Beryllium-10 concentrations of tektites from the Ivory Coast and from Central Europe: Evidence for near-surface residence of precursor materials

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Abstract

By using accelerator mass spectrometry, we measured ^{10}Be ($T_{1/2} = 1.5$ Ma) concentrations in nine Ivory Coast (IVC) tektites, in six soil samples collected near the Bosumtwi impact crater, the likely source region, and in a depth profile taken through a 23 g moldavite. In the core of the moldavite sample we also measured an upper limit on the ^{36}Cl ($T_{1/2} = 0.3$ My) concentration. The average ^{10}Be concentration in IVC tektites of $(22 \pm 11) \times 10^6$ atom/g exceeds reasonable limits for a meteoritic component or cosmic-ray production *in situ* after tektite formation. The ^{10}Be must be meteoric, which implies that IVC tektites formed from soils or sediments. Corrected to the time of formation (ToF) 1.07 Ma ago and for a small *in situ* component, the average ^{10}Be concentration of $(35 \pm 7) \times 10^6$ atom/g $(1 - \sigma$ mean) is considerably lower than those of contemporary Bosumtwi soils, $\sim 250 \times 10^6$ atom/g, or of Australasian tektites at their ToF, 0.8 Ma B.P. near Lake Bosumtwi today the soil column is only ~ 1 m thick. If the landscape was similar 1.07 Ma ago, then the total thickness of the tektite formation zone probably did not exceed 10 m. With increasing depth below the surface of the moldavite, the ^{10}Be concentrations decrease rapidly owing to the presence of a surface component, probably of recent origin. The main interior mass of the sample contains $\sim 0.8 \times 10^6$ atom ^{10}Be/g and fewer than 0.1×10^6 atom ^{36}Cl/g, little of which can be meteoritic. Although not definitive, consideration of several possible cosmic-ray exposure histories suggests that about half the interior ^{10}Be has a meteoric origin, which if corrected to the time of formation yields a concentration compatible with those measured in typical contemporary soils. The observations are consistent with the formation of three of the four main tektite groups from surface soils or sediments.

1. INTRODUCTION

Studies of the cosmogenic nuclide ^{10}Be ($T_{1/2} = 1.5$ Ma) support the view that impact-associated melting of surface materials produced the Australasian tektites (Koeberl, 1986, 1994; Wasson, 2003). In particular, the concentrations of ^{10}Be in Australasian tektites overlap with values measured in contemporary terrestrial sediments and soils

(Ma et al., 2004), but not with those in rocks collected at comparable elevations and latitudes (Stone, 2000), or in extraterrestrial materials (Vogt et al., 1990). If tektites from the Ivory Coast, Central Europe, and North America also formed from surface soils or sediments, then they, too, once may have contained as much ^{10}Be as the Australasian tektites. We set out to test this hypothesis for the Ivory Coast and Central European tektites. With an age of 35 Ma, North American tektites preserve about 1 part in 10^7 of any original meteoric ^{10}Be, too little to measure in a sample of reasonable size with present day capabilities.

The first Ivory Coast (IVC) tektites described came from a relatively restricted area in République de Côte d'Ivoire (Lacroix, 1934). Later, Glass (1968, 1969) found microtek-

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tites in the Atlantic Ocean off the coast of West Africa with the same composition and age as the IVC tektites. The commonalities implied that the tektites and microtektites formed in a single event that spread material over a much larger strewn field than originally imagined (e.g., Glass and Zwart, 1979; Glass et al., 1979, 1991). As determined by Ar–Ar and by fission track dating, the currently accepted age of the IVC tektites and microtektites is 1.07 Ma (Koeberl et al., 1997). The source crater, based on age and geochemical data, is the Bosumtwi impact structure in Ghana (e.g., Schnetzler et al., 1966, 1967; Gentner et al., 1967; Kolbe et al., 1967; Shaw and Wasserburg, 1982; Jones, 1985; Koeberl et al., 1998).

If the IVC tektites were closed to the exchange of ^{10}Be, they should retain today $\sim$61% of the ^{10}Be originally present. Taking the mean ^{10}Be concentration of Australasian tektites as a guide (see Ma et al., 2004) and allowing for 1.07 Ma of decay, we would expect the IVC tektites to contain $\sim$85 × 10^6 atom ^{10}Be/g. Englert et al. (1984) reported ^{10}Be concentrations of 20–40 × 10^6 atom/g in three IVC tektites. Although these results seem close to the expected answer, Englert et al. quoted Middleton, Klein, and colleagues at the University of Pennsylvania as having measured ^{10}Be concentrations some three times lower in comparable objects. The small number and inconsistencies of the available data called for further study.

There were three other reasons for re-opening the investigation of cosmogenic radionuclides in the IVC tektites. First, the measurement technique for ^{10}Be, accelerator mass spectrometry, has improved since the original studies 20 years ago. The minimum sample size needed for an analysis has decreased, which made it easier to obtain specimens, and precision is better. Second, during the last 10 years interest in and the pace of research at the Bosumtwi crater have intensified. Recent efforts have led to a new geological map (Koeberl and Reimold, 2005); to the drilling in 1999 of cores into the fallout suevites and breccias outside the northern crater rim (Boamah and Koeberl, 2002, 2003, 2006); and, in 2004, to a multinational and interdisciplinary drilling program into the crater lake itself in order to study the sediments and the underlying impactite deposits (e.g., Koeberl et al., 2006). As part of these studies, soils were collected from two areas near the Bosumtwi crater, providing an opportunity for comparing the ^{10}Be concentrations of IVC tektites with those of plausible sources. Third and relatedly, efforts are under way to identify in the impact structure the IVC tektite formation zone and to characterize its stratigraphy, pre-impact depth, and petrography. A constraint on the IVC source region inferred from ^{10}Be matched with ground truth from Bosumtwi would inspire confidence in generalizing to other tektite strewn fields the key conclusion from the study of ^{10}Be in Australasian tektites: that near-surface materials were an important or even the main source of material.

Like the IVC tektites, the Central European tektites ("moldavites") are mainly of the splash-form variety. They were produced about 14.4 Ma ago (Schwarz and Lippolt, 2002; Laurenzi et al., 2003) as a result of the Ries–Steinheim impact event into a region capped by a discontinuous layer of sand, clay, and limestone (e.g., Engelhardt et al.,

1987, 2005; Stöffler et al., 2002); geochemical evidence indicates that the tektites were derived from near-surface sediments called the Upper Freshwater Molasse (e.g., Engelhardt et al., 1987). After the passage of 14.4 Ma, 1 atom in 776 of any ^{10}Be originally present would have survived decay. Assuming that a moldavite had approximately the same initial ^{10}Be concentration as did Australasian tektites and remained closed, it would contain today $\sim$0.2 × 10^6 atom ^{10}Be/g. Pal et al. (1982) used a 3-g sample of a moldavite as a procedural blank for a study of tektites, and reported an upper limit of 2 × 10^6 atom ^{10}Be/g.

In the course of more than 14 Ma near the Earth's surface, moldavites must have been exposed to cosmic rays bombardment to some degree. To help monitor the effects of cosmic rays during this period, we analyzed for a second cosmogenic nuclide, ^{36}Cl ($T_{1/2} = 0.3$ Ma). In the 14 Ma since the moldavites formed, the concentration of any ^{36}Cl originally present in the moldavite interiors would have decreased to a level well below our detection limit as a result of radioactive decay. We therefore expected that any ^{36}Cl measured would be the result of recent cosmic-ray irradiation.

2. EXPERIMENTAL METHODS

2.1. Samples

We analyzed nine Ivory Coast tektites for their ^{10}Be content (Table 1). Samples IVC2096, IVC3395, and IVC3396, originally came from the collection of the Museum National d'Histoire Naturelle, Paris; and samples IVC8901 and IVC8902 from the University, Abidjan, Ivory Coast, but all these samples had been at the University of Vienna collection. Koeberl et al. (1997) previously analyzed the chemical and the isotopic compositions of these samples. Unfortunately, details concerning the provenance of four remaining samples, from the Rutgers University collection, here labeled IV0xxxx, were lost. The only two likely sources, however, are the Max-Planck Institut für Kernphysik at Heidelberg (T. Kirsten) or the U.S. National Museum (R. Clarke and G. MacPherson). We obtained a moldavite with a mass of 23.1985 g from the Natural History Museum in Vienna.

Table 1
^{10}Be concentrations (10^6 atoms/g) of tektites from Ivory Coast

Sample ID	^{10}Be	
	Measured	ToF
IVC2096	24.1 ± 0.5	47.1 ± 1.0
IVC3395	5.6 ± 0.3	7.0 ± 0.4
IVC3396	25.3 ± 1.3	49.7 ± 2.7
IVC8901	40.6 ± 0.8	82.9 ± 1.8
IVC8902	13.3 ± 0.3	23.8 ± 0.5
IV06022304	19.9 ± 0.9	38.0 ± 1.7
IV07022304B	12.7 ± 0.7	22.5 ± 1.3
IV07022304D	17.0 ± 0.9	31.8 ± 1.6
IV07022304F	17.2 ± 0.9	32.1 ± 1.8
Average	18 ± 11	29 ± 18

ToF, time of formation, 1.07 Ma B.P. (see text).

Dense tropical rain forest largely covers the region around Bosumtwi; annual rainfall is ∼150 cm/a (see, Gyau-Boakye and Tumbulto (2006), also available at: http://www.ansti.org/volume/8-Gyau.pdf#search=%22rainfall%20Kumasi%22). The impact excavated lower greenschist facies metasediments (greywacke, quartzitic greywacke, meta-tuffs, phyllites, shales and schists) of the 2.1–2.2 Ga Birimian Supergroup. Rocks to the southeast of the crater contain altered basic intrusives (Birimian metavolcanics) in addition to metasediments. Further to the east and southeast occur clastic Tarkwaian sediments, formed, in all likelihood, by erosion of Birimian rocks. Soils up to 1 m thick, some of which are lateritic, have evolved from these rocks and cover most of the surface area around Bosumtwi. During an expedition in 1997, one of us (C.K.) collected soil samples for the purpose of ^{10}Be measurements and comparison with the respective values in Ivory Coast tektites, with the assumption that similar soils covered the target surface at the time of the tektite-forming impact event. Samples LB-29 were collected at 6°33.96′ N and 1°25.86′ W, about 1.5 km north of the northern part of the crater rim near the village of Nyameani; three subsamples were collected, one from the surface (LB-29A), one by digging down about 50 cm (LB-29B), and one from about 80–90 cm depth (LB-29C). Samples LB-52A and LB-52B were collected about 6 km to the east of the eastern crater rim, near the road between Akronwe and Pemenase, at 6°29.94′ N and 1°18.37′ W, at depths of about 20 and 50 cm below the present-day surface, respectively (see map in Koeberl and Reimold, 2005).

2.2. Chemical preparation and accelerator mass spectrometry

The IVC tektites looked extremely clean and in most cases appeared to have fresh fracture surfaces. All of them were rinsed briefly with 1 M HCl. We extracted ^{10}Be from 500–1500 mg of each Ivory Coast tektite and Bosumtwi soil sample by dissolution in mineral acids followed by ion exchange procedures (Vogt et al., 1991). Measurements of ^{10}Be/^{9}Be ratios were made at the accelerator mass spectrometer of PRIME Laboratory, Purdue University. Because of an unresolved uncertainty of 10% concerning the ^{9}Be concentration of our carrier solution, we used the meteorite Dhurmsala as a standard. The ^{10}Be activity of this material, 21.3 dpm/kg, is well-known from analyses at many laboratories. The ^{10}Be/^{9}Be blank for the chemical procedure was less than 2×10^{-14} (atom/atom).

Because of the risk of surface contamination from ^{10}Be in adhering modern soils or adsorbed from groundwater, we took extra precautions in processing the moldavite. Surface material was removed in several steps. First we abraded ∼3 g from the surface with a Dremel tool, recovering 1.2 g of powder (sample J2388ZA) and several chips. To remove additional material, we etched the samples six times as outlined in Table 2, rinsing each time to ensure the capture of all dissolved material and to clean the newly exposed surface. The masses of the etched samples were determined by difference. After etching a mass of 19.95 g remained of which we took 19.14 g for the analysis of ^{10}Be and ^{36}Cl.

3. RESULTS

3.1. Ivory Coast tektites

The ^{10}Be concentrations (10^6 atom/g) measured in nine Ivory Coast tektites range from 5.6 to 40.6 with an average of 19 ± 9 (1σ) (Table 1). Three analyses of Englert et al. (1984) had a mean of 31 ± 10. Considering the variability of the results from sample to sample, the agreement seems satisfactory. The mean for all 12 IVC tektites is 22 ± 11, which corresponds to 37 ± 18 ($1 - \sigma$) corrected to the time of formation (ToF) 1.07 Ma ago.

3.2. Bosumtwi soils

Table 3 shows the ^{10}Be concentrations of the Bosumtwi soils. Agreement for the replicate samples of LB 29 is excellent. The range of ^{10}Be concentrations, from ∼100 to 400×10^6 atom/g, is fairly typical of Earth surface materials (e.g., Table 5 of Ma et al., 2004). The surface sample LB29A contains about three times *less* ^{10}Be than the lower-lying samples B and C, which may seem surprising given that precipitation delivers the ^{10}Be to the surface. Barg et al.

Table 3
^{10}Be concentrations in soils collected near Bosumtwi crater

Sample	Location	Depth (cm)	^{10}Be (10^6 atom/g)
LB29A	6°33.96′ N, 1°25.86′ W	0	154 ± 8
LB29B		50	395 ± 23
LB29B			386 ± 25
LB29C		80–90	437 ± 23
LB52A	6°29.94′ N 1°18.37′ W	20	149 ± 60
LB52B		50	133 ± 12

Table 2
^{10}Be concentrations in samples from a 23-g moldavite

Sample	Preparation	Mass (g)	Depth (cm)	^{10}Be (10^6 atom/g)
J2388ZA	Abrasion	2.9471	2.72×10^{-2}	9.6 ± 4.8
J2388ZB	1 M HCl; low heat; 15 min	0.0009	5.43×10^{-2}	$(6 \pm 6) \times 10^2$
J2388ZC	1 M HF; 15 min	0.0466	5.48×10^{-2}	12.1 ± 5.0
J2388ZD	1 M HF; 20 min	0.0689	5.59×10^{-2}	24.2 ± 9.9
J2388ZE	1 M HF; 20 min	0.0565	5.71×10^{-2}	5.9 ± 4.2
J2388ZF	1 M HF; 20 min	0.0654	5.83×10^{-2}	2.6 ± 3.6
J2388ZG	1 M HF; 30 min	0.0579	5.95×10^{-2}	3.0 ± 3.9
J2388ZH	None	19.9552	64.34×10^{-2}	0.8 ± 0.1

(1997, Table 6), reported an even more extreme surface depletion in a soil profile from South Mali that they described variously as oxide-rich, bauxite, and ferricrete. The most likely explanation is leaching at the surface.

3.3. Moldavite

Fig. 1 and Table 2 show the [10]Be concentrations of the moldavite samples. We calculated a nominal depth and layer thickness for each sample from the sample masses by treating the original object as a sphere with a mass of 23.2 g and a density of 3.0 g/cm³; each layer as a perfect spherical shell; and the residual mass as a sphere. The nominal width of each layer is shown as a horizontal line in Fig. 1.

The procedural blank for the moldavite samples had a [10]Be/[9]Be ratio of 9×10^{-15}, which, based on both experience and counting statistics, we take to have an uncertainty of $\pm 4 \times 10^{-15}$. The measured [10]Be/[9]Be ratios of the samples span a factor of twenty, from $\sim 12 \times 10^{-15}$ for the mg-size etches J2388F and J2388G to $\sim 200 \times 10^{-15}$ for the gram-sizes samples J2388A and J2388Z. The vertical lines in Fig. 1 are one-sigma error bars that fold together the uncertainties in sample and blank. Except for the first etch, J2388B, the uncertainties in the measured [10]Be/[9]Be ratios dominate. The first etch removed so little material, ~ 1 mg, that in this case we have assigned an additional uncertainty of 100% to the sample mass. In converting the blank-corrected [10]Be/[9]Be ratios to numbers of [10]Be atoms, we included in the number of [9]Be atoms a small contribution from 2 ppm wt. native Be, an estimate based on published elemental analyses of Australasian tektites (cf. Koeberl, 1986).

The measured [36]Cl/Cl ratio of the main interior mass of the moldavite, J2388H, was $(15.7 \pm 2.5) \times 10^{-15}$; the mean ratio for four blanks measured at different times was $(14 \pm 15) \times 10^{-15}$. The [36]Cl concentration calculated for the sample is $(3 \pm 11) \times 10^4$ atom/g. We adopt 0.1×10^6 atom/g as an approximate upper limit for the [36]Cl concentration of J2388H.

4. DISCUSSION

4.1. Ivory Coast tektites

4.1.1. Meteoritic component?
At saturation, typical stony meteorites contain about 2.3×10^{10} atom [10]Be/g (20 dpm/kg). Surface concentrations in impactors big enough to make craters are about half as large and volume-averaged concentrations much lower. For example, in a stony impactor 80 m in diameter, the mean production rate is about 2% of the value at the surface. If the impactor contributes less than 1% of the tektite mass, then we would expect at most 4×10^6 atom [10]Be/g from the meteorite itself.

4.1.2. Cosmogenic contribution
A portion of the [10]Be in the IVC tektites probably owes to production by cosmic rays *in situ*. We can set an upper limit on this contribution with the aid of a [10]Be production rate, P_{cos}^{10}, and the added assumptions that the IVC tektites spent all their time at the surface and suffered little or no erosion. Using the production rates of Masarik (2002) (see below) and the average IVC tektite composition of Koeberl et al. (1998), we find a [10]Be production rate of 5.17 atom (g tektite)$^{-1}$ a^{-1} at sea level and high latitudes. At the latitude, 6°30′ N, and elevation (~ 200–300 m → $P = 984$ hPa) of the Bosumtwi impact structure, we obtain a correction factor (Stone, 2000) of 0.81, giving a production rate of 4.2 atom (g tektite)$^{-1}$ a^{-1}.

With no erosion, the concentration of cosmogenic [10]Be, N_{cos}, in an Ivory Coast tektite exposed at the surface increases over time, T, according to the relation

$$N_{cos} = \frac{P_{cos}^{10}}{\lambda_{10}}(1 - e^{-\lambda_{10}T}) \qquad (1)$$

For $T = 1.07$ Ma and $P_{cos}^{10} = 4.2$ atom [10]Be (g tektite)$^{-1}$ a^{-1} we find for the present ($T = \infty$) $N_{cos} = 3.5 \times 10^6$ atom [10]Be/g. The *in situ* production rate (and hence the value of N_{cos}) would be smaller if the IVC tektites lay buried for long, as did, for example, Australites (Chalmers et al., 1979). For this reason, we adopt the value $N_{cos} = (2 \pm 2) \times 10^6$ atom [10]Be/g for *in situ* [10]Be production that postdated the formation event.

Twelve Ivory Coast tektites have an average [10]Be concentration of $(37 \pm 6) \times 10^6$ atom/g (σ_{mean}) after adjustment to the time of formation. *In situ* production of $(2 \pm 2) \times 10^6$ atom/g therefore accounts for not more than $7 \pm 7\%$ of the average value, leaving $(35 \pm 7) \times 10^6$ atom/g of [10]Be at the time of formation to be explained.

4.1.3. Meteoric [10]Be in Ivory Coast tektites
If neither a meteoritic component nor cosmic rays can account for the observed concentrations of [10]Be in IVC tektites, then by elimination the [10]Be must be meteoric, i.e., produced in the Earth's atmosphere, just as in Australasian tektites. Further, and again as in the Australasian tektites,
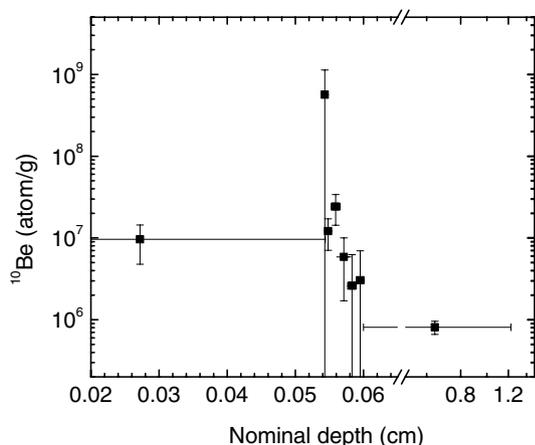

Fig. 1. The [10]Be concentrations in successive layers and in the remaining, interior portion of a moldavite decrease with increasing depth. Higher values at the surface probably reflect contamination from meteoric (precipitation-borne) [10]Be. The lowest value measured, the one for the interior portion, is taken to represent [10]Be that was present when the moldavite formed about 14.4 Ma ago.

the IVC tektite source material must have been loosely consolidated within, say, ten ^{10}Be half-lives of the ToF. Were the grains cemented together earlier, adsorption of ^{10}Be would have ceased, and any ^{10}Be present would have decayed by the time of the impact. Although we do not know the nature of the landscape at Bosumtwi 1.07 Ma ago, the main rock types there have ages of about 2 Ga (Koeberl et al., 1998), much too large to retain ^{10}Be at the levels observed in IVC tektites, even with initial concentrations of 1000×10^6 atom/g. Thus, if IVC tektites came from Bosumtwi, they formed at least in part from soils or sediments.

Observed variations in the ^{10}Be concentrations of recent soils and sediments worldwide range over a factor of 100, from 10 to 1000×10^6 atom/g (Barg et al., 1997; Ma et al., 2004) and encompass the values for IVC tektites. Even so, the mean concentration of meteoric ^{10}Be in IVC tektites, $(35 \pm 7) \times 10^6$ atom/g ToF, is lower than expected, about seven times less than the mean for present-day Bosumtwi soils, 253 ± 66. On average, Australasian tektites contained about $(143 \pm 5) \times 10^6$ (σ_{mean}) atom ^{10}Be/g (ToF). Calculations similar to those made above for IVC tektites show that *in situ* production accounts for less than 3% of the ^{10}Be in Australasian tektites. Thus, the average meteoric ^{10}Be concentration (ToF) in Australasian tektites exceeds the one in IVC tektites by a factor of about 4.

What might have lowered the ^{10}Be concentration in IVC tektites? Global factors influencing production and ultimately accumulation of ^{10}Be include the cosmic-ray flux, the Sun's magnetic field, and the geomagnetic field. We know of no evidence for significant changes in the cosmic-ray flux or the Sun's magnetic field at the three relevant time points, namely, the present (Bosumtwi soils), 0.8 before the present (Australasian tektites), and 1.07 before the present (IVC tektites). A geomagnetic reversal or excursion may have raised production rates at the time the Australasian tektites were produced (Glass et al., 1979), but probably accounts for at most half the difference between IVC and Australasian tektites (e.g., Ticich et al., 1986).

Several local factors could explain the spread in concentrations: climate, through its influence on latitude-dependent transport from the stratosphere to the troposphere, precipitation rates, aeolian particle transport, and soil erosion (or development); duration of exposure; pH; sample depth; and the type or particle size of material present. Lower ^{10}Be concentrations may result when erosion is rapid, or precipitation low, or burial at depth lengthy; we consider the possibility of dilution by local rocks below. The Australasian tektites formed at a time of warmer, wetter climatic conditions (interglacial isotope stage 19), whereas the climate was colder and drier (glacial isotope stage 20) when the IVC tektites were created. Presumably rates of erosion were correspondingly lower in Ghana 1.1 Ma ago, leaving lower delivery rates of ^{10}Be and/or radioactive decay during burial as viable explanations for the low ^{10}Be concentrations of IVC tektites. Assuming a one-crater origin for Australasian tektites, Ma et al. (2004) made use of systematic differences in the ^{10}Be concentrations of indochinites and australites to constrain the range of burial depths of the source materials. The limited number of IVC tektite analyses, and the absence of different tektite types preclude the use of this approach here: Australasian tektites occur as Muong Nong-type, splash form, and aerodynamically shaped variety, all of which show different ^{10}Be contents, whereas all IVC tektites known to date are of the splash form variety.

A final possible explanation for the low ^{10}Be concentrations of the IVC tektites deserves consideration. Blum et al. (1992) argued for making Australasian tektites by mixing bedrock essentially devoid of ^{10}Be with surface materials rich in ^{10}Be. Ma et al. (2004) doubted that the volumes of materials required would have mixed well enough to explain the limited observed range of ^{10}Be concentrations. They also pointed to the absence of the 'intermediate' objects consisting of both glass and bedrock that one might expect. As the location of the Australasian tektite source region remains unknown, Ma et al. could argue plausibly that it might include sedimentary deposits of considerable thickness—perhaps on the order of 50 m or more—consistent with current models for the formation of Central European tektites (Stöffler et al., 2002). Knowledge of the terrain in Ghana leaves less latitude for discussion. Currently, soils there that are rich in ^{10}Be extend downward to only 1 m or so; below them lie somewhat weathered, but more competent metamorphic rocks of Precambrian age. Setting mixing difficulties aside, a mixture of 1 part of contemporary soils with ~7 parts of ^{10}Be-free bedrock would make IVC tektites with approximately the observed ^{10}Be concentration. This result implies that the tektite-forming region was no more than 10 m thick.

Koeberl (1994) estimated the recovered mass of the IVC strewn field as 20×10^6 t. The present diameter of Lake Bosumtwi is ~8 km, which corresponds to an area of ~5×10^7 m^2. Assuming a density of 2.5 g/cm^3, a disk 1 m thick with this area would have a mass of 130×10^6 t, some six times larger than that of the IVC strewn field. Admixture of seven parts of rock increases the mass and hence the discrepancy by another factor of 10 or so. These considerations suggest that tektite formation region took place in an area much smaller than the Lake.

4.2. Moldavite

4.2.1. ^{10}Be depth profile

In the moldavite the measured ^{10}Be concentrations decrease with increasing depth in the sample (Fig. 1). Flat profiles of elemental concentrations obtained by electron microprobe analyses imply good mixing of the melts prior to quenching, from which we infer that any ^{10}Be initially present should also be uniformly distributed. It follows that the trend in Fig. 1 results from the presence of a surface component, which was probably introduced by adhering grains of modern soil and/or by exposure to ground water.

The etching procedures removed some of the surface contamination from the moldavite, but perhaps not all of it. A contamination zone extending for another 2 mm with the same ^{10}Be concentration as measured in the last etch would account for all the ^{10}Be and leave little to write save that ^{10}Be in ground water can penetrate samples to a depth of 2 mm or so. On the other hand, the concentration data for the last five etches (J2588C–G) show a rapid decrease

with increasing nominal depth. A linear fit to these five data points has the form $^{10}Be = 2.0 \pm 1.1 - (3.4 \pm 2.0) \times$ nominal depth. If we assume that the ^{10}Be in samples C–G consists entirely of surface contamination and extrapolate the fitted line to the nominal depth of the innermost sample, then we would predict a ^{10}Be concentration due to contamination that is much lower than the measured concentration. We therefore prefer to take the view that etching removed most of the contamination, although in retrospect, etching the sample even more deeply would have provided a more decisive answer.

We have no reason to suspect that surface contamination would have much effect on the ^{36}Cl present in the sample. Atmospheric production of ^{36}Cl is much lower than of ^{10}Be and chlorine normally reacts to form soluble compounds, which would wash away in the field.

4.2.2. Meteoritic contribution

We estimated a meteoritic contribution of about 4×10^6 atom $^{10}Be/g$ for the IVC tektites above. The moldavites are associated with a larger crater and presumably, therefore a larger impactor with a smaller average ^{10}Be concentration. Decay over 14.4 Ma would reduce any meteoritic component in the moldavite to negligible proportion.

4.2.3. Cosmogenic nuclide production rates

The instantaneous production rate of a cosmogenic nuclide depends mainly on the composition, latitude, elevation, and burial depth of the sample. Updating the work of Masarik and Reedy (1995), Masarik (2002) calculated production rates, P_{cos} (atom g^{-1} y^{-1}), at sea level and high latitudes for several cosmogenic nuclides as a function of elemental composition (mass fractions), among them

$$P_{cos}^{10} = 9.82[O] + 1.74[Mg] + 1.03[Al] + 0.89[Si] + 0.35[Fe]$$

$$P_{cos}^{36} = 122[K] + 68[Ca] + 13.5[Ti] + 6.75[Fe] + 2.03[Ni]$$

Engelhardt et al. (2005) presented the following data for mean elemental concentrations (mass %) in moldavites:

$O = 50.0$ (by difference), $Mg = 1.08$, $Al = 5.03$, $Si = 37.26$, $K = 2.78$, $Ca = 2.00$, $Ti = 0.20$, and $Fe = 1.33$. For a moldavite of average composition we find $P_{cos}^{10} = 5.3$ (atom g^{-1} y^{-1}) and $P_{cos}^{36} = 4.9$ (atom g^{-1} y^{-1}). According to the formulation of Stone (2000), at the location of the Ries Crater, 48°53′ N, 10°37′ E and ~400 m elevation ($P = 965$ hPa), the production rates of ^{10}Be and ^{36}Cl are higher by 48% and 49%, respectively yielding $P_{cos}^{10} = 7.96$ (atom g^{-1} y^{-1}) and $P_{cos}^{36} = 7.22$ (atom g^{-1} y^{-1}).

These production rates occur only at the surface and decrease rapidly with depth below it. For a column of silicate rock, an attenuation length, Λ, of 160 g/cm^2 is widely quoted (Lal and Peters, 1967; Nishiizumi et al., 1984; Lal, 1991); it corresponds to a half thickness of 111 g/cm^2, or about 0.6 m in a sediment with a density of 2 g/cm^3. We will adopt a half-thickness of 111 g/cm^2 for both P_{cos}^{10} and P_{cos}^{36}.

4.2.4. Exposure histories

The goal in constructing exposure histories for the moldavite is to match the measured ^{10}Be concentration of 0.8×10^6 atom/g, and to satisfy the constraint that the ^{36}Cl concentration be less than 0.1×10^6 atom/g. As this problem has an infinite number of possible solutions, we consider only a few limiting cases, starting with a one-stage irradiation under fixed conditions (Fig. 2).

4.2.5. Case 1a—One-stage irradiation at the surface

In the simplest one-stage exposure history, the moldavite lies at the surface for 14.4 Ma, where cosmic-ray irradiation produces 17×10^6 atom $^{10}Be/g$ and 3×10^6 atom $^{36}Cl/g$, concentrations that are 20× and 30× more, respectively, than observed. We conclude that the moldavite did not spend 14.4 Ma at the surface.

4.2.6. Case 1b—One-stage irradiation at depth

In the next simplest one-stage history, the moldavite stays for 14.4 Ma at a depth of 490–550 g/cm^2 (2–3 m), with instantaneous excavation just prior to recovery. Although the match to the measured concentrations is not compel-
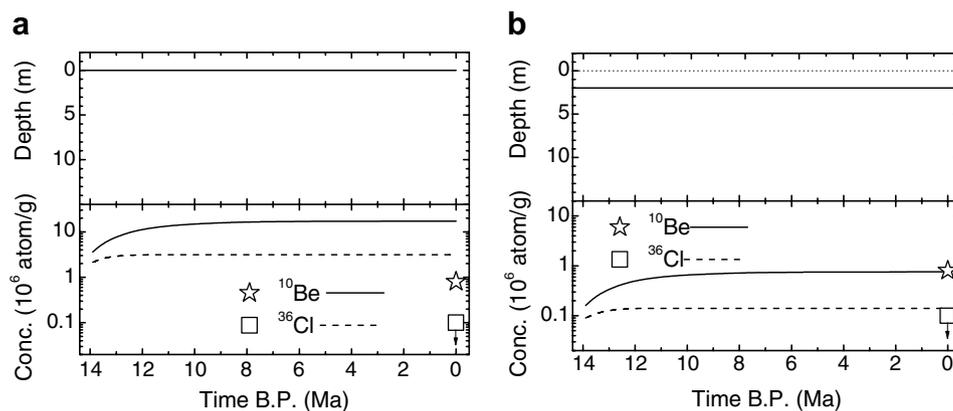

Fig. 2. Hypothetical exposure histories for the moldavite. The upper graphs show the depth of the sample over time: a depth of 0 represents the surface of the Earth. The lower graphs show how the concentrations of ^{10}Be and ^{36}Cl increase with time under the assumed (b) irradiation conditions. (a) A one-stage irradiation at the surface greatly overestimates the ^{10}Be and ^{36}Cl concentrations; irradiation at a constant depth of approximately 2 m or 500 g/cm^2 matches the ^{10}Be concentration (☆) but overestimates ^{36}Cl (□) by 40% or more.

ling—a good match for ^{10}Be but 50% too much ^{36}Cl at 490 g/cm^2, or 40% too little ^{10}Be but a good match to the upper limit for ^{36}Cl at 550 g/cm^2—we do not rule out such a scenario. The disagreements become progressively worse for exposures at smaller depths. At greater depths, the irradiation cannot produce enough ^{10}Be.

4.2.7. Case 2a—Burial followed by a one-stage irradiation

A simple two-stage exposure history may begin at a large depth with the tektite covered by a thick layer of ejecta and end with it close to the surface, perhaps as a result of erosion rapid enough to be considered instantaneous. The upper limit on the ^{36}Cl concentration limits any recent irradiation at the surface to ~20 ka, long enough to make only about 1/8 of the ^{10}Be observed. If the second stage took place a little below the surface, however, the match can be improved up to the limiting case of a second stage lasting 14.4 Ma at a depth of ~500 g/cm^2, which is equivalent to Case 1b. As the limiting match is no *better* than for Case 1b, we see no advantage to this class of exposure histories.

4.2.8. Case 2b—One-stage irradiation followed by burial

Reversing Case 2a, a 'two-stage' history may begin with the tektite at or near the surface, followed by a relatively long period of deep burial (as a result, perhaps, of a mudslide) and terminated by a quick excavation (as a result, perhaps, of a second mudslide). Initial exposure at the surface for 7.8 My followed by 6.6 My of burial would satisfy the observational constraints. Surface exposures of such long duration are rare among meteorites (Jull, 2006), and on terrestrial surfaces in temperate climates (e.g., Schaefer et al., 2006). In a geomorphologically more plausible variant, the tektite might start out below the surface and remain there until even deeper interment took place some time within the last 7.8 Ma. Case 1b sets an upper limit on the depth (~500/cm^2) of the first stage. As the first-stage depth approaches this limit, the duration of irradiation increases and the fit to the experimental data worsens.

4.2.9. Case 3—Constant erosion

Erosion lowers effective production rates. If the attenuation length, Λ, and erosion rate, ε, of a soil or sediment column remain constant, then the concentration, C, of a cosmogenic radionuclide grows in according to the equation:

$$C(x,t) = P_{\cos}e^{-\rho x/\Lambda}(1 - e^{-(\lambda+\varepsilon\rho/\Lambda)t})/(\lambda + \varepsilon\rho/\Lambda)$$

where x is the depth of the sample when C is measured. Setting $x = 0$ and $t = T$ corresponds physically to placing the moldavite at a depth equal to $T\,\text{Ma}\times\varepsilon$ (cm/Ma) when it formed so that it would have reached the surface, $x = 0$, only recently. Compared to the two-stage Case 2a, this model smoothes over the abrupt change in production rate, and lowers average production during the second stage of irradiation. To be specific, a high average erosion rate of 1 cm/ka sustained for 14.4 Ma would excavate a sample initially at a depth of 144 m. Under these conditions we find for $C(^{10}\text{Be})$ 0.8×10^6 atom/g and for $C(^{36}\text{Cl})$, 1.4×10^5 atom/g, values similar to those obtained in Case 1b. Higher erosion rates lower the ^{10}Be concentration and are

ruled out. Lower erosion rates are possible, but only if taken in conjunction with more complex sequences of events: deep burial, rapid partial excavation, steady erosion.

4.2.10. Meteoric ^{10}Be in moldavite?

In sum, a constant irradiation at a mean depth of ~500 g/cm^2 (~2 m below the surface) seems to capture the essential features of the moldavite's terrestrial exposure to cosmic rays. As a side benefit, burial at 500 g/cm^2 might help protect the object from weathering. In the context of this exposure history, if the experimental upper limit on the ^{36}Cl concentration is taken at face value, it implies that no more than half the ^{10}Be in the moldavite can be cosmogenic. By elimination, then, a concentration of ~4×10^5 atom/g may be meteoric. At the time of moldavite formation, the concentration of meteoric ^{10}Be would have been 300×10^6 atom/g, a value squarely in the range of typical terrestrial sediments. This is our preferred interpretation.

5. CONCLUSIONS

Nine Ivory Coast (IVC) tektites contain on average 22×10^6 atom ^{10}Be/g. As this value exceeds greatly the maximum possible one from cosmic ray production *in situ*, the only plausible source for most of the ^{10}Be is meteoric, i.e., ^{10}Be made in the atmosphere, brought down by precipitation, and adsorbed onto the surfaces of relatively small grains at the site of the impact. After correction to the time of tektite creation, the concentrations of ^{10}Be in the IVC tektites are considerably lower than those measured in contemporary soils from the Lake Bosumtwi area or in Australasian tektites. The lower concentrations may reflect any of several factors, but we are drawn to the possibility that IVC tektite formation took place in a region where cover by particles in the right size range was thin and leaching and/or erosion limited the inventory of ^{10}Be. It seems clear, however, that the IVC tektites, like the Australasian tektites, formed at least in part from loosely consolidated surface materials.

Etching experiments show that the ^{10}Be concentration decreases rapidly with depth in the outermost 0.2 cm of a 23-g moldavite originally ~2.5 cm in diameter. The shape of the depth profile demonstrates the presence of a surface component, probably associated with adhering grains of modern soil and, to a lesser degree, penetration of ^{10}Be in ground water. The innermost portion of the moldavite, which comprised ~85% of the total mass, contained 0.8×10^6 atom ^{10}Be/g, but too little ^{36}Cl to detect. We argue that the ^{10}Be was not due to surface contamination, and therefore was either present when the tektite formed or was produced later, in the moldavite itself, by cosmic-ray irradiation. The absence of detectable ^{36}Cl, which comes largely from production *in situ*, constrains the range of possible irradiation histories for the sample. The simplest and most compelling exposure histories make only about half the measured ^{10}Be concentration, although it is possible to construct more elaborate ones that account for all of it. If we assume that half the measured ^{10}Be is meteoric and that the moldavite behaved as a closed system, then the precursor grains had a ^{10}Be concentration of about

300 × 10^6 atom/g 14.4 Ma ago. Beryllium-10 concentrations in modern soils are comparable. Confirmation that moldavite interiors contained ^{10}Be when they formed would be desirable. A more extensive series of etches and the measurement of additional cosmogenic radionuclides such as ^{26}Al and ^{53}Mn could supply the necessary evidence. For now we conclude that the available data are consistent with formation of Central European tektites from loosely consolidated surface materials. This reinforces the conclusion (e.g., Koeberl, 1994) that tektites formed early in the crater formation process, before the transient cavity was excavated.

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