Bohor and others, 1984; Izett and Pillmore, 1985; Bohor and Izett, 1986; Izett, 1990).

The recent discovery of tektites at the K-T boundary in marine sedimentary rocks of the Beloc Formation of southern Haiti has further strengthened the impact hypothesis (Izett and others, 1990; Izett, 1991; Sigurdsson and others, 1991). Tektites are unusual glassy melt droplets formed by instantaneous fusion of terrestrial rocks during the hypervelocity impacts of large, extraterrestrial objects (asteroids or comets). The Haitian tektites, which occur at the paleontological K-T boundary, are accompanied by shocked quartz (Hildebrand and Boynton, 1990; Izett and others, 1990; Izett, 1991) and an iridium anomaly (Alvarez and others, 1982). They were the first certain tektites found in K-T boundary sediments and among the oldest tektites found on Earth. Recently, Officer and others

(1992), Lyons and Officer (1992), and Jéhanno and others (1992) claimed that the Haitian tektites are of volcanic, rather than impact, origin, but their arguments are unconvincing and ignore considerable data indicating the glass is different in its physical and chemical properties from any volcanic glass on Earth (Izett and others, 1990; Izett, 1991; Sigurdsson and others, 1991). Moreover, recent oxygen isotope analyses have shown that the Haitian tektites were formed from a mixture of carbonate and silicate rocks and preclude derivation of the glass by volcanic processes (Blum and Chamberlain, 1992)

Since the discovery of the K-T tektites on Haiti, tektites accompanied by an Ir anomaly have also been found in K-T boundary deposits at Arroyo el Mimbral in northeastern Mexico (Smit and others, 1992) and in cores at DSDP sites 536 and 540 in the southeast Gulf of Mexico (Alvarez and others, 1992). The DSDP tektites have not been dated but the Mimbral tektites have an ^{40}Ar/^{39}Ar age (65.06±0.25 Ma) compatible with that for the K-T boundary (Swisher and others, 1992).

It now appears that the site of the impact that produced the tektites found in Haiti and Mexico was the Chicxulub structure on the Yucutan platform (Hildebrand and Boynton, 1990), which has an ^{40}Ar/^{39}Ar age indistinguishable from those measured for the Haitian tektites (Swisher and others, 1992; Sharpton and others, 1992). The Manson structure in Iowa (Hartung and others, 1990) may also be of K-T age (Kunk and others, 1989).

There seems little doubt that one or more asteroids or comets struck the Earth at the end of the Cretaceous Period and caused the deposition of impact materials worldwide in a K-T boundary layer that contains unusually high abundances of Ir and, in some localities, shocked minerals and tektites. Whether or not this impact was responsible for the mass faunal extinctions at the end of the Cretaceous Period is still a subject of lively debate.

The Haitian tektite glasses are non-hydrated and have K$_2$O contents of 0.5 percent to nearly 2.0 percent and thus are datable by ^{40}Ar/^{39}Ar methods. In 1991 we published two brief reports on the ^{40}Ar/^{39}Ar ages of these tektites (Izett and others, 1991a, 1991b), showing that the age of the tektites, and hence the age of the K-T impact that formed them, is 64.5±0.1 Ma. The purpose of this report is to provide complete documentation for these important radiometric ages and to report new data.

DESCRIPTION OF THE TEKTITES

The Beloc Formation of southern Haiti consists of a 1–2-m-thick basal basaltic conglomerate overlain by a 150-m-thick sequence of interbedded fossiliferous pelagic limestone, marl, chalk, and chert (Maurasse, 1982a, 1982b). The K-T boundary occurs about 40–50 m above the base of the formation and is marked by a 0.5-m-thick

volcanogenic turbidite referred to as the "K-T marker bed" (Izett, 1991). This K-T-marker bed consists of air-fall impact ejecta mixed with a small component of locally derived volcanogenic, biogenic, and sedimentary material (Izett, 1991; Maurasse and Sen, 1991). Latest Maestrichtian planktonic foraminifera occur immediately below and earliest Danian foraminifera occur directly above the turbidite (Maurasse, 1982a; Sigurdsson and others, 1991; Maurasse and Sen, 1991). An iridium abundance anomaly occurs in the upper two-thirds of the marker bed and extends into a 2-cm-thick marl bed that immediately overlies the marker bed (Maurasse, 1982a; Alvarez and others 1982; Frank Asaro, oral commun., 1991). Analysis by Izett (1991) of the acid-insoluble residue (0.006 percent by weight) obtained from the turbidite revealed that it contains 45 percent shocked quartz and 2 percent of shocked quartzite and metaquartzite grains along with locally derived volcanogenic silicates.

The tektites, which occur within iron-rich smectite clay spherules that are pseudomorphs of the original tektites, have been described in detail by Izett and others (1990), Sigurdsson and others (1991), and Izett (1991). Altered tektites are abundant (~40 percent) throughout the K-T marker bed but those containing relict glass are concentrated in the lower 2 cm of the bed (fig. 1). The spherules are very well preserved and about 20 percent of them have shapes typical of small tektites, including spheroids, oblate spheroids, ellipsoids, discoids, spindles, teardrops, rods, and dumbells; the rest are irregular in shape. They vary in diameter from a few tenths of a millimeter to as much as 1 cm. Many of the larger spherules are hollow. Similar clay spherules that may be tektite pseudomorphs occur in other K-T boundary rocks in Wyoming, Mexico, Alabama, Mississippi, and DSDP site 603B off the coast of North Carolina (see Izett, 1991, for discussion and references; also Pitakpaivan and Hazel, 1992).

The Haitian clay spherules were tentatively identified as tektites by Maurasse (1982b). The significance of his report, however, was largely unappreciated until Hildebrand and Boynton (1990a) positively identified the spherules as altered tektites on the basis of their shapes. Izett and others (1990) and Izett (1991) provided unequivocal proof that the pellets are pseudomorphs of tektites when they found that about 2 percent of the pellets in the lower 2 cm of the K-T marker bed contain relict, unaltered glass cores whose properties are unique to tektites (fig. 2).

In reflected light, most of the relict tektites appear dark brown to black in color but in transmitted light they range from pale brown to pale yellow brown; a few have a golden honey color. The tektites are devoid of microlites and crystallites, characteristically found in volcanic glass, but some contain spherical and almond-shaped bubbles. The major- and trace-element compositions of the tektites (Izett and others, 1990; Sigurdsson and others, 1991; Izett,

1991; Koeberl and Sigurdsson, 1992) are broadly similar to those of other tektite groups, except that the Haitian tektites have lower Si (50–68 percent), Cr, Ni, Co, B, Mn, and Hf, and higher Fe, Ca, Na, Sc, V, Cu, Zn, Ba, Sr, Sn, and Ba. The honey-colored tektites have unusually high contents of Ca (as much as 30 percent CaO) and very high S (0.1–0.4 percent). The rare earth element contents are within the range of the other tektite groups; their Sr- and Nd-isotopic compositions, however, are distinct (Premo and Izett, 1992). Oxygen isotope analyses have shown that the tektites fall on a mixing line between an isotopically heavy ($\delta^{18}O=14$ per mil) high-calcium sedimentary composition and an isotopically light ($\delta^{18}O=6$ per mil) high-

silica igneous composition, which precludes origin from a volcanic source (Blum and Chamberlain, 1992) and supports their origin from an impact.

ANALYTICAL METHODS

Several hundred tektites, ranging in size from 0.3 to 4.5 mm, were extracted for $^{40}Ar/^{39}Ar$ dating from a slabbed sample of the K-T marker bed. The tektites were scrubbed ultrasonically in dilute HF (~5 percent) to remove adhering clay and then washed in distilled water. Most of the tektites were equant and ranged in diameter from about 0.7 to 1.2 mm and in mass from about 0.3 to 1.2 mg. Sanidine crystals (~150 μm in diameter) from two of the Z-coal bentonites (ZCB) of local usage from the Hell Creek locality in Garfield County, Montana (Baadsgaard and others, 1988), were also analyzed. One sample (JFL–500C) was the same material used by Baadsgaard and his colleagues; the other (83–O–05) was collected from the same locality by one of us (JDO) in 1983. Sample 83–O–05 is from a bentonite (sanidine-bearing only) that occurs approximately 50 cm above the K-T boundary in the Hells Creek area, whereas sample JFL–500C is from a bentonite (sanidine and biotite-bearing) that occurs ~70 cm above the K-T boundary (Carl Swisher, oral commun., 1983). An Ir anomaly and shocked quartz occurs in this section at the K-T boundary (Izett, 1990). Sanidine and other minerals from the ZCB have been dated previously by the K-Ar, $^{40}Ar/^{39}Ar$, Rb-Sr, and U-Pb methods, with results ranging from about 63.5 to 66.0 Ma (Obradovich, 1984; Baadsgaard and others, 1983, 1988). The ZCB sample was included in the sample array in order to provide a direct tie between the Haitian tektites and a well-studied continental K-T section in Montana.

The age of the tektites was determined by $^{40}Ar/^{39}Ar$ dating using two different U.S. Geological Survey laboratories that employ different instrumentation. Single and multiple tektites were analyzed with the GLM continuous laser system in Menlo Park, California, and two samples consisting of about 50–70 tektites each were analyzed using a double-vacuum resistance furnace system in Denver, Colorado. The methods and procedures used by these two laboratories are described separately below.

The samples for this study were irradiated in six separate irradiations (table 1) in the cores of the U.S. Geological Survey TRIGA reactor (GSTR) and the Los Alamos National Laboratory Omega West Reactor (OWR). Irradiation procedures, methods used to correct for interfering Ar isotopes generated by undesirable reactions with Ca and K, and the GSTR flux characteristics are described in detail by Dalrymple and others (1981) and Dalrymple and Duffield (1988).

Irradiation GLN3 contained two quartz vials. One of the quartz vials contained the samples used for the laser

Figure 1. Photograph of polished slab of the "K-T marker bed" (Izett, 1991), Beloc Formation, southern Haiti. The spherical and ovoid pellets are tektites that have been altered to smectitic clay. About 2 percent of the tektites have relic, unaltered glass cores.

system analyses. These consisted of an aluminum-foil packet of 32 tektites and a packet of about 31 mg of sanidine crystals from the ZCB. These two packets were sandwiched between packets of monitor minerals as shown in figure 3. The second vial contained a packet of about 50 tektites (67 mg), which were used for one of the two resistance furnace analyses (90G15L–1), sandwiched between packets of monitor minerals.

Irradiation DD27 contained six quartz vials. In one of these was a single cylindrical aluminum packet (7 mm diameter by 9 mm long) of about 70 tektites (83.4 mg), which were used for the second resistance furnace analysis (90G15L–2). The vial containing the tektites included 6 packets of MMhb-1 (~7 mg each) with the tektite adjacent to and above the fifth packet from the bottom and below but separated from the sixth packet of MMhb–1 by another sample (fig. 3).

In irradiations 105 and 108, the ZCB sanidine, the tektites, and the monitor minerals were contained in a single stack of uniformly spaced, small aluminum cups. One cup in irradiation 105 contained both ZCB sanidine and tek-

tites. In irradiation 108 the tektites were placed in the same cups as the sanidine monitor mineral (fig. 3). Irradiations JDO6 and JDO8 consisted of a single quartz vial each containing aluminum-foil packets; the tektites and the ZCB sanidine were contained in the same packets in these two irradiations.

The errors calculated for individual ages in this paper are estimates of the analytical precision at the 67 percent (1σ) level and include the estimated error in the precision of the irradiation parameter J but do not include possible errors in the values used for the ages of the monitor minerals, discussed below. Plateau ages are the weighted means and weighted errors (1 σ_{best}) of the plateau increments, where weighting is by the inverse of the variance (Taylor, 1982). Weighted means are sometimes preferable to simple means because weighting takes into account the quality of the individual analyses. We generally report ages to a precision of four numerals, but round the grand weighted mean to three numerals, which is the maximum precision justified considering the various uncertainties involved in the age measurements and associated calibrations.

Figure 2. A, Photograph of clay tektite pseudomorph with relic glass core. The pseudomorph is approximately 1.8 mm in diameter. B, A representative selection of unaltered glass tektite cores, like those that were dated. The largest of the cores is about 4.5 mm long.

Table 1. Parameters for the six irradiations that contained Haitian tektites.

Irradiation No.	Reactor[a]	Irradiation time (hr)	Neutron flux (n/cm²)	Cd shielding
GLN3	GSTR	20.0	~2.2x10¹⁸	no
DD27	GSTR	60.0	~6.6x10¹⁸	no
105	OWR	14.3	~5.2x10¹⁸	yes
108	OWR	14.0	~5.1x10¹⁸	yes
JDO6	GSTR	30.0	~3.3x10¹⁸	no
JDO8	GSTR	30.0	~3.3x10¹⁸	no

Irradiation No.	Reactor[a]	Irradiation time (hr)	Neutron flux (n/cm²)	Cd shielding
GLN3	GSTR	20.0	$\sim2.2\times10^{18}$	no
DD27	GSTR	60.0	$\sim6.6\times10^{18}$	no
105	OWR	14.3	$\sim5.2\times10^{18}$	yes
108	OWR	14.0	$\sim5.1\times10^{18}$	yes
JDO6	GSTR	30.0	$\sim3.3\times10^{18}$	no
JDO8	GSTR	30.0	$\sim3.3\times10^{18}$	no

[a] GSTR: Geological Survey TRIGA Reactor, Denver, CO.
OWR: Omega West Reactor, Los Alamos National Laboratory, Los Alamos, NM

CONTINUOUS LASER SYSTEM (MENLO PARK)

The GLM laser system consists of a 5W continuous Ar-ion laser, laser optics, a small-volume, ultra-high vacuum sample chamber and extraction line, an IR microscopic radiometer/thermometer, and a very sensitive, low-background rare gas mass spectrometer equipped with a Baur-Signer source and electron multiplier detector (Dalrymple and Duffield, 1988; Dalrymple, 1989). The laser beam, which is used to heat (or melt) the sample, is focused with a Galilean beam expander and directed with steering mirrors through the sapphire window of the sample chamber onto the irradiated sample (fig. 4). The sample chamber is moved with a motorized X-Y stage to bring each sample under the laser beam for heating and

Figure 3. J-curves for the six irradiations that included Haitian tektites (HT) and ZCB sanidine samples. The monitor minerals are shown by open circles with the calculated standard deviations of precision of five or six measurements. TCR, Taylor Creek Rhyolite; FCT, Fish Canyon Tuff sanidine; MMhb–1, Minnesota hornblende; GSTR, Geological Survey TRIGA Reactor; OWR, Los Alamos National Laboratory Omega West Reactor.

analysis. The gas released during heating or fusion is cleaned with Zr-Al and Zr-V-Fe getters and isotopically analyzed with the mass spectrometer.

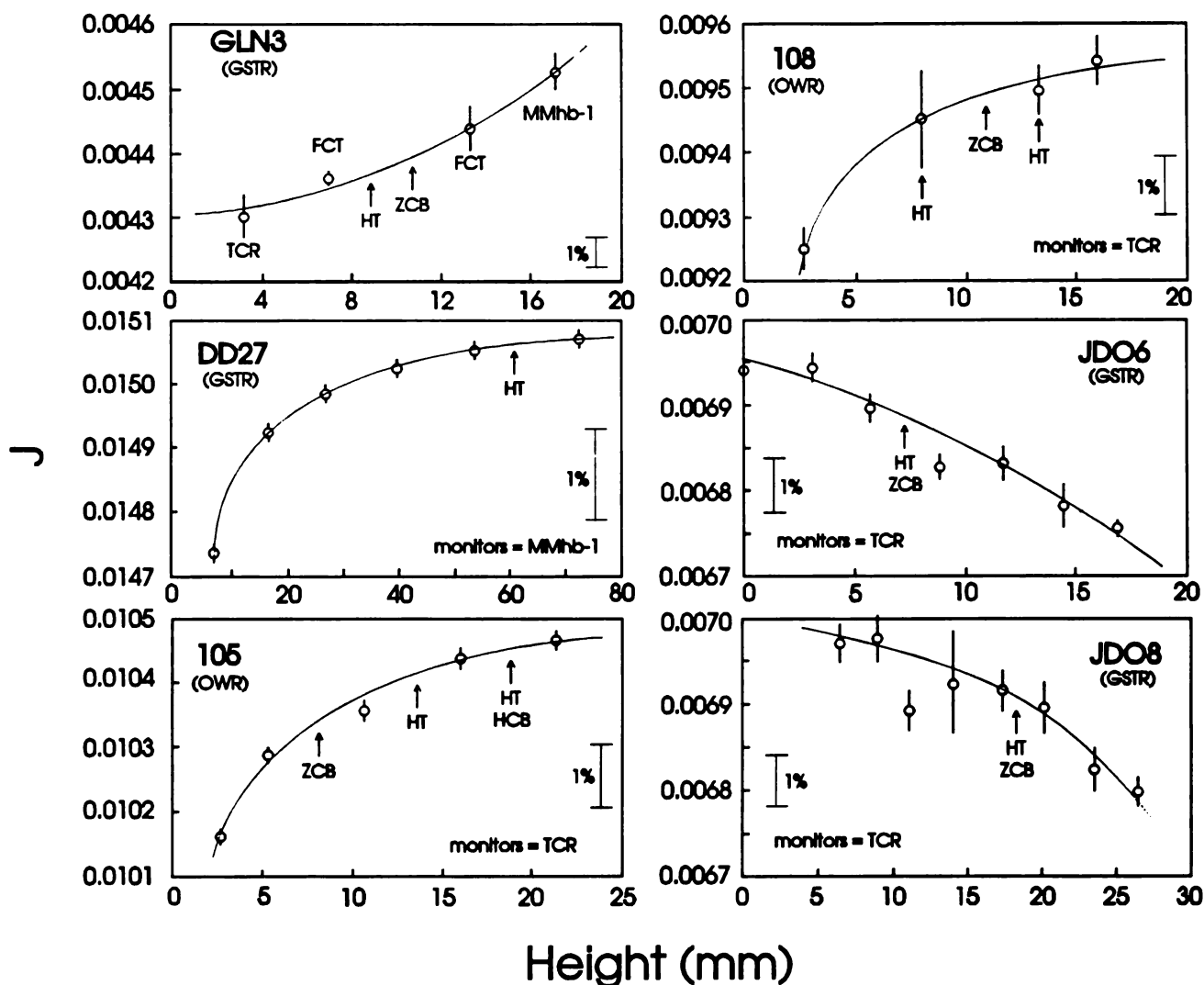The irradiated Haitian tektites were placed in small wells in a Cu planchet; some of the tektites were weighed with an electromicrobalance. The planchet was placed into the sample chamber and the chamber and extraction line were evacuated and baked overnight at 300°C. The pressure in the sample chamber and extraction line after bakeout was $<1 \times 10^{-8}$ torr. Procedures for the sanidine analyses were similar.

Two types of $^{40}Ar/^{39}Ar$ analyses were done—total fusion analysis, which results in a single $^{40}Ar/^{39}Ar$ age for either an individual tektite or a small number of tektites, and incremetal heating analyses, which results in an age spectrum or Ar release diagram for a single tektite. For the incremental heating analyses, individual tektites, ranging in mass from 0.9 to 1.2 mg (0.8–1.2 mm diameter), were progressively heated for 60 seconds per increment with a broadened (defocused) laser beam. Hall (1990) has shown that temperature gradients within small grains heated in this way are negligible. At and below 1200°C the sample temperature was measured with the IR radiometer. It operates in the wavelength band of 1.0 μm to 5.8 μm and measures temperature relative to an internal blackbody cavity over an area of the sample surface 35 μm in diameter. The radiometer was malfunctioning above 1200°C so we controlled the gas release at higher temperatures by increasing incrementally the power setting of the laser. Because the radiometer is used only to help control the fractional gas release, the malfunction had no effect on the resulting ages calculated from the incremental-heating measurements.

For the total fusion analyses, the tektites, sanidine, and hornblende were melted and held for about 60 seconds at the maximum temperature achievable, estimated to be about 1500°C.

Figure 4. Cross section of sample chamber, laser beam, and IR microscope used for $^{40}Ar/^{39}Ar$ dating of the single tektites with the Menlo Park continuous laser system.

INTERNAL RESISTANCE FURNACE SYSTEM (DENVER)

The internal resistance furnace system at Denver consists of a low blank, double-vacuum resistance furnace, an ultra-high vacuum extraction line, and a rare-gas mass spectrometer equipped with a Nier-type source and a Faraday detector. The double-vacuum resistance furnace comprises a tantalum crucible with molybdenum liner surrounded by an outer can cooled with a water jacket. Within the outer can and around the crucible are two tungsten heating elements that are shielded from the outer can by two heat shields. The volume containing the heating elements is evacuated to less than 1×10^{-7} torr. The crucible is on-line with the extraction line. A furnace controller provides power to the heating elements and can drive the furnace to the specified temperature in two minutes. The temperature of the crucible is monitored by a thermocouple whose feedback to the controller ensures that the set temperature during any heating step is maintained to within ±10°C. The gas released during each heating step is cleaned with Zr-Al, Zr-V-Fe, and Ti getters, and with molecular sieve dessicant. The extraction system includes three compartments and gas is transferred between compartments by freezing on charcoal fingers with liquid nitrogen. After cleaning, the Ar is expanded into the mass spectrometer and analyzed.

The packets containing the irradiated Haitian tektites were placed in a glass side-arm located above the crucible. For both analyses, the furnace, sidearm, and extraction line were evacuated and baked for six hours at 260°C.

Both experiments done in the resistance furnace were incremental heating analyses during which each sample was progressively heated for 20 minutes per heating step. After each heating step the furnace was turned off for 10 minutes while the gas released during that step was transferred from the furnace section to the getter section of the extraction line.

MONITOR MINERALS

$^{40}Ar/^{39}Ar$ dating is a relative method and so requires the use of one or more neutron fluence monitor minerals, or standards, whose ages are known. Aliquants of the monitor minerals are irradiated alongside the unknown samples and their Ar ratios measured by the same procedures. The $^{40}Ar/^{39}Ar$ ratios of the monitor minerals are used along with their known age to calculate a conversion efficiency factor, J, which is a measure of the fraction of ^{39}K converted to ^{39}Ar by the fast neutron reaction $^{39}K(n,p)^{39}Ar$. J is then used in the age equation to calculate the age of the unknown samples. The calibration of the monitor minerals, therefore, has a direct effect on the accuracy of the $^{40}Ar/^{39}Ar$ ages calculated for the unknown

samples. New methods and instrumentation developed over the past few years for ^{40}Ar/^{39}Ar dating have resulted in the ability to acquire age data with a precision that exceeds the accuracy of the age of any fluence monitor mineral currently available. In addition, there is not universal agreement on the ages used for the monitor minerals, and different laboratories, including Menlo Park and Denver, sometimes use slightly different values (ages) for the same monitor mineral. Thus we feel that it is important to describe the monitor minerals used in this study and the values adopted for their age in some detail.

Three different fluence-monitor minerals were used in our irradiations: Fish Canyon Tuff sanidine, sanidine from the Taylor Creek Rhyolite, and MMhb–1 hornblende (fig. 3). MMhb-1 hornblende is used worldwide as an interlaboratory ^{40}Ar/^{39}Ar standard (Alexander and others, 1978; Samson and Alexander, 1987). Fish Canyon Tuff sanidine is used by some laboratories as an interlaboratory standard, whereas Taylor Creek Rhyolite sanidine is used by the Menlo Park laboratory as an intralaboratory standard.

In the Menlo Park laboratory, the primary standard mineral is SB–3, a biotite from a rock with an age of 162.9±0.8 Ma (Lanphere and others, 1990). The age of SB–3 is based on 24 K$_2$O measurements by flame photometry and 11 measurements of the radiogenic ^{40}Ar content by isotope dilution using ^{38}Ar tracers that can be tied to absolute air calibrations. The ages for Fish Canyon Tuff (27.55±0.10 Ma; Lanphere and others, 1990) and Taylor Creek Rhyolite (27.92±0.04 Ma; Duffield and Dalrymple, 1990) sanidine crystals were determined at Menlo Park by ^{40}Ar/^{39}Ar methods (multiple measurements) using SB–3 as the neutron fluence monitor mineral. Menlo Park has also obtained a value of 27.55±0.12 Ma for Fish Canyon Tuff biotite by ^{40}Ar/^{39}Ar incremental heating (Lanphere and others, 1990). The Menlo Park group has measured a conventional K-Ar age of 513.9±2.3 Ma for MMhb-1 hornblende based on 16 K$_2$O measurements by flame photometry and 5 measurements of the radiogenic ^{40}Ar content by isotope dilution using the ^{38}Ar tracers described above. The Menlo Park group has also measured the age of MMhb–1 by ^{40}Ar/^{39}Ar techniques using SB–3 as the monitor mineral and the mean of the 19 ages is 514.7± 2.5Ma, which is not significantly different from the value of 513.9 Ma measured by K-Ar techniques. Thus, the ages used for SB–3, MMhb–1, Taylor Creek Rhyolite sanidine, and Fish Canyon Tuff sanidine in the Menlo Park laboratory constitute an internally consistent set of values.

The published "international" mean for MMhb–1 is 520.4±1.7 Ma (Samson and Alexander, 1987). This age is based on data from 18 laboratories, including the USGS laboratories at Menlo Park and Denver. The K and Ar values for MMhb–1 are not, however, known with either the precision or accuracy needed for a good ^{40}Ar/^{39}Ar standard. The range of the mean values obtained by the various laboratories is 3.3 percent for K and 6.5 percent for radiogenic ^{40}Ar. In addition, the Menlo Park data included in the international mean age for MMhb–1 contain some incorrect data.

Because the published "best" age for MMhb–1 is based in part on some incorrect values and because of the wide range in the values used to calculate this age, the workers in the Menlo Park laboratory have elected to use the value of 513.9 Ma for MMhb–1. This is done to preserve the self-consistent set of monitor mineral ages within the Menlo Park laboratory rather than to artificially adjust the measured values of all of the other Menlo Park monitor minerals, whose ages were determined independently of MMhb–1, simply in order to bring them into conformity with the published mean age of MMhb–1. Foland and others (1986) have also found a ^{40}Ar/^{39}Ar age of 513.5 Ma for MMhb–1 based on comparison with their intralaboratory standard biotite.

The age of MMhb–1 was also measured in the Denver laboratory with a result of 515.3 Ma on the basis of two K$_2$O and two Ar measurements (Samson and Alexander, 1987). Denver personnel have not measured the age of Taylor Creek Rhyolite sanidine but obtained a conventional K-Ar age of 28.5±0.8 Ma for Fish Canyon Tuff sanidine (Steven and others, 1967). The Denver laboratory normally uses the published mean value of 520.4 Ma for MMhb–1 and adjusts the ages of Fish Canyon Tuff and Taylor Creek Rhyolite upward from the Menlo Park values to account for the difference between 513.9 Ma and 520.4 Ma for MMhb–1.

For the purposes of this paper, we have calculated all ages measured in both Menlo Park and Denver using the monitor mineral values measured by the Menlo Park laboratory. Conversion of a ^{40}Ar/^{39}Ar age for an unknown sample from one monitor value to another can be done using

$$t_2 = \frac{1}{\lambda} \log_e \left[\frac{e^{\lambda t_{m2}} - 1}{e^{\lambda t_{m1}} - 1} (e^{\lambda t_1} - 1) + 1 \right]$$

where t_1=original age, t_2=converted age, t_{m1}=monitor age used for t_1, t_{m2}=monitor age used for t_2, and λ (decay constant)=5.543x10^{-10} yr^{-1}.

Although the conversion is not linear, the middle Tertiary to K-T boundary ages in this paper may be converted, without significant error, from a MMhb–1 value of 513.9 Ma to one of 520.4 Ma by multiplying the ages by 1.0144.

RESULTS

LASER TOTAL FUSION ANALYSES

The results of 53 laser total fusion analyses of single tektites, ranging (of those weighed) in mass from 0.28 to

0.92 mg, and of small groups (2–3) of tektites are given in table 2 and figure 5. The analyses all have high yields of radiogenic ^{40}Ar, typically above 98 percent, and estimated standard deviations of precision of 0.6–0.7 percent, which includes the estimated error in J. The K/Ca ratios of the measured tektites, as calculated from the ^{39}Ar/^{37}Ar ratios, range from 0.14 to 0.36, and thus the dated tektites represent a range of compositions (fig. 6). We did not, however, analyze any of the high Ca (honey-colored) tektites, which have K/Ca ratios as low as 0.02 (Sigurdsson and others, 1991; Izett, 1991).

The total range of the calculated ^{40}Ar/^{39}Ar ages is from 63.34±0.40 Ma to 66.30±1.33 Ma, or 4.7 percent. Excluding the greatest age, which appears anomalous (fig. 5), the remaining 52 ^{40}Ar/^{39}Ar ages have a mean and standard deviation of 64.42±0.41 Ma and a weighted mean and standard error of the mean (σ_{best}) of 64.42±0.06 Ma. The rather large range of ages is not entirely due to analytical error. Much of it is due to biases in the irradiation parameter, J, caused at least in part by using two different reactors and five different irradiations. The tektite ages from irradiation JDO6, for example, are biased toward younger values relative to the ages from the other irradiations (fig.

5). Ages from irradiation 108 have a wider range of values than those from the other irradiations, which is probably due, at least partly, to imprecision in determining the J-values for that irradiation (fig. 3). The tektites analyzed in irradiations 105, 108, JDO6, and JDO8 were small fragments with high surface/volume ratios, the best material having been used for irradiation GLN3. Some of the dispersion in the ages may also be due to slight alteration of

Figure 5. Histogram of ^{40}Ar/^{39}Ar laser system total fusion ages on 53 single Haitian tektites and on 28 samples of the Z-coal bentonite (ZCB) sanidine. The arithmetic means and standard deviations of the two data populations are shown by the filled circles with bars. The two ages >66 Ma are not included in the means.

Figure 6. K/Ca ratios for the 53 laser system total fusion measurements on individual tektites, as calculated from the ^{39}Ar/^{37}Ar ratios.

Table 2. $^{40}Ar/^{39}Ar$ laser total fusion age data on single Haiti tektites and Z-coal bentonite sanidine.

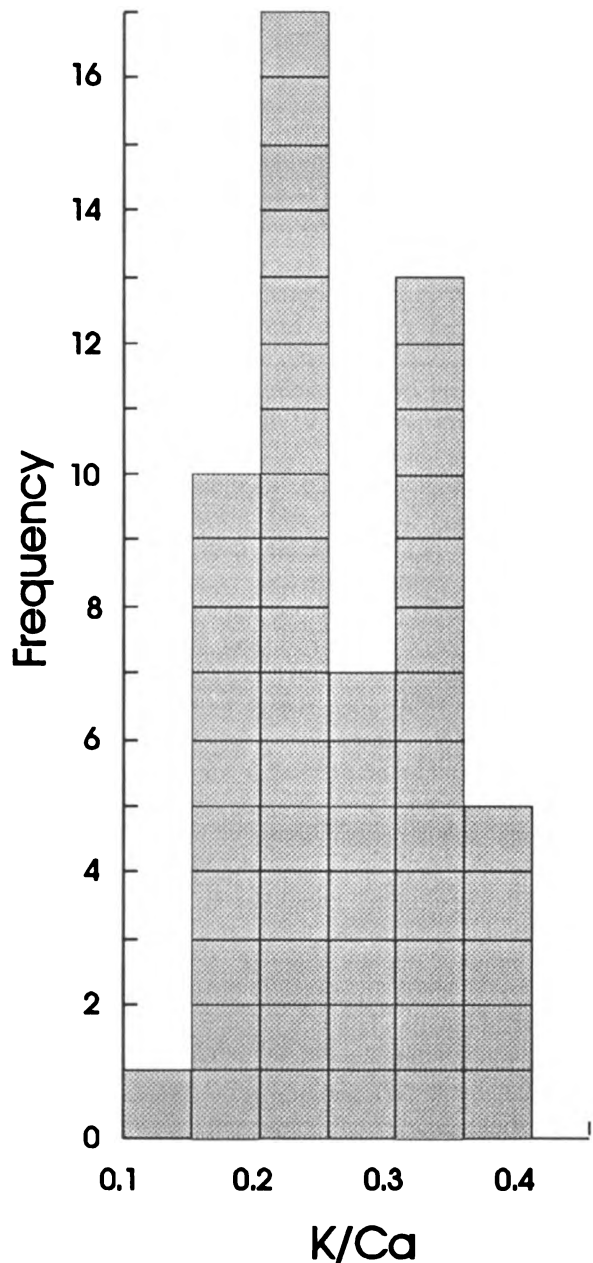| Sample No.	Weight[a] (mg)	$^{40}Ar/^{39}Ar$[b]	$^{37}Ar/^{39}Ar$[b]	$^{36}Ar/^{39}Ar$[b]	$^{40}Ar_{rad}$[c] (%)	$^{39}Ar_{Ca}$[c] (%)	$^{36}Ar_{Ca}$[c] (%)	Age[d] (Ma)
				Haiti tektites				
(Irradiation GLN3, J=0.004376)								
90G15K-5	n.d.	8.544	3.4411	0.001722	97.1	0.2	53.8	64.50 ± 0.43
90G15K-6	n.d.(2)	8.990	2.8409	0.003196	91.9	0.2	23.9	64.19 ± 0.39
90G15K-7	n.d.	8.728	3.3032	0.002443	94.6	0.2	36.4	64.19 ± 0.47
90G15K-8	0.316	8.369	1.3805	0.000618	99.0	0.1	60.1	64.32 ± 0.39
90G15K-9	0.376	8.334	1.4455	0.000597	99.2	0.1	65.2	64.14 ± 0.38
90G15K-10	0.49	8.325	1.4264	0.000379	99.9	0.1	100.0	64.55 ± 0.41
90G15K-11	0.279	8.377	1.6067	0.000697	99.0	0.1	62.0	64.35 ± 0.41
90G15K-12	0.33	8.467	2.0101	0.000980	98.4	0.1	55.2	64.66 ± 0.39
90G15K-13	0.548	8.374	1.4377	0.000686	98.8	0.1	56.4	64.24 ± 0.38
90G15K-14	0.452	8.346	2.7090	0.000752	99.8	0.2	96.9	64.70 ± 0.39
90G15K-15	0.514	8.370	2.9835	0.000885	99.6	0.2	90.7	64.77 ± 0.39
90G15K-16	0.772	8.409	1.5404	0.000643	99.1	0.1	64.5	64.67 ± 0.38
90G15K-17	0.537	8.373	1.5350	0.000695	98.9	0.1	59.4	64.28 ± 0.38
90G15K-18	0.39	8.369	1.6373	0.000769	98.7	0.1	57.3	64.15 ± 0.38
90G15K-19	0.548	8.383	1.6028	0.000565	99.4	0.1	76.3	64.69 ± 0.38
90G15K-20	0.759	8.694	2.7776	0.001927	95.9	0.2	38.8	64.75 ± 0.38
90G15K-21	0.602	8.344	1.5262	0.000428	99.8	0.1	96.0	64.65 ± 0.38
90G15K-22	0.496	8.363	1.4912	0.000607	99.2	0.1	66.1	64.37 ± 0.38
90G15K-23	0.436	8.355	2.0282	0.000617	99.6	0.1	88.4	64.63 ± 0.38
90G15K-24	0.631	8.360	1.5753	0.000432	99.9	0.1	98.1	64.80 ± 0.38
90G15K-25	0.923	8.371	1.5931	0.000640	99.1	0.1	66.9	64.42 ± 0.38
90G15K-26	0.748	8.375	1.4649	0.000541	99.4	0.1	72.8	64.59 ± 0.37
90G15K-27	0.411	8.342	1.3645	0.000558	99.2	0.1	65.8	64.24 ± 0.38
				weighted mean ± σ_{best} =			64.48 ± 0.08	
				mean ± σ =				64.47 ± 0.22
(Irradiation 105, J=0.010398)								
90G15K-28	0.410	3.573	2.001	0.000830	97.6	0.1	66.3	64.35 ± 0.44
90G15K-29	0.117	3.610	1.875	0.000722	98.2	0.1	71.4	65.42 ± 0.62
90G15K-30	0.212	3.576	2.302	0.001114	96.0	0.2	56.8	63.34 ± 0.40
90G15K-31	0.241	3.539	1.522	0.000551	98.8	0.1	76.0	64.50 ± 0.56
90G15K-32	0.371	3.594	2.057	0.000900	97.2	0.1	62.9	64.45 ± 0.38
				weighted mean ± σ_{best} =			64.25 ± 0.20	
				mean ± σ =				64.41 ± 0.74
(Irradiation 105, J=0.010452)								
90G15K-33	0.173	3.529	1.857	0.000598	99.2	0.1	85.4	64.91 ± 0.42
90G15K-34	0.280	3.519	1.378	0.000548	98.5	0.1	69.2	64.26 ± 0.38
90G15K-35	0.390	3.589	2.381	0.001010	97.0	0.2	64.8	64.59 ± 0.42
90G15K-36	0.292	3.530	2.011	0.000761	98.2	0.1	72.6	64.29 ± 0.43
90G15K-37	0.221	3.669	2.592	0.001374	94.6	0.2	51.9	64.40 ± 0.56
				weighted mean ± σ_{best} =			64.49 ± 0.19	
				mean ± σ =				64.49 ± 0.27

individual tektites, but the dated tektites optically appear unaltered and we have no way to quantitatively evaluate the magnitude of this effect, if any. None of these factors affect the mean tektite age appreciably, but they do affect the dispersion and hence the precision of the mean age.

Our analyses show no significant difference in age between the ZCB sanidines from JFL–500C and 83–O–05, and we treat them as a single data set even though the two bentonites are separated stratigraphically by 20 cm. The 28 measurements from the two ZCB sanidine samples (table 2; fig. 5) have a mean and standard deviation of 64.75±0.33 Ma and a weighted mean and standard error (σ_{best}) of 64.77±0.07 Ma (value of 66.52 Ma excluded), which is not significantly different from the mean of the tektite total fusion ages at the 95 percent level of confidence. As with the tektites, there are apparent biases between irradiations—irradiation 108, for example, is biased toward higher ages relative to irradiations GLN3 and

Table 2. Continued.

Sample No.	Weight[a] (mg)	$^{40}Ar/^{39}Ar$[b]	$^{37}Ar/^{39}Ar$[b]	$^{36}Ar/^{39}Ar$[b]	$^{40}Ar_{rad}$[c] (%)	$^{39}Ar_{Ca}$[c] (%)	$^{36}Ar_{Ca}$[c] (%)	Age[d] (Ma)
				Haiti tektites				
(Irradiation 108, J=0.009452)								
90G15K-38	n.d.	4.055	2.321	0.001196	95.9	0.2	53.4	65.20 ± 0.37
90G15K-39	n.d.	3.905	1.433	0.000532	98.9	0.1	74.1	64.74 ± 0.62
90G15K-40	n.d.	3.917	2.240	0.000713	99.2	0.2	86.4	65.17 ± 0.93
90G15K-41	n.d.	4.104	2.579	0.001615	93.4	0.2	43.9	64.33 ± 0.66
90G15K-42	n.d.	3.976	2.393	0.000725	99.4	0.2	90.7	(66.30 ± 1.33)
				weighted mean ± σ_{best} =			64.96 ± 0.27	
				mean ± σ =				64.86 ± 0.41
(Irradiation 108, J=0.009495)								
90G15K-43	n.d.	3.858	1.990	0.000775	98.2	0.1	70.6	63.84 ± 0.82
90G15K-44	n.d.	3.891	1.924	0.000749	98.3	0.1	70.6	64.42 ± 0.35
90G15K-45	n.d.	3.868	3.068	0.000964	99.1	0.2	87.5	64.57 ± 1.01
90G15K-46	n.d.	3.932	2.179	0.000755	98.8	0.1	79.4	65.41 ± 0.42
90G15K-47	n.d.	3.920	2.867	0.001170	97.1	0.2	67.4	64.15 ± 0.79
				weighted mean ± σ_{best} =			64.67 ± 0.24	
				mean ± σ =				64.48 ± 0.59
(Irradiation JDO6, J=0.006862)								
90G15R-1	1.017	5.369	1.667	0.000725	98.1	0.1	53.6	64.13 ± 0.40
90G15R-2	1.089 (2)	5.348	2.000	0.000930	97.4	0.1	50.1	63.44 ± 0.45
90G15R-3	1.343 (2)	5.393	2.157	0.000914	97.7	0.1	55.0	64.17 ± 0.38
90G15R-4	1.066	5.386	1.814	0.000923	97.2	0.1	54.2	63.76 ± 0.40
90G15R-5	1.468 (2)	5.400	2.052	0.000905	97.6	0.1	52.8	64.20 ± 0.38
90G15R-6	1.187 (2)	5.429	1.832	0.001007	96.8	0.1	42.4	63.99 ± 0.40
				weighted mean ± σ_{best} =			63.97 ± 0.16	
				mean ± σ =				63.95 ± 0.30
(Irradiation JDO8, J=0.006910)								
90G15R-7	0.352 (2)	5.893	2.660	0.002708	89.9	0.2	26.4	64.94 ± 0.48
90G15R-8	0,277 (3)	5.442	2.303	0.001297	96.2	0.2	47.8	64.17 ± 0.46
90G15R-9	0.388 (2)	5.545	1.691	0.001525	94.1	0.1	29.8	64.00 ± 0.45
90G15R-10	0.379 (3)	5.401	2.145	0.001137	96.8	0.1	50.7	64.09 ± 0.46
				weighted mean ± σ_{best} =			64.28 ± 0.23	
				mean ± σ =				64.30 ± 0.43
				Z-coal bentonite sanidine				
(Irradiation GLN3, J=0.004404)								
JFL-500C	n.d. (m)	8.365	0.0060	0.000345	98.7	0.0	0.5	64.42 ± 0.42
JFL-500C	n.d. (m)	8.318	0.0062	0.000138	99.4	0.0	1.2	64.52 ± 0.38
JFL-500C	n.d. (m)	8.337	0.0065	0.000110	99.5	0.0	1.6	64.73 ± 0.38
				weighted mean ± σ_{best} =			64.57 ± 0.23	
				mean ± σ =				64.56 ± 0.16
(Irradiation 105, J=0.010322)								
JFL-500C	n.d.(m)	3.585	0.0066	0.000192	98.4	0.0	0.9	64.50 ± 0.44
JFL-500C	n.d.(m)	3.574	0.0068	0.000095	99.2	0.0	2.0	64.82 ± 0.38
JFL-500C	n.d.(m)	3.586	0.0081	0.000142	98.8	0.0	1.6	64.79 ± 0.38
JFL-500C	n.d.(m)	3.570	0.0063	0.000105	99.1	0.0	1.7	64.69 ± 0.46
JFL-500C	n.d.(m)	3.591	0.0083	0.000195	98.4	0.0	1.2	64.60 ± 0.43
JFL-500C	n.d.(m)	3.586	0.0064	0.000050	99.5	0.0	3.5	65.27 ± 0.39
				weighted mean ± σ_{best} =			64.80 ± 0.17	
				mean ± σ =				64.79 ± 0.27

Table 2. Continued.

Sample No.	Weight[a] (mg)	$^{40}Ar/^{39}Ar$[b]	$^{37}Ar/^{39}Ar$[b]	$^{36}Ar/^{39}Ar$[b]	$^{40}Ar_{rad}$[c] (%)	$^{39}Ar_{Ca}$[c] (%)	$^{36}Ar_{Ca}$[c] (%)	Age[d] (Ma)
				Z-coal bentonite sanidine				
(Irradiation 105, J=0.010452)								
JFL-500C	n.d.(m)	3.526	0.0069	0.000070	99.4	0.0	2.7	64.86 ± 0.37
JFL-500C	n.d.(m)	3.525	0.0061	0.000058	99.5	0.0	2.9	64.91 ± 0.37
JFL-500C	n.d.(m)	3.525	0.0064	0.000073	99.3	0.0	2.4	64.84 ± 0.37
JFL-500C	n.d.(m)	3.523	0.0063	0.000023	99.8	0.0	7.7	65.07 ± 0.38
JFL-500C	n.d.(m)	3.533	0.0077	0.000099	99.1	0.0	2.1	64.83 ± 0.37
				weighted mean ± σ_{best} =				64.90 ± 0.17
				mean ± σ =				64.90 ± 0.10
(Irradiation 108, J=0.009474)								
JFL-500C	n.d.(m)	3.899	0.0064	0.000093	99.2	0.0	1.9	64.95 ± 0.42
JFL-500C	n.d.(m)	3.926	0.0073	0.000054	99.5	0.0	3.7	65.59 ± 0.37
JFL-500C	n.d.(m)	3.980	0.0076	0.000290	97.8	0.0	0.7	65.32 ± 0.35
JFL-500C	n.d.(m)	4.026	0.00066	0.000451	96.6	0.0	0.4	65.31 ± 0.48
JFL-500C	n.d.(m)	3.908	0.00740	0.000149	98.8	0.0	1.4	64.82 ± 0.36
				weighted mean ± σ_{best} =				65.20 ± 0.17
				mean ± σ =				65.20 ± 0.31
(Irradiation JDO6, J=0.006862)								
83-O-05	0.192(12)	5.350	0.00588	0.0001704	99.0	0.0	0.8	64.43 ± 0.37
83-O-05	0.147(9)	5.341	0.02839	0.0001024	99.4	0.0	6.5	64.57 ± 0.38
83-O-05	0.177(8)	5.349	0.02687	0.0001423	99.2	0.0	4.4	64.53 ± 0.40
83-O-05	0.113(8)	5.524	0.02752	0.0001688	99.1	0.0	3.8	(66.52 ± 0.42)
83-O-05	0.145(9)	5.344	0.00546	0.0001330	99.2	0.0	1.0	64.48 ± 0.38
				weighted mean ± σ_{best} =				64.50 ± 0.19
				mean ± σ =				64.50 ± 0.06
(Irradiation JDO8, J=0.006910)								
83-O-05	0.188(10)	5.401	0.01809	0.000296	98.2	0.0	1.6	64.96 ± 0.38
83-O-05	0.074(5)	5.358	0.00532	0.000366	97.8	0.0	0.4	64.18 ± 0.42
83-O-05	0.062(5)	5.421	0.00523	0.000542	96.9	0.0	0.3	64.31 ± 0.46
83-O-05	0.083(6)	5.514	0.00547	0.000816	95.5	0.0	0.2	64.46 ± 0.44
83-O-05	0.076(6)	5.355	0.03895	0.000306	98.2	0.0	3.4	64.39 ± 0.43
				weighted mean ± σ_{best} =				64.49 ± 0.19
				mean ± σ =				64.46 ± 0.30
Haiti tektites, all data				weighted mean ± σ_{best} =				**64.42 ± 0.06 Ma**
(n=52)				mean ± σ =				**64.42 ± 0.41 Ma**
				std. error of mean =				**0.07 Ma**
Z-coal bentonite sanidine, all data				weighted mean ± σ_{best} =				**64.77 ± 0.07 Ma**
(n=28)				mean ± σ =				**64.75 ± 0.33 Ma**
				std. error of mean =				**0.06 Ma**

[a] Number of tektites or crystals in parentheses where n>1; n.d., not determined;. m, multiple crystals, number not determined

[b] Corrected for ^{37}Ar decay (half-life=35.1 days) and ^{39}Ar decay (half-life = 269 years).

[c] Subscripts: rad, radiogenic; K, potassium-derived; Ca, calcium derived.

[d] Decay constants: λ_ϵ=0.581x10^{-10}yr^{-1}, λ_β=4.692x10^{-10}yr^{-1}. Errors assigned to individual ages are estimates of the standard deviation of analytical precision. Weighted means and σ_{best} are weighted by the inverse of the variance (Taylor, 1982). Value in () not included in means. Reactor corrections for irradiation GLN-3: $(^{36}Ar/^{37}Ar)_{Ca}$=0.000251 ± 8, $(^{39}Ar/^{37}Ar)_{Ca}$ = 0.000671 ± 13, $(^{40}Ar/^{39}Ar)_K$ = 0.0285 ± 47. Reactor corrections for irradiations 105 and 108: $(^{36}Ar/^{37}Ar)_{Ca}$=0.000275 ± 3, $(^{39}Ar/^{37}Ar)_{Ca}$ = 0.000675 ± 3, $(^{40}Ar/^{39}Ar)_K$ = 0.00240 ± 2. Reactor corrections for irradiations JDO-6 and JDO-8: $(^{36}Ar/^{37}Ar)_{Ca}$=0.000269 ± 2, $(^{39}Ar/^{37}Ar)_{Ca}$ = 0.000670 ± 5, $(^{40}Ar/^{39}Ar)_K$ = 0.0091 ± 54.

Table 3. Means and standard deviations of $^{40}Ar/^{39}Ar$ laser total-fusion ages on Z-coal bentonite sanidine and single Haitian tektites (HT), in Ma.

[Where |HT-ZCB|>CV, the means are significantly different at the 95% level of confidence.]

Irradiation	HT	N	ZCB	N	|HT-ZCB|	CV
GLN3	64.47 ± 0.22	23	64.56 ± 0.16	3	0.09	0.20
105	64.45 ± 0.52	10	64.83 ± 0.21	11	0.38	0.34 ·
108	64.65 ± 0.53	9	65.20 ± 0.31	5	0.55	0.44
JDO6	63.95 ± 0.30	6	64.50 ± 0.06	4	0.55	0.25
JDO8	64.30 ± 0.43	4	64.46 ± 0.30	5	0.16	0.49
All data	64.42 ± 0.41	52	64.75 ± 0.33	28	0.33	0.17

CV, critical value.

JDO8—but these biases probably do not have an appreciable effect on the mean age calculated from all 28 measurements.

Taken at face value, the statistics indicate that the mean age of the tektites and the mean age of the ZCB sanidine is significantly different at the 95 percent level of confidence (table 3). As discussed above, however, the two sets of data do not represent homogeneous populations. Comparing the means of the tektites and the ZCB sanidine obtained from the individual irradiations makes the apparent age differences less clear. The means from irradiations GLN3 and JDO8 are not significantly different at the 95 percent level of confidence, whereas those from irradiations 105, 108, and JDO6 are (table 3). Thus, although there is a tendency in our data for higher ages from the ZCB sanidine, we think that it is primarily due to imprecision in determining the neutron-efficiency factor, J, for the different irradiations and different sample positions and do not think that it is geologically significant.

LASER INCREMENTAL HEATING ANALYSES

Incremental heating analyses were done with the laser system on four single tektites weighing from 0.87 to 1.24 mg (table 4). All four of the age spectra have plateaus over 96 percent or more of the ^{39}Ar released and show no evidence that the tektite glass has been subjected to post-solidification alteration or thermal disturbance (fig. 7). The K/Ca ratios of the various gas fractions, as calcuated from the $^{39}Ar/^{37}Ar$ values, are uniform over the full range of ^{39}Ar released (fig. 8), indicating that the tektite glass is an unaltered, homogeneous phase. The plateau ages range from 64.35±0.35 Ma to 64.45±0.35 Ma and have a weighted mean of 64.38±0.18 Ma, which is not different from the weighted mean of the total fusion ages

(64.42±0.07 Ma) at the 95 percent level of confidence. The isochron ages calculated from the incremental heating data are concordant with the age spectrum plateau ages, have $^{40}Ar/^{36}Ar$ intercepts indistinguishable from the atmospheric value, and have good statistical fits (table 6; · fig. 9).

Because the infrared microscope is equipped for optical viewing, it was possible to observe the behavior of the tektite glass during incremental heating. Physical changes in the tektites as temperature increased are of interest and provide information about the tektite glass as a $^{40}Ar/^{39}Ar$ geochronometer. From room temperature to about 900°C, no visible change occurred in the general shape (equant) and color (opaque and black) of the tektites. Moreover, <1 percent of the ^{39}Ar was liberated during the low temperature heating steps. At 900°C, slight changes in the surface reflectivity of the tektites occurred. At about 1,000°C, the surfaces of the tektites changed from rough to smooth and angular ridges separating sculptured areas disappeared, but the original shape and color of the tektites were unchanged. Near 1,200°C, their surfaces were completely smooth and their overall shapes were oviform or spherical. Heating above 1,200°C converted the tektites to perfect spheres although only a cumulative 10–15 percent of their total ^{39}Ar content had been expelled by that and the lower temperature increments. From 1,200 to 1,500°C, the shape and color of the tektites did not change. At the maximum temperature (~1,500°C) the glass abruptly became clear and small patches of a black crust appeared on the surfaces of the glass spheres. Unlike diffusion of Ar from most minerals, the diffusion of Ar from the tektite glass was surprisingly slow even at very high (>1,200°C) temperatures, despite the fact that the glass was soft enough to be reshaped into perfect spheres by surface tension. This indicates that unaltered tektite glass remains a closed system to Ar even at low and moderate temperatures and is, therefore, an excellent $^{40}Ar/^{39}Ar$ geochronometer.

Table 4. Analytical data for ^{40}Ar/^{39}Ar laser age spectra on single K-T tektites from Haiti.

Temp.[a] (°C)	^{40}Ar/^{39}Ar	^{37}Ar/^{39}Ar[b]	^{36}Ar/^{39}Ar	^{40}Ar$_{rad}$[c] (%)	^{39}Ar$_{Ca}$[c] (%)	^{36}Ar$_{Ca}$[c] (%)	^{39}Ar (% of total)	Age[d] (Ma)
90G15K-1, 0.870 mg (Irradiation GLN-3, J=0.004376)								
600	107.7	4.361	0.3101	15.2	0.3	0.4	0.03	125. ± 175
650	19.09	2.179	0.0442	32.5	0.1	1.3	0.03	48.4 ± 201
700	15.46	1.855	0.0230	57.0	0.1	2.2	0.05	68.4 ± 103
750	10.24	2.037	0.01094	69.9	0.1	5.0	0.1	55.7 ± 25
800	8.109	1.964	0.00718	75.6	0.1	7.4	0.2	47.8 ± 16
850	8.360	2.227	0.01380	53.2	0.1	4.4	0.3	34.8 ± 18
900	8.179	2.268	0.00921	68.8	0.2	6.6	0.4	44.0 ± 14
950	8.431	2.243	0.00518	83.8	0.2	11.6	0.7	55.0 ± 7.9
1000	8.281	2.217	0.001074	98.1	0.1	55.5	1.1	63.16 ± 4.8
1050	8.335	2.259	0.000843	99.1	0.2	72.1	1.5	64.13 ± 1.91
1100	8.306	2.294	0.000789	99.3	0.2	78.2	1.6	64.05 ± 1.79
1140	8.225	2.338	0.000895	98.9	0.2	70.3	1.4	63.21 ± 2.03
1200	8.230	2.366	0.000766	99.4	0.2	83.1	1.6	63.57 ± 1.74
120X	8.364	2.327	0.000765	99.4	0.2	81.9	2.9	64.57 ± 1.91
121X	8.243	2.358	0.000979	98.7	0.2	64.8	2.5	63.18 ± 1.12
122X	8.265	2.361	0.000854	99.1	0.2	74.3	4.3	63.63 ± 1.94
123X	8.299	2.342	0.000792	99.3	0.2	79.5	4.6	64.02 ± 1.80
124X	8.300	2.381	0.000753	99.5	0.2	85.0	6.5	64.14 ± 0.46
125X	8.329	2.388	0.000705	99.7	0.2	91.1	12.2	64.48 ± 0.56
126X	8.352	2.381	0.000671	99.8	0.2	95.4	18.3	64.72 ± 0.36
127X	8.354	2.373	0.000869	99.1	0.2	73.4	17.4	64.29 ± 0.37
128X	8.353	2.415	0.000827	99.3	0.2	78.5	15.3	64.40 ± 0.41
129X	8.356	2.381	0.000766	99.4	0.2	83.6	4.8	64.53 ± 3.3
130X	8.365	2.396	0.00410	87.7	0.2	15.7	1.7	57.08 ± 3.2
131X	8.639	2.291	0.00417	87.4	0.2	13.8	0.5	58.8 ± 11
90G15K-2, 1.117 mg (Irradiation GLN-3, J=0.004376)								
800	10.55	2.282	0.00474	88.4	0.2	13.0	0.2	72.2 ± 11
900	8.429	2.381	0.00209	94.8	0.2	30.6	0.5	62.1 ± 4.7
1000	8.422	2.550	0.000864	99.3	0.2	79.4	1.2	64.93 ± 1.96
1090	8.372	2.551	0.000950	99.0	0.2	72.2	2.1	64.36 ± 2.15
1200	8.334	2.567	0.000701	99.9	0.2	98.6	4.3	64.64 ± 1.59
121X	8.306	2.561	0.000889	99.2	0.2	77.4	3.4	63.99 ± 1.02
122X	8.365	2.596	0.001100	98.5	0.2	63.5	5.5	63.99 ± 2.49
123X	8.320	2.562	0.000727	99.8	0.2	94.8	9.7	64.47 ± 0.51
124X	8.339	2.522	0.000850	99.3	0.2	79.9	16.6	64.31 ± 0.33
125X	8.339	2.511	0.000807	99.4	0.2	83.7	20.0	64.40 ± 0.29
126X	8.327	2.492	0.000708	99.8	0.2	94.7	15.7	64.52 ± 0.37
127X	8.362	2.475	0.000867	99.2	0.2	76.8	10.1	64.42 ± 0.48
128X	8.394	2.457	0.000776	99.5	0.2	85.2	9.1	64.85 ± 0.48
129X	8.447	2.512	0.00341	90.3	0.2	19.8	1.5	59.36 ± 2.17
130X	9.281	2.708	0.0302	0.1	0.2	0.2	0.1	4.4 ± 33
90G15K-3, 1.240 mg (Irradiation GLN-3, J=0.004376)								
900	8.586	1.524	0.000606	99.2	0.1	67.6	1.2	66.10 ± 1.38
1000	8.283	1.574	0.000478	99.7	0.1	88.7	1.6	64.11 ± 1.09
1100	8.283	1.579	0.000510	99.6	0.1	83.3	2.9	64.03 ± 1.16
1200	8.328	1.577	0.000858	98.4	0.1	49.4	4.7	63.59 ± 0.73
121X	8.304	1.570	0.000512	99.6	0.1	82.5	5.0	64.19 ± 0.69
122X	8.324	1.557	0.000456	99.8	0.1	91.9	8.1	64.46 ± 0.45
123X	8.326	1.541	0.000444	99.8	0.1	93.5	10.0	64.49 ± 0.38
124X	8.335	1.513	0.000499	99.6	0.1	81.6	11.3	64.41 ± 0.35
125X	8.324	1.504	0.000503	99.5	0.1	80.4	10.8	64.31 ± 0.36

Table 4. Continued.

Temp.[a] (°C)	$^{40}Ar/^{39}Ar$	$^{37}Ar/^{39}Ar$[b]	$^{36}Ar/^{39}Ar$	$^{40}Ar_{rad}$[c] (%)	$^{39}Ar_{Ca}$[c] (%)	$^{36}Ar_{Ca}$[c] (%)	^{39}Ar (% of total)	Age[d] (Ma)
126X	8.335	1.499	0.000651	99.0	0.1	61.9	9.7	64.06 ± 0.39
127X	8.359	1.478	0.000406	99.9	0.1	98.0	9.1	64.79 ± 0.41
128X	8.327	1.481	0.000480	99.6	0.1	82.9	7.7	64.38 ± 1.10
129X	8.357	1.467	0.000489	99.6	0.1	80.7	7.6	64.58 ± 0.48
130X	8.370	1.467	0.000745	98.7	0.1	53.0	8.9	64.10 ± 0.42
131X	8.718	1.489	0.00386	88.2	0.1	10.4	1.3	59.75 ± 2.68
90G15K-4, 1.082 mg (Irradiation GLN-3, J=0.004376)								
900	8.641	1.615	0.000820	98.6	0.1	53.0	2.2	66.09 ± 1.85
1000	8.322	1.614	0.000649	99.1	0.1	66.9	2.8	64.05 ± 1.47
1100	8.307	1.612	0.000440	99.9	0.1	98.5	4.1	64.40 ± 1.00
1200	8.287	1.614	0.000751	98.8	0.1	57.8	5.5	63.55 ± 0.77
121X	8.307	1.614	0.000646	99.1	0.1	67.2	5.9	63.94 ± 0.71
122X	8.362	1.613	0.000544	99.5	0.1	79.8	8.3	64.59 ± 0.64
123X	8.310	1.628	0.000600	99.3	0.1	73.0	14.6	64.07 ± 0.33
124X	8.313	1.651	0.000465	99.8	0.1	95.5	13.6	64.41 ± 0.35
125X	8.320	1.665	0.000466	99.8	0.1	96.1	11.7	64.48 ± 0.39
126X	8.345	1.676	0.000488	99.8	0.1	92.4	10.8	64.62 ± 0.42
127X	8.317	1.661	0.000468	99.8	0.1	95.4	15.5	64.44 ± 0.32
128X	8.354	1.652	0.000447	99.9	0.1	99.4	4.1	64.77 ± 1.02
129X	8.719	1.611	0.000544	82.9	0.1	8.0	0.9	56.26 ± 4.6

[a] Plateau increments indicated in bold type. Increments extracted above 1200°C are numbered sequentially, terminated with an "X", and have no temperature significance.

[b] Corrected for ^{37}Ar decay, half-life=35.1 days.

[c] Subscripts: rad, radiogenic; K, potassium-derived; Ca, calcium derived.

[d] Decay constants: λ_ϵ=0.581x10^{-10}yr^{-1}, λ_β=4.692x10^{-10}yr^{-1}. Errors assigned to individual ages are estimates of the standard deviation of analytical precision. Reactor corrections for irradiation GLN-3: $(^{36}Ar/^{37}Ar)_{Ca}$=0.000251 ± 8, $(^{39}Ar/^{37}Ar)_{Ca}$ = 0.000671 ± 13, $(^{40}Ar/^{39}Ar)_K$ = 0.0285 ± 47.

VACUUM FURNACE INCREMENTAL HEATING ANALYSES

Incremental heating analyses were done on two bulk samples of tektites (67.3 mg and 83.4 mg) using a double-vacuum resistance furnace (fig. 10; tables 5, 6). Both of the resulting age spectra are flat with similar plateau ages of 64.65±0.22 Ma and 64.46±0.11 Ma over 56.5 percent and 74.8 percent of the ^{39}Ar released, respectively, and a weighted mean for the pair of measurements of 64.50±0.10 Ma. The total-gas ages for the two analyses are 64.50±0.79 Ma and 64.80±0.40 Ma, respectively. Unlike the age spectra obtained with the laser system, both of the furnace age spectra exhibit minor excess ^{40}Ar in the first 5 percent of the ^{39}Ar released, which may be due to ^{39}Ar recoil from a very small amount of non-glass phases (clays?) in the bulk sample. The isochron ages for the plateau parts of each analysis are 64.98±0.10 Ma and 64.52±0.08 Ma, respectively, and have $^{40}Ar/^{36}Ar$ intercepts indistinguishable from the atmospheric value.

DISCUSSION

The tektites we analyzed give $^{40}Ar/^{39}Ar$ ages that indicate that the fresh tektite glass cores have remained undisturbed K-Ar systems since they were formed by the K-T impact event at the close of the Cretaceous Period. The weighted mean of 58 of our our 59 analyses (52 total fusion, 6 incremental heating, one anomalous total fusion value excluded) is 64.43±0.05 Ma, which is our best estimate for the age of the tektites and, therefore of both the K-T impact and the K-T boundary.

Since we first reported our results (Izett and others, 1991a, 1991b), three other laboratories have reported ages for the Haiti tektites (fig. 11). Gillot and others (1991) measured two conventional K-Ar ages on ground, bulk tektite samples using the peak-intensity method, which does not require the use of a ^{38}Ar tracer. Their results were concordant (64.27±0.40 Ma, 63.63±0.40 Ma) with a mean value of 64.0±0.35 Ma (1σ).

Hall and others (1991) obtained flat and concordant age spectra on four single tektites using a continuous laser system and methods similar to ours. The mean of their four values, 64.75±0.08Ma (1s), is based on a monitor mineral (3gr hornblende=1,071 Ma) that does not depend for its calibration on MMhb–1. Hall and his colleagues commented that a comparison of their tektite results with ours (Izett and others, 1991a) and two analyses of

MMhb–1 using 3gr as the monitor mineral suggest that the correct age for MMhb–1 may be 517 Ma, which is midway between the Menlo Park USGS value of 513.9 Ma and the international mean of 520.4 Ma.

McWilliams and others (1992) recently reported a mean age for Haiti tektites of 64.91±0.06 Ma (1σ) using Taylor Creek Rhyolite sanidine (27.92 Ma) as the monitor. They claim that this age is marginally older than their mean value for sanidine from three bentonite beds that lie immediately above the K-T boundary at three localities in western North America (see table below).

Swisher and others (1992) reported weighted mean ages of 65.07±0.11 Ma and 65.01±0.08 Ma for three ^{40}Ar/^{39}Ar total fusion and nine ^{40}Ar/^{39}Ar incremental heating experiments on single Haitian tektites. They also determined a weighted mean age of 65.06±0.25 Ma for ^{40}Ar/^{39}Ar total fusion ages on two single tektites from the Arroyo el Mimbral K-T locality in northeastern Mexico. Their ages are based on a MMhb–1 value of 520.4 Ma and convert to values of 64.15 Ma (total fusion) and 64.09 Ma (incremental heating) for the Haitian tektites, and 64.14 Ma for the Arroyo el Mimbral tektites.

In addition to the ages for the Haitian tektites, there have been several other recent studies directed toward determining the age of the K-T boundary (fig. 11). Obradovich (1984) and Obradovich and Sutter (1984) reported a single ^{40}Ar/^{39}Ar age spectrum age of 66.0±0.27 Ma (1σ) for sanidine from JFL–500C, which occurs in the Z-coal ~70 cm above the K-T boundary near Hell Creek, Montana. Their age for the sanidine is based on a MMhb–1 age of 519.5 Ma and converts to an age of 65.1 Ma for MMhb–1=513.9 Ma.

Baadsgaard and others (1988; also Baadsgaard and Lerbekmo, 1983) measured K-Ar, Rb-Sr, and U-Pb ages on minerals from bentonites associated with three coal seams that lie stratigraphically above, but very close to, the
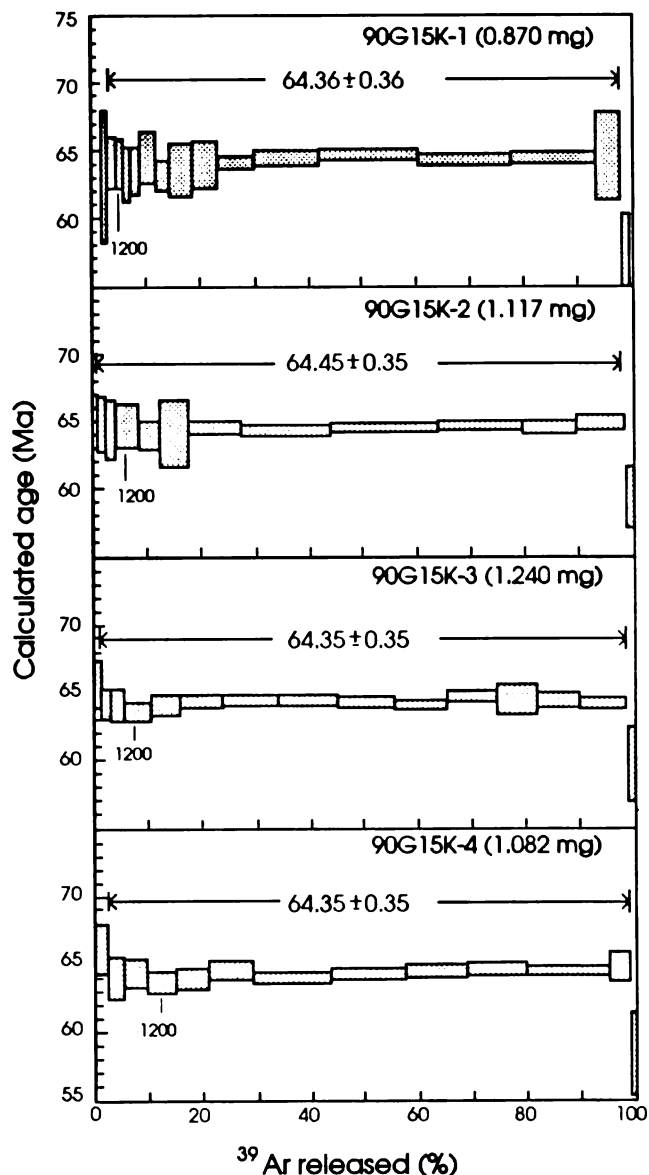

Figure 7. ^{40}Ar/^{39}Ar age spectra for four single Haitian tektites measured with the laser system. The weighted means and standard deviations of the plateau increments are shown for each age spectrum. The 1,200°C increment, above which the IR microscope was not functioning properly, is labeled. Some of the lowest temperature increments have been omitted from the age spectra because their ^{39}Ar content was too small to plot.
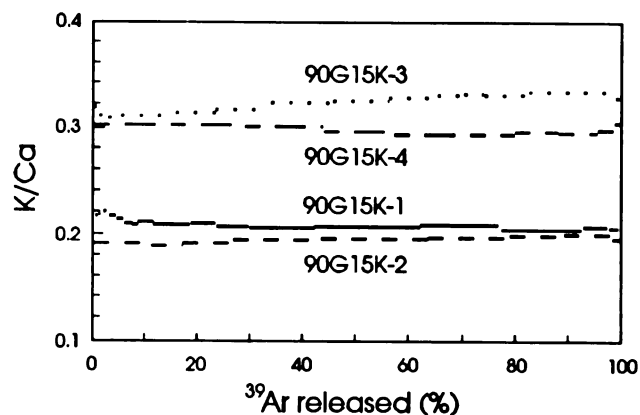

Figure 8. K/Ca diagrams for the four tektites measured with the laser system. The K/Ca ratios for each increment are calculated from the ^{39}Ar/^{37}Ar ratios.

K-T boundary. These include the Z-coal near Hell Creek, Montana (70 cm above the K-T boundary in the upper part of the Z-coal), the Ferris coal near Frenchman River, Saskatchewan (50 cm above the K-T boundary immediately above the Ferris coal), and the Nevis coal (40 cm above the K-T boundary immediately above Nevis coal). They obtained the following mean ages (1σ errors):

	K-Ar (sanidine)	Rb-Sr isochron (biotite)	U-Pb discordia (zircon)
Z-coal	64.6±0.5	63.7±0.3	63.9±0.3
Ferris coal	65.8±0.6	64.5±0.2	64.4±0.3
Nevis coal	65.8±0.7	63.9±0.3	64.3±0.3

Their weighted mean age for the nine values is 64.3±0.6 Ma. The K-Ar ages were done by Ian McDougall, who measured an age of 524.2 Ma for MMhb–1 hornblende (Samson and Alexander, 1987).

Carl Swisher has reported $^{40}Ar/^{39}Ar$ ages of 66.1–66.2 Ma for sanidine crystals from bentonites within the Z-coal (Berggren and others, 1992) using an MMhb-1 age of 520.4 Ma, but these ages now appear to be invalid because of difficulties in sample preparaton (Carl Swisher, oral commun., 1992).

McWilliams and others (1991a, 1991b, 1992) have reported $^{40}Ar/^{39}Ar$ total fusion and age spectrum ages for sanidine crystals from splits of the same mineral concentrates used by Baadsgaard and others (1988). Their mean ages, which are based on the USGS Menlo Park monitor values, are:

	$^{40}Ar/^{39}Ar$ total fusion	$^{40}Ar/^{39}Ar$ age spectrum
Z-coal	64.79±0.08	64.66±0.06
Ferris	64.71±0.06	64.56±0.08
Nevis	64.81±0.12	64.72±0.08

Their weighted mean value for the three K-T localities is 64.71±0.05 Ma.

The age data for North American and Caribbean K-T boundary sediments is relatively consistent considering the variety of laboratories and methods involved in the mea-
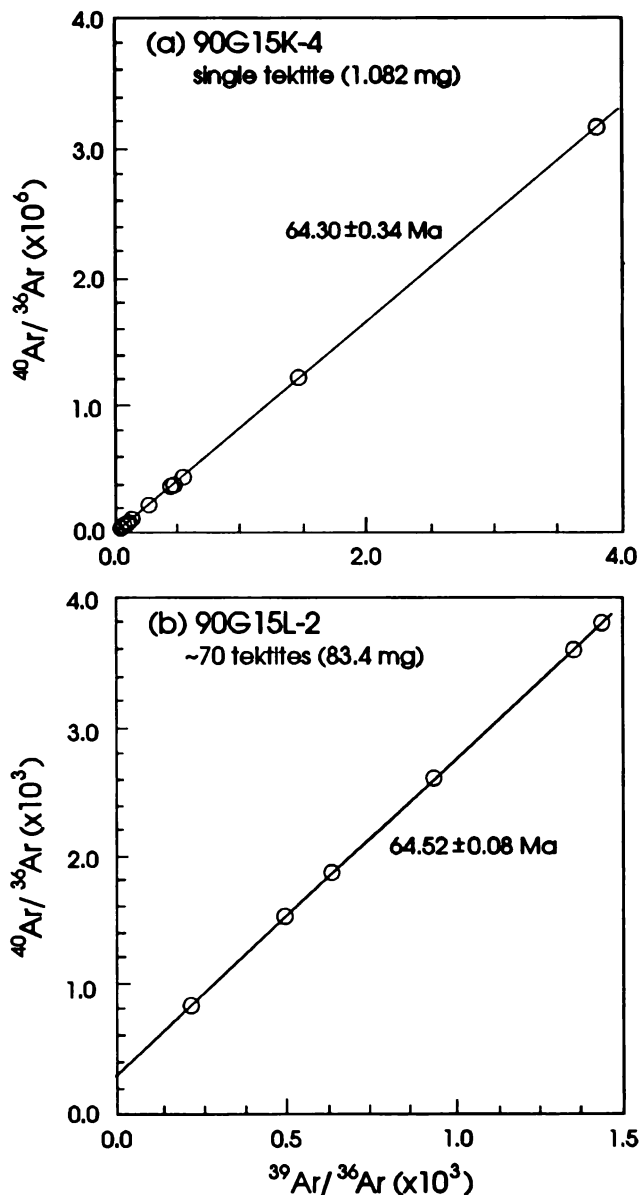

Figure 9. $^{40}Ar/^{36}Ar$ vs $^{39}Ar/^{36}Ar$ isochron diagrams for (a) one of the laser incremental heating measurements on single tektites, and (b) one of the resistance furnace incremental heating experiments on a bulk tektite samples. The isochron diagrams for the other incremental heating experiments are similar (table 5).
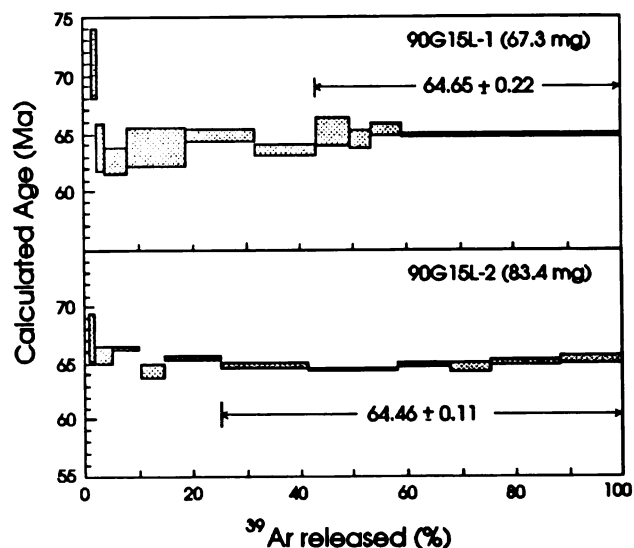

Figure 10. $^{40}Ar/^{39}Ar$ age spectra for tektite samples analyzed with the resistance furnace system.

Table 5. Analytical data for ^{40}Ar/^{39}Ar resistance furnace age spectra on K-T boundary tektites from Haiti.

Temp.[a] (°C)	^{40}Ar/^{39}Ar	^{37}Ar/^{39}Ar[b]	^{36}Ar/^{39}Ar	^{40}Ar$_{rad}$[c] (%)	^{39}Ar$_{Ca}$[c] (%)	^{36}Ar$_{Ca}$[c] (%)	^{39}Ar (% of total)	Age[d] (Ma)
90G15L-1, 67.3 mg (Irradiation GLN-3, J=0.004546)								
800	36.10	1.788	0.0896	27.1	<0.1	<0.1	0.3	77.5 ± 6.5
850	12.67	1.873	0.0166	61.2	<0.1	<0.1	0.3	62. ± 19.
900	10.61	1.840	0.00802	79.0	<0.1	<0.1	0.6	66.6 ± 7.6
950	10.99	1.977	0.00429	90.1	0.1	<0.1	1.1	78. ± 10
1000	9.839	1.808	0.00704	81.6	0.1	<0.1	1.6	63.8 ± 2.1
1050	8.594	1.698	0.00272	91.6	0.1	12.5	4.6	62.6 ± 1.1
1100	8.307	1.747	0.00139	96.5	0.1	33.3	10.2	63.7 ± 1.6
1150	12.38	1.729	0.0148	65.8	0.1	3.2	13.2	64.74 ± 0.50
1200	4.247	1.779	0.00201	94.3	0.1	20.0	11.7	63.31.± 0.46
1250	9.084	1.782	0.00361	90.0	0.1	13.3	6.1	64.9 ± 1.2
1300	10.49	1.780	0.0084	77.1	0.1	5.3	3.5	64.27 ± 0.76
1350	9.826	2.286	0.00617	83.2	0.2	8.7	5.9	65.00 ± 0.56
1450	8.718	1.714	0.00319	93.2	<0.1	14.5	41.0	64.61 ± 0.26
90G15L-2, 83.4 mg (Irradiation DD27, J=0.015052)								
550	1.082	0.2084	0.00305	19.9	0.1	<0.1	0.1	57. ± 32.
600	6.109	1.943	0.01364	34.6	0.2	<0.1	0.1	56. ± 10.
650	11.01	1.880	0.0309	18.2	0.2	<0.1	0.1	53. ± 19.
700	218.5	2.831	0.706	4.4	<0.1	<0.1	<0.1	241. ± 69.
750	13.61	2.055	0.0401	11.8	<0.1	<0.1	0.1	42. ± 31.
800	5.186	2.048	0.00813	56.3	0.1	4.8	0.6	76.56 ± 0.64
850	2.967	2.032	0.00185	86.0	0.1	33.3	1.2	67.1 ± 2.1
900	2.857	2.074	0.00180	87.0	0.1	30.4	3.2	65.41 ± 0.82
950	2.714	2.069	0.00120	92.8	0.1	45.8	4.9	66.24 ± 0.18
1000	2.671	2.071	0.00133	91.0	0.1	42.3	4.8	63.99 ± 0.60
1050	2.621	2.120	0.00101	94.7	0.1	56.1	10.0	65.29 ± 0.23
1100	2.685	2.189	0.00134	91.3	0.1	42.7	16.4	64.51 ± 0.23
1150	2.658	2.130	0.00128	91.7	0.1	44.0	16.2	64.16 ± 0.20
1200	2.792	2.080	0.00168	87.9	0.1	32.4	10.0	64.56 ± 0.27
1250	2.949	2.103	0.00226	82.7	0.1	23.9	7.8	64.21 ± 0.61
1350	3.122	2.002	0.00275	78.7	0.1	18.9	12.8	64.70 ± 0.27
1450	4.141	2.149	0.00622	59.6	0.1	9.2	11.6	64.91 ± 0.41

[a] Plateau increments indicated in bold type.

[b] Corrected for ^{37}Ar decay, half-life=35.1 days.

[c] Subscripts: rad, radiogenic; K, potassium-derived; Ca, calcium derived.

[d] Decay constants: λ_ε=0.581x10^{-10}yr^{-1}, λ_β=4.692x10^{-10}yr^{-1}. Errors assigned to individual ages are estimates of the standard deviation of analytical precision. Reactor corrections for irradiation GLN-3: $(^{36}$Ar/^{37}Ar$)_{Ca}$=0.000261 ± 2, $(^{39}$Ar/^{37}Ar$)_{Ca}$ = 0.000675 ± 4, $(^{40}$Ar/^{39}Ar$)_K$ = 0.00497 ± 37. Reactor corrections for irradiation DD27: $(^{36}$Ar/^{37}Ar$)_{Ca}$=0.000263 ± 2, $(^{39}$Ar/^{37}Ar$)_{Ca}$ = 0.000641 ± 3, $(^{40}$Ar/^{39}Ar$)_K$ = 0.00770 ± 25.

surements, and the difficulties of calibrations both within and between laboratories. When the single age reported by Obradovich (1984) and Obradovich and Sutter (1984) is converted to an MMhb–1 value of 513.9 Ma, all of the values fall between 64.5 Ma and 65.2 Ma or are not significantly different from an age within that range (that is, the age of Baadsgaard and others, 1988). Because of the uncertainties introduced by different sample collections, preparation methods, and irradiations, as well as differences between laboratory calibrations and instrumentation, we think that this agreement is good. We do not think that

there is any significant difference between the tektite ages and the sanidine ages for the continental K-T sections despite small differences in the numerical values. Instead, we think that these differences are most likely due to calibration and irradiation differences and do not have any real geological significance.

Our best age for the Haiti tektites, which are found at the K-T boundary and provide a direct age for the K-T bolide impact, is 64.4±0.1 Ma. If the age of Obradovich (1984) is converted to a MMhb–1 value of 513.9 Ma, then the weighted mean of the 26 ages shown in Figure 11 is

Table 6. Summary of $^{40}Ar/^{39}Ar$ age spectra and isochron results on K-T boundary tektites from Haiti.

Sample[a] No.	Weight (mg)	Plateau		Isochron		
		^{39}Ar (%[steps])	Age[b] (Ma)	Age[c] (Ma)	SUMS/(n-2)	$^{40}Ar/^{36}Ar$[c]
90G15K-1	0.870	95.9[15 of 25]	64.36 ± 0.36	64.00 ± 0.45	0.32	22 ± 139
-2	1.117	98.2[12 of 15]	64.45 ± 0.35	64.25 ± 0.34	0.16	200 ± 68
-3	1.240	97.5[13 of 15]	64.35 ± 0.35	64.27 ± 0.33	0.16	146 ± 44
-4	1.082	96.9[11 of 13]	64.35 ± 0.35	64.30 ± 0.34	0.10	21 ± 64
90G15L-1	67.3	56.5 [4 of 13]	64.69 ± 0.28	64.98 ± 0.20	0.05	291 ± 2
-2	83.4	74.8[6 of 17]	64.46 ± 0.11	64.52 ± 0.08	0.01	300 ± 1

[a] Data for 90G15K obtained with laser system, 90G15L with resistance furnace system.

[b] Weighted mean plateau age and σ_{best}.

[c] 1σ errors.

64.6±0.1 Ma (σ_{best}). This value, because it is based on measurements made in several laboratories using several dating methods and includes several calibrations that are independent of the value chosen for MMhb-1 hornblende monitor, is probably the best value for the age of the K-T boundary and the K-T impact.

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Figure 11. Summary of age measurements on deposits related to the K-T boundary impact marker bed in North America and Haiti. Errors shown are 2σ level ($2\ \sigma_{best}$ for weighted means). The ages are plotted as reported and have not been adjusted for differences in monitor mineral values. **BLM88**, Baadsgaard and others (1988); Baadsgaard and Lerbekmo (1983); **MBB91**, McWilliams and others, 1991a, 1991b; **MBB92**, McWilliams and others, 1992; **O84**, Obradovich, 1984; Obradovich and Sutter, 1984; **IDS91**, Izett and others, 1991a, 1991b, this paper; **GJRS91**, Gillot and others, 1991; **HYS91**, Hall and others, 1991; **SGM92**, Swisher and others, 1992. **IH**, incremental heating; **TF**, total fusion; **isoc**, isochron; **C-D**, concordia-discordia.

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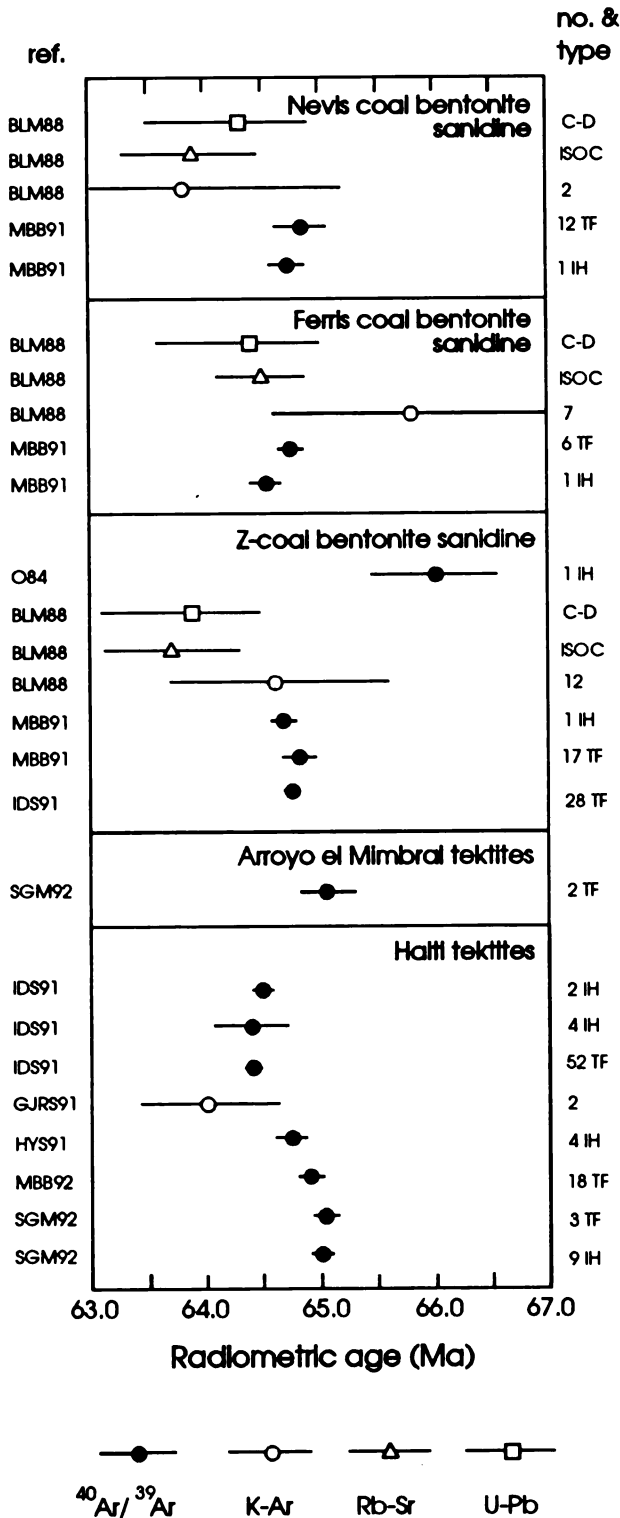
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