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Research paper

Authigenic Be as a tool to date river terrace sediments? – An example from a Late Miocene hominid locality in Bulgaria

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ABSTRACT

A hominid tooth found in a river terrace layer from Azmaka (Bulgaria) has been biochronologically dated to ~7 Ma. This age is younger than expected and indicates that hominids became extinct in Europe later than previously thought. In this study, authigenic $^{10}Be/^{9}Be$ is applied to potentially determine the absolute age of the Miocene river terrace layers containing the hominid tooth. Modern fluvial channel bed deposits provide the initial starting value for the geochronological clock. Homogeneity of modern fluvial channel bed deposits and closed-system behavior of the authigenic minerals in the river terrace layers are required. $^{10}Be/^{9}Be$ ratios analyzed for modern fluvial channel beds vary by a factor of two. The initial starting value for the geochronological clock is not well-constrained and age calculations uncertain. Furthermore, the $^{10}Be/^{9}Be$ ratios analyzed for different cycles of the terrace layers are variable within different layers and do not decrease with formation depth. The mean authigenic age based on the mean $^{10}Be/^{9}Be$ ratio from six terrace layers and using the mean initial ratio from measured modern fluvial channel bed samples is 5.80 ± 0.70 Ma. An authigenic $^{10}Be/^{9}Be$ age of 6.20 ± 0.41 Ma is calculated for the river terrace layer associated with the hominid tooth. Despite these first promising ages, the method of authigenic minerals to date river terrace sediments needs further and more detailed investigations.

1. Introduction

The knowledge of the appearance and extinction of European hominids is of great importance to understand the evolution of human kind. To date, it is widely assumed that great apes became extinct on the European continent during the Late Miocene, between 9.5 and 8.7 Ma (Koufos, 2003; Agusti et al., 2003), due to climate (increasing seasonality) and vegetational changes (from evergreen to deciduous; Agusti et al., 2003). However, a single tooth of a hominid (attributed to cf. *Ouranopithecus* sp.), found in Bulgaria in a proto-savannah biome, is biochronologically dated to ~7 Ma (Spassov et al., 2012). This age challenges the commonly held assumption and indicates that European hominids had a much larger environmental plasticity than previously assumed. This unexpected result opens new research avenues and supports the hypothesis that a significant part of human evolution might have also happened outside of Africa, e.g., in Europe or Western Asia (Begun et al., 2012).

However, the absolute dating of Miocene vertebrate fossils remains difficult. Relative and absolute age determinations are usually done by fossil assemblages (biochronology), magnetostratigraphy, and Ar/Ar-dating of ash layers in terrestrial sediments. Unfortunately, these techniques are not always applicable. Meteoric ^{10}Be concentrations in soils of a chronosequence have been applied to date the formation age of soils (Pavich et al., 1984). However, this attempt to date soil formation with meteoric ^{10}Be was subjected to some difficulties, which were addressed step by step in the following years (e.g., Maejima et al., 2004; Pavich and Vidic, 1993). In the last years, meteoric ^{10}Be measurements have been applied more and more frequently. As for instance, the applications range from: 1) catchment-wide denudation rates (e.g.,

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von Blanckenburg et al., 2012); 2) tracking of sediment sources (e.g., Reusser and Bierman, 2010); 3) soil denudation rates (e.g., Graly et al., 2010); and 4) regolith production and transport (e.g., Jungers et al., 2009; Bacon et al., 2012; West et al., 2013, 2014). Another application to date sediment deposits is the use of $^{10}Be/^{9}Be$ ratios measured in authigenic minerals (Barg et al., 1997). This technique has been successfully applied in lacustrine sediment deposits to date the age of hominids in Chad (Lebatard et al., 2008, 2010). Remains of *Australopithecus bahrelghazal* and *Sahelanthropus tchadensis* had been found in two locations. Biochronological estimates indicate ages of late Pliocene (3–3.5 Ma) and Late Miocene (~7 Ma), respectively. Based on $^{10}Be/^{9}Be$ ratios in authigenic minerals, *A. bahrelghazali* is dated to 3.58 ± 0.27 Ma, whereas the age of *S. tchadensis* is bracketed between 6.8 and 7.2 Ma (Lebatard et al., 2008, 2010). In order to use the $^{10}Be/^{9}Be$ ratios in authigenic minerals for age determinations, two conditions need to be fulfilled: a) closed system behavior and b) known initial concentration. Therefore, Lebatard and co-workers (2008 and 2010) applied the technique in a deflation basin which allows the prerequisite of closed system behavior and the input signal to be fairly well constrained. These special conditions encountered in the northern Chad Basin demonstrate that the $^{10}Be/^{9}Be$ ratios in authigenic minerals can be used to date the deposition of continental sediments from 1 to 8 Ma.

In this study, the method of authigenic $^{10}Be/^{9}Be$ to determine deposition ages has been expanded to clastic sediments of fluvial terraces with the goal to determine absolute ages of clastic sediments up to 10 Ma. The initial ratio of Be isotopes needed for age determination is derived from modern fluvial channel beds. River terrace samples analyzed for this study are collected from the Ahmatovo Formation (Upper Thrace Basin) in the quarries of Azmaka near Chirpan, Bulgaria (see Fig. 1), yielding the tooth cf. *Ouranopithecus* (Spassov et al., 2012). The Ahmatovo Formation (Kojumdgieva and Dragomanov 1979) represents fluvial deposits of the Neogene palaeo-Maritsa river and its tributaries (Dragomanov et al., 1981; for the distribution of the Ahmatovo Formation in the study area see Fig. 1). The age determination presented in this study is based on $^{10}Be/^{9}Be$ ratios measured with the novel carrier-free method (Christl et al., 2010; Lachner et al., 2013). In order to cross-check the validity of the carrier-free method in clastic sediments, several samples were measured with the traditional method using ^{9}Be carrier.

2. Study area and characteristics of sample material

The study area, belonging to the Upper Thrace Basin (Central Bulgaria), is drained by the Maritsa River and is bordered to the north by the Sredna Gora Mountain, where all northern tributaries of the Maritsa River originate (Fig. 1 after map of Boyanov et al., 1990). The present-day climate is continental to continental-mediterranean (Kopralev, 2002). The mean temperature is 11.5–12.5 °C with about 550 mm rain a year. Today, the region is drained by several small to very small northern tributaries of the Maritsa River (Fig. 1). The Sazliika River is one of the largest and has a length of 145 km and a drainage area of 3.298 km^2. Several other small rivers such as the Starata River (267 km^2) and Omurov River (308 km^2) drain the area around Chirpan. The mean slope for the entire catchment area is 6.0° for the Omurov River, 6.7° for the Starata River, and 3.4° for the Sazliika River. These three rivers in the area near Azmaka have been selected to retrieve a regional $^{10}Be/^{9}Be$ ratio potentially similar to the Miocene initial ratio.

Land use within the catchment area of the selected rivers upstream of the sampling points is limited to local and non-industrial pasture and crop farming and local digging for Late Cretaceous limestone and Proterozoic granite in the Sredna Gora Mountains (Kopralev, 2010). Furthermore, this area is protected as a natural landmark (Kopralev, 2010). Archaeological investigations along the Omurov River (about 8 km to the northwest of the Azmaka outcrop) revealed, that the area has been settled by farmers at least since the late Neolithic, about 7.500 years before present (Nikolov, 2011). Physical erosion rates based on sediment load data from the Maritsa River indicate values ranging between 4 and 16 mm/ka (after Rousseva et al., 2006). These are relatively low erosion rate values. In contrast, extreme erosion rate values from grassland and crop farming in other regions of Bulgaria may be as high as ~200 mm/ka (after Rousseva et al., 2006).

The catchment areas of the Omurov and Starata Rivers comprise Cretaceous and Eocene marine sediments, whereupon the uppermost reaches of the Omurov River flow through Proterozoic gneisses and granites. The catchment of the Sazliika River (upstream of the sampling point) comprises mainly Cretaceous flysch and Quaternary fluvial clastics, but reaches into gneisses and granites (see Fig. 1).

The investigated Ahmatovo Formation, consisting of fluvial sands and gravel of Late Miocene and younger and may be earliest Pleistocene age (Kojumdgieva and Dragomanov, 1979; Dragomanov et al., 1981), can be up to 300 m thick, but is generally less than 100 m thick. According to the paleo-geographic reconstruction of Dragomanov et al. (1981) their deposits in our working area, north of Chirpan, represent a northern tributary of the Paleo-Maritsa River. The Ahmatovo Formation in the Azmaka outcrop (abandoned sand-pits, Fig. 1, Table 1) represents six fining up-ward cycles in a 26 m thick stratigraphy (Fig. 2A). All six cycles are covered by generally weakly developed paleo-soils. Only cycles 1 and 6 contain abundant pedogenic carbonate. The lower 13 m of the Ahmatovo Formation in the Azmaka Quarry, formed by cycles 1 and 2, are characterized by medium to coarse gravels (up to boulder size) and are attributed to a braided river. The upper 13 m contain cycles 3, 4, 5, and 6. Cross-bedding structures and finer grain-size fractions than in the lower 13 m indicate that the river depositing these cycles was partly meandering. The sedimentary archive provides no indication of an unconformity within the different cycles. Sedimentation in one cycle is believed to be rather fast within ten thousands of years and the whole 26 m of the Ahmatovo Formation in the Azmaka Quarry within several hundred thousands of years (no major faunal development).

Within the petrographic composition of the terrace sediments (gravel fraction) granites and vein quartz dominate equally (31–47 % and 29–49 % respectively), whereas sedimentary clasts (usually Cretaceous flysch) and gneiss are sub-ordinate (11–27 % and 0–3 %, respectively; Bonitz, 2013). This data indicates that the paleo-catchment area of this northern paleo-Maritsa tributary involves mainly proterozoic granites and metamorphites, as well as Cretaceous flysch, and is, therefore, best comparable to the present-day catchment of the Omurov River (Fig. 1).

Many fossil mammals are excavated in the terrace material, and they also appear to be biochronologically homogeneous (Spassov et al., 2012). The most interesting discovery is the cf. *Ouranopithecus* tooth from cycle 4 with a biochronologic age constraint to ~7 Ma (Spassov et al., 2012). The paleo-climatic conditions in southeast Europe at around 7 Ma were not well-constrained, but mammalian faunas suggest a savannah type ecosystem (Spassov et al., 2012).

3. Methods

3.1. Age determination with authigenic ^{10}Be

In pioneering studies, Monaghan et al. (1983) and Pavich et al. (1984, 1985, 1986) used the inventory of meteoric ^{10}Be depth

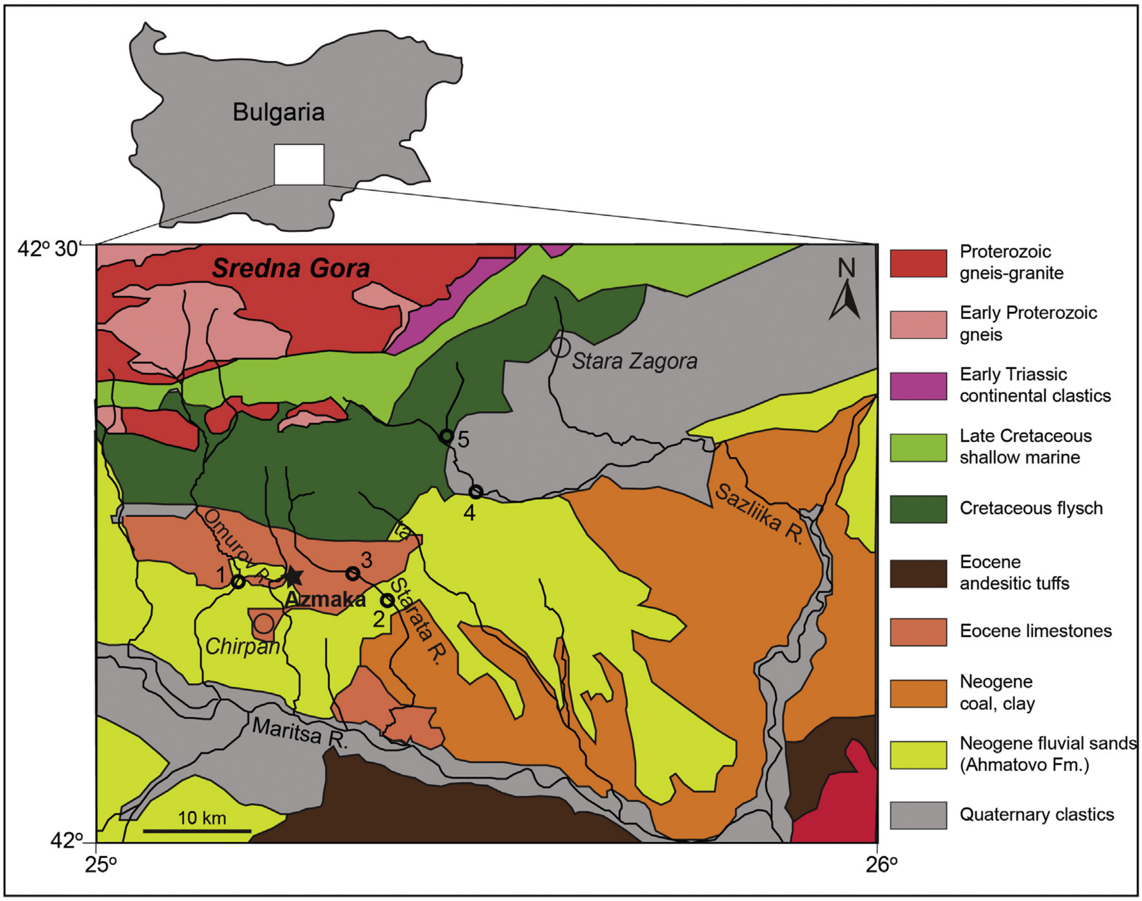

Fig. 1. Geologic map (after Boyanov et al., 1990) showing an overview of sample locations. Miocene terrace samples are collected in the Azmaka Quarry near Chirpan, Bulgaria (black star). River sediment samples are from three different rivers draining the area around Chirpan (circles).

profiles in soils for the age determination of soil formation. The model calculation they presented, called the open system (e.g., Barg et al., 1997), needed more refinement in order to be a reliable method to date soil formation ages. Lal et al. (1991) suggested to use the so called closedsystem method where ^{10}Be/^{9}Be ratios in authigenic minerals are used as chronometers. Barg et al. (1997) addressed this model to calculate soil formation ages with experimental data. However, they concluded that the present work still has to be pushed considerably. Ten years later, Lebatard et al. (2008 and 2010) applied the authigenic ^{10}Be measured in Holocene lake and Miocene and Pliocene sedimentary deposits to date the age of hominids.

^{10}Be is mainly produced in the atmosphere and locked into authigenic minerals at the time of mineral formation. Due to radioactive decay the amount of ^{10}Be decreases. If the decrease in concentration can be determined, a formation age of the authigenic mineral can be assessed. If the transport of the authigenic mineral is short (e.g., in a river) or non-existing (e.g., in a terrace), then the formation age is a deposition age of the fluvial sediment. However, two critical assumptions need to be made for an age determination: a) closed system behavior and b) known initial concentration. Closed system behavior is achieved when no ^{10}Be is added or lost after deposition except by radioactive decay. Conditions, which favor such closed system behavior, exist in arid regions or for samples collected at depth and, hence, shielded from surface processes and climatic influence. The initial concentration of ^{10}Be in sediment deposited in fluvial terraces can potentially be deciphered from the load transported in modern river channel beds. The absolute ^{10}Be concentration depends on additional parameters. The measured ^{10}Be concentration can be affected by parameters such as scavenging efficiency during mineral formation and/or the specific surface area of the sedimentary particles. In order to correct for such effects, a normalizing isotope needs to be used: stable ^{9}Be.

^{10}Be and ^{9}Be have different sources (atmospheric versus detrital), but they behave the same during authigenic mineral formation. Therefore, only the fraction accumulated during authigenic mineral formation needs to be extracted. The measured ^{10}Be/^{9}Be ratio can then be used to determine formation ages. For a successful age determination t (a), the initial ratio ^{10}Be/^{9}Be$_{init}$, the present ratio of the terrace material ^{10}Be/^{9}Be$_{present}$ as well as the decay constant λ (1/a) need to be known:

$$t = -\left(\frac{1}{\lambda}\right) \times \ln\left[\frac{(^{10}Be/^{9}Be)_{present}}{(^{10}Be/^{9}Be)_{init}}\right] \quad (1)$$

The initial ratio of sediment deposit can be derived from, e.g., modern fluvial channel bed deposits. Modern fluvial channel bed deposits can represent the erosion product, which is stored in river terraces. River sediments from one location and the authigenic signature are expected to be relatively well-mixed and homogeneous. However, the authigenic signature of the fluvial channel bed deposit from different locations and rivers might be variable due to variable rates and styles of denudation, and variable lithologies eroded. In addition, the authigenic mineral might not yet be in equilibrium with the river water. The possible inhomogeneities in the material providing the initial ratio will lead to a scatter in

Table 1
Sample information from the Azmaka terraces and modern river bed deposits, Bulgaria.

Sample	Location	Coordinates		Altitude	Cycle	Profile depth	Sample depth
		N	E	m		m	m
Azmaka terrace sediments							
10AZM016	Azmaka 4	42.2317	25.3328	218	5	17–22	2.6
10AZM017							
10AZM019	Azmaka 4	42.2317	25.3328	218	5	17–22	2.6
10AZM020							
10AZM021							
10AZM013	Azmaka 4	42.2317	25.3328	218	4	15–17	3.0
10AZM014							
10AZM015							
10AZM031	Azmaka 2	42.2336	25.3374	226	3	13–15	5.0
10AZM032							
10AZM033							
10AZM028	Azmaka 2	42.2340	25.3372	224	2	7–13	3.0
10AZM029							
10AZM030							
10AZM034	Azmaka 2	42.2342	25.3367	223	2	7–13	1.0
10AZM035							
10AZM036							
Active river sediment							
10OMU001	Omur (1 in Fig. 1)	42.2303	25.2561	165			
10OMU002							
10OMU003							
10STA001	Starata (2 in Fig. 1)	42.2243	25.4196	185			
10STA002							
10STA003							
10STA004	Starata (3 in Fig. 1)	42.2393	25.3900	206			
10STA005							
10STA006							
10SAZ001	Sazliika (4 in Fig. 1)	42.3393	25.5114	220			
10SAZ002							
10SAZ003							
10SAZ004	Sazliika (5 in Fig. 1)	42.3674	25.4756	247			
10SAZ005							
10SAZ006							

measured $^{10}Be/^{9}Be$ ratios. As a result, the starting point of the decay clock is not precisely known, and uncertainties on the calculated deposition ages could be large (see results and discussion).

3.2. Sample collection and preparation

The 6 sedimentary cycles of the Ahmatovo Formation in Azmaka were collected from as deep as possible below the present surface. However, the local outcrop situation provided several constraints (Fig. 2B). Cycles 2, 3, 4, and 5 were sampled from reasonable depths (>2 m). However, samples 10AZM034 to 036 from cycle 2 were collected from only 1 m below the present surface (Table 1). No samples from deep below the present surface were available for cycles 1 and 6. Each depth in the profile was sampled three times in order to average out possible inhomogeneities in the sediment deposit. A total of six different locations were sampled and treated for Be-analysis.

Three modern rivers draining present-day catchments of the region were chosen to represent the initial $^{10}Be/^{9}Be$ ratio for age calculations: Starata River (10STA001 to 006) and Sazliika River (10SAZ001 to 006) were sampled at two different locations, and Omurov at one location (10OMU001 to 003, see Fig. 1). At each location three samples were collected out of the modern fluvial channel bed deposits. Samples from the same location were measured either individually or as a mixture of three samples contributing equal amounts. A total of five different locations were sampled and treated for Be-analysis to retrieve a regional $^{10}Be/^{9}Be$ ratio potentially similar to the Miocene initial ratio.

One gram of the powdered <2 mm size fractions of alluvial and terrace sediments were weighed in as individual samples. In the case of mixed samples, 1 g of mixed powder consisting of equal parts of each sample material was used. Two mixed terrace samples and two mixed river samples were prepared the traditional way using ^{9}Be carrier. The traditional method is based on the addition of some ^{9}Be carrier in order to handle the sample for $^{10}Be/^{9}Be$ ratio measurement by accelerator mass spectrometry (AMS). For the traditional sample preparation with carrier (e.g., Bourles et al., 1989), the sample is leached for 3.5 h at 95 °C with 20 ml of 0.04 M NH_2OH-HCl in 20 ml 25% acetic acid. The leachate is separated from the solid sample by centrifugation. After separation of 2 ml of leachate for ^{9}Be concentration measurement, the remaining leachate is spiked with 0.3 ml of a 1 mg/g ^{9}Be spike. The spiked solution is transferred into hydrochloric acid. Fe is separated from Be with a 2 ml BioRad AG1x8 column. The dry sample is mixed with oxalic acid and centrifuged. The supernate solution is dried down. A 1 ml BioRad AG50x8 column is used to clean Be further from other elements in the sample. After a precipitation with NH_4OH, the sample is rinsed several times with H_2O. The precipitate is baked to BeO. The $^{10}Be/^{9}Be$ ratios of the spiked samples were measured at the Tandy AMS facility (Müller et al., 2010). The measured $^{9}Be/^{10}Be$ ratios of the spiked samples were normalized to the ETH Zurich in house standard S2007N with a nominal ratio of 28.1×10^{-12} (Christl et al., 2012). The ^{9}Be concentrations of the sample materials were determined by standard addition with a Quadrupol ICP-MS at ETH Zurich.

In the case of the carrier-free sample preparation, samples were treated as described in Lachner et al. (2013). This procedure is comparable to the traditional sample preparation, just that no ^{9}Be carrier is added and that before the final precipitation 1 mg of Fe-carrier is added. After mixing with 4 mg Nb powder (325 mesh),

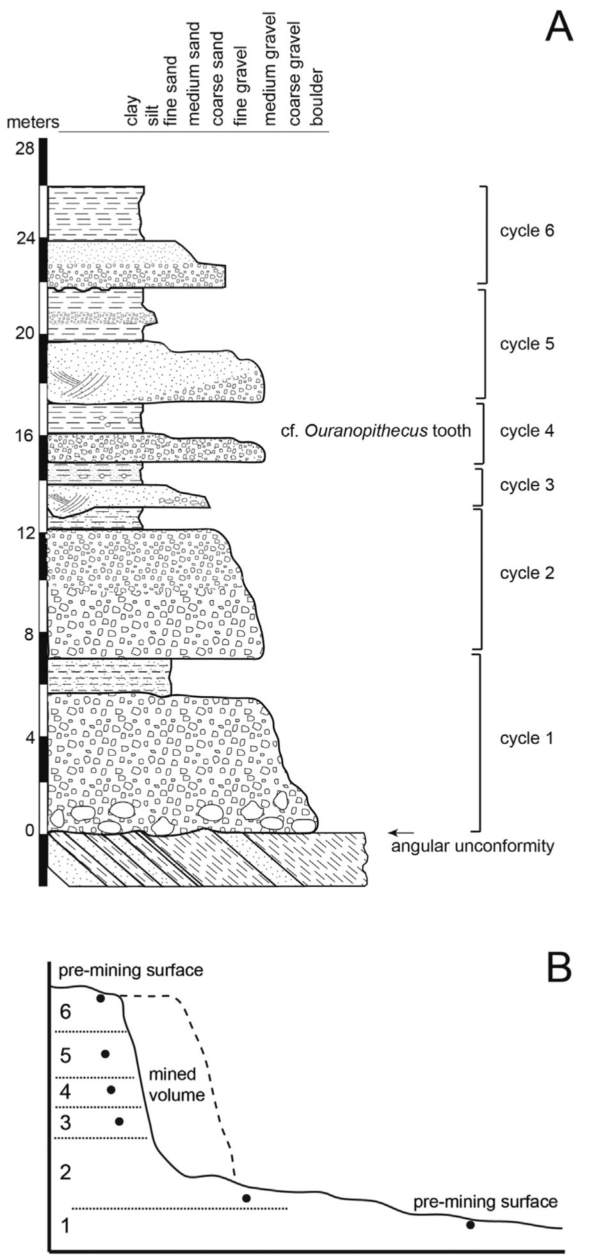

Fig. 2. Stratigraphy of the Ahmatovo Formation observed in the Azmaka Quarry near Chirpan, Bulgaria. A) Miocene sedimentation starts with angular unconformity over latest Oligocene to early Miocene sediments (Dragoynovo Formation, Kojumdgieva and Dragomanov, 1979). The Ahmatovo Formation consists of 6 cycles. Cycles 1 and 2 were formed by a braided river system, whereas cycles 3 to 6 developed under meandering river conditions. The hominid tooth is attributed to cycle 4. B) Sketch of the actual outcrop situation in the abandoned quarry. Most samples of cycles 2, 3, 4, and 5 could be collected from acceptable depths below present-day surface (>2 m). Some samples of cycle 2 were collected close to the present-day surface and are possibly affected by open-system behavior.

the sample is pressed into a cleaned titanium holder and $^{10}Be/^{9}Be$ ratios are measured at the Tandy AMS facility (Christl et al., 2010; Lachner et al., 2013). The measured ratios were normalized to the ETH Zurich in house standard S1 with a nominal ratio of 95.1×10^{-9} (Christl et al., 2012). All errors in this study are 1σ errors.

3.3. Data treatment of carrier-free measurements

Samples for initial ratio and age determination were prepared for measurement in two different ways: a) samples from one location were mixed in equal parts before chemical treatment and analysis, and b) samples from one location were prepared and measured individually and averaged afterwards. Consequently, a variety of averaging steps had to be employed while determining the quantities required for age calculation (eq. (1)) in order to include as much data as possible but still give fair weights to all results.

The initial $^{10}Be/^{9}Be$ ratio for the age calculation was determined based on the $^{10}Be/^{9}Be$ ratio measurements of mixed and individually measured samples from modern fluvial channel beds. Individually prepared and measured samples (a) were combined via an arithmetic average to a combined sample ratio in order to get results comparable to the mixed samples (b). Replicate measurements of the same sample were combined as an error-weighted average. A combination of averaged replicate ratios and averaged individually measured sample ratios was also based on an error-weighted ratio (e.g., 10STA004/005/006). The mean initial ratio was then estimated as the arithmetic mean of the internally averaged five modern sample locations.

Ages of different terrace locations are calculated from the related $^{10}Be/^{9}Be$ ratios by internally averaging the measured ratios of a sampling location according to the procedure explained above for the initial ratios of the river sediments (mixed and individual samples). The thus averaged ratios were then used with the mean initial ratio and the half-life of ^{10}Be (1.387 ± 0.012 Ma; Chmeleff et al., 2010; Korschinek et al., 2010) to calculate the ages of the individual sampling locations (eq. (1)).

Additionally, a mean terrace age (an analog to the mean initial ratio) calculated from the mean $^{10}Be/^{9}Be$ ratio of the six different sample locations is presented. This approach of giving only one age for the terrace is motivated and justified by the observation of no major faunal development in all six terrace cycles indicating a duration of the terrace formation of less than 1 Ma.

Errors of the mean ratios are estimated via the error weighted deviations of the single ratios to the mean ratio. The error of an age is derived by Gaussian, independent error propagation of ratios and ^{10}Be half-life. All errors presented in this study are 1σ errors. In order to illustrate the influence of the heterogeneous initial ratios on the calculated ages, additionally, the lowest and highest measured initial ratios were used to determine minimum and maximum ages, respectively (see results).

4. Results

4.1. Comparison of traditional and carrier-free methods

Two fluvial terrace samples (10AZM016/017 and 10AZM031/032/033) and two modern fluvial channel bed deposit samples (10SAZ001/002/003 and 10AZM031/032/033) were measured for comparison of the traditional and the carrier-free methods (Tables 2 and 3, Fig. 3). For the analysis of the traditional method all samples were mixed before Be-extraction. Values based on the traditional method from fluvial terrace cycle 3 (10AZM031/032/033) and 5 (10AZM016/017) differ by almost an order of magnitude. The values of two river samples analyzed with the traditional method agree within error. In the case of the carrier-free method, some samples were analyzed separately, whereas others were mixed before analysis. The separately analyzed, carrier-free samples agree within errors in the case of the river sample, but lie just outside statistical agreement in the case of the samples from cycle 3 (Samples 10AZM031/032/033 have a chi-square value of 6.32 with 2 degrees of freedom (p-value = 0.042)).

The first terrace sample (10AZM016/017) was analyzed by the traditional and carrier-free methods and samples prepared as

Table 2
Traditional authigenic $^{10}Be/^{9}Be$ measurements.

Sample	Weight	m (^{9}Be) sample	Error	m(^{9}Be) carrier	$^{10}Be/^{9}Be$ meas.	Error	$^{10}Be/^{9}Be$ authigenic	Error
	g	g	g	g	10^{-12}	%	10^{-12}	%
Azmaka terrace sediments								
10AZM016/017	0.9810	4.14E−07	1.23E−08	2.95E−04	0.759	2.9	539	4.1
10AZM031/032/033	1.0372	1.74E−07	5.20E−09	2.97E−04	0.042	13.8	66.7	15.3
Modern river bedload								
10SAZ001/002/003	0.9936	1.43E−07	4.66E−09	2.96E−04	2.50	1.5	5166	3.6
10OMU001/002/003	0.9709	1.53E−07	4.32E−09	2.96E−04	2.82	1.5	5443	3.2

Table 3
Carrier-free authigenic $^{10}Be/^{9}Be$ measurements of modern fluvial channel bed deposits (initial ratio).

Sample	Map location	$^{10}Be/^{9}Be$ authigenic[a]	$^{10}Be/^{9}Be$ authigenic[b]
		10^{-10}	10^{-10}
10OMU001	1	57.8 ± 1.1	
10OMU002	1	58.5 ± 1.4	57.3 ± 1.4
10OMU003	1	55.6 ± 1.4	
10STA001/002/003	2	128 ± 5	
10STA001/002/003B	2	120 ± 4	124 ± 3
10STA004/005/006	3	68.3 ± 1.6	
10STA004/005/006B	3	106 ± 2	
10STA004	3	103 ± 2	94.9 ± 12.5
10STA005	3	107 ± 2	
10STA006	3	107 ± 2	
10SAZ001/002/003	4	53.1 ± 1.5	53.1 ± 1.5
10SAZ004	5	67.4 ± 3.0	
10SAZ005	5	58.8 ± 2.2	64.6 ± 3.2
10SAZ006	5	67.7 ± 3.6	
		Mean[c]	78.7 ± 15.6

[a] Measured values of mixed and individual samples.
[b] Average value of sample location. Individual samples are combined as an arithmetic average. Replicates are combined as an error-weighted average. Combination of replicate values and averaged individual sample values are error-weighted averages.
[c] Arithmetic mean; errors are all one sigma errors.

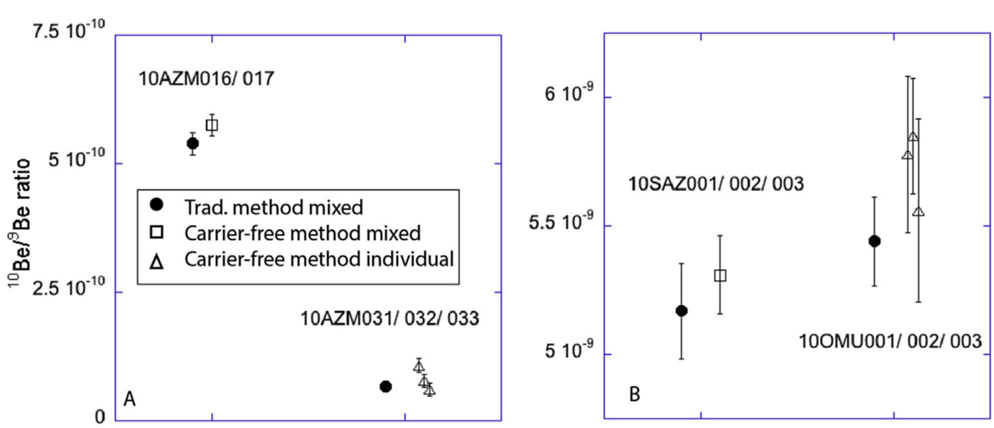

Fig. 3. Comparison of $^{10}Be/^{9}Be$ ratios measured with the traditional ^{9}Be-carrier method and the carrier-free method. A) Two samples from the terrace sequence were analyzed. While a combined sample 10AZM016/017 was analyzed for both methods, sample 10AZM031/032/033 was analyzed as individual samples with the carrier-free method and a combined sample with the traditional method. B) Two samples from modern fluvial channel bed deposits were selected and analyzed the same way as described in A). Note the change in scale of the y-axes. Errors are 1 sigma.

mixed samples. The two methods agree within error (Fig. 3A). The second terrace sample (10AZM031/032/033) was analyzed separately for the carrier-free method, where as the traditional method used a mixed sample. The average of the individual carrier-free analyses agrees with the value from the traditional method. For the first river sample (10SAZ001/002/003) a sample mixture was analyzed for both methods and the results agree within error. For the second river sample (10AZM031/032/033) the powders were analyzed separately by the carrier-free method, but as a mixture by the traditional method. The average of the carrier-free measurements of the individual samples agrees well with the value determined by the traditional method (Fig. 3B).

After successful comparison of these traditionally analyzed samples with the carrier-free method, further samples were analyzed with the carrier-free method only. The carrier-free method determines the natural $^{10}Be/^{9}Be$ ratios directly by only one AMS measurement. The information of the ^{10}Be and ^{9}Be concentrations, however, is not available by measuring with the carrier-free method.

4.2. Initial $^{10}Be/^{9}Be$ ratio

The determination of the initial $^{10}Be/^{9}Be$ ratio is based on the analysis of bed deposits from modern fluvial channels. The measured $^{10}Be/^{9}Be$ ratios are highly variable. They range from as low as 53.1×10^{-10} (e.g., 10SAZ001/002/003, see Table 3 and Fig. 4) to values as high as 128×10^{-10} (e.g., 10STA001/002/003). In Table 3, individually measured samples from one location were combined as an arithmetic average for further initial ratio calculation. The mean $^{10}Be/^{9}Be$ ratio of all the combined data is $(78.7 \pm 15.6) \times 10^{-10}$. Due to the heterogeneity in the ratios from the different rivers, the error on the mean initial ratio is relatively large. The general trend is that the rivers Sazliika and Omurov give low values (lower than 100×10^{-10}). In contrast, the river Starata produces all the high values (higher than 100×10^{-10}). Only 10STA004/005/006 shows a $^{10}Be/^{9}Be$ ratio comparable to the ratios measured in samples from the Sazliika and Omurov rivers.

4.3. Age determination

$^{10}Be/^{9}Be$ ratios measured on individual terrace samples from a given terrace generally agree well with each other and also with mixed terrace samples from the same terrace (Table 4 and Fig. 5). The $^{10}Be/^{9}Be$ ratios across all terrace samples are variable and range from 0.77×10^{-10} (10AZM032) to 13.4×10^{-10} (10AZM019). An expected clear trend in decreasing $^{10}Be/^{9}Be$ ratios with stratigraphic depth cannot be observed. The ratios decrease from the top of the stratigraphy to the samples collected in cycle 3. Ratios in samples from cycle 2, which is stratigraphically below cycle 3, are higher than in cycle 3. Individual samples from one sampling depth are averaged to yield one value.

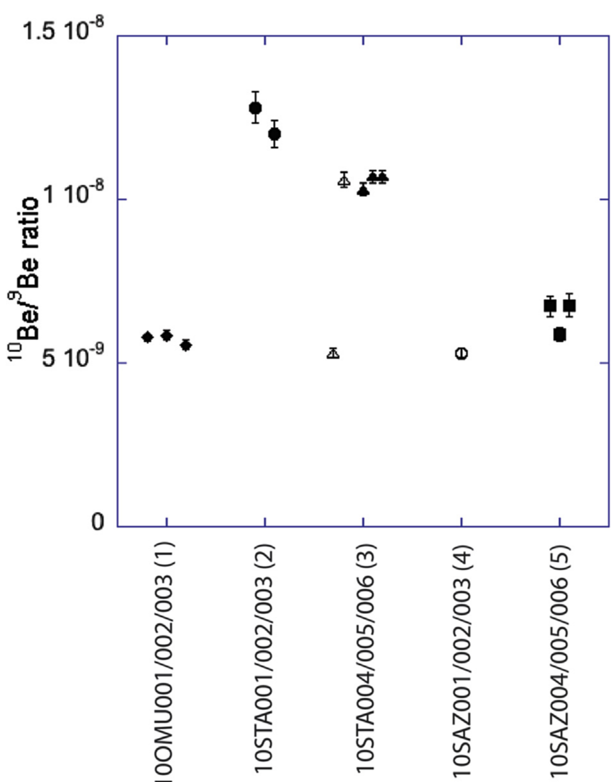

Fig. 4. $^{10}Be/^{9}Be$ ratio measurements for individual and mixed samples from modern fluvial channel bed deposits of three different rivers. Two rivers were collected at two different locations. The $^{10}Be/^{9}Be$ ratios are very inconsistent. The initial $^{10}Be/^{9}Be$ ratio used for the starting clock in the age calculation is determined by the mean of the presented values (see also Table 3).

Using the mean initial ratio, the youngest age is determined in cycle 5 (5.24 ± 0.41 Ma) and the oldest age in cycle 3 (9.15 ± 0.54 Ma). However, as $^{10}Be/^{9}Be$ ratios are higher in terrace cycle 2 than cycle 3, the ages also decrease to 5.66 ± 046 Ma for cycle 2 (Fig. 6). The error weighted average age for the samples 10AZM013 to 015 collected in cycle 4 is 6.20 ± 0.41 Ma. The mean terrace age estimated from the mean ratio of the different terrace locations amounts to 5.80 ± 0.70 Ma.

A minimum age calculation using the lowest measured initial $^{10}Be/^{9}Be$ value decreases the ages by a constant offset of 0.79 Ma. The use of the highest measured value as the initial $^{10}Be/^{9}Be$ ratio increases the ages by an offset of 0.90 Ma (maximum age). For instance, the minimum age for the combined sample 10AZM013/014/015 (Cycle 4 associated with the hominid tooth) is 5.41 Ma, whereas the maximum age is 7.10 Ma. Some reasons for this large scatter in $^{10}Be/^{9}Be$ ratios in modern river sediments and terraces and the resulting uncertainties are discussed below. Certainly, more detailed investigations, which go beyond the scope of this paper, are needed to better constrain the systematic uncertainties of this method.

5. Discussion

5.1. Initial $^{10}Be/^{9}Be$ ratio

One of the crucial assumptions for the age determination with authigenic $^{10}Be/^{9}Be$ ratios from river terraces is the knowledge of the initial $^{10}Be/^{9}Be$ ratio. In this study, the $^{10}Be/^{9}Be$ ratios measured in modern fluvial channel bed deposits range from 53.1×10^{-10} to ratios as high as 128×10^{-10}. In comparison, $^{10}Be/^{9}Be$ ratios in the reactive fraction from river sediment of the Amazon basin range from 1.95 up to 60.1×10^{-10} (Wittmann et al., 2012). The $^{10}Be/^{9}Be$ ratios show no dependence on different grain sizes (Wittmann et al., 2012). The highest ratio measured for the Amazon basin is comparable to the minimum ratio measured for the modern fluvial channel bed deposits in this study. Lebatard et al. (2008, 2010) measured $^{10}Be/^{9}Be$ ratios in Holocene Lake Mega Chad to be relatively homogeneous at 272, 246, 266, and 244×10^{-10}. These ratios are a factor of two larger than the maximum value determined in this study.

The ratios measured in the three different rivers of this study vary by a factor of two. The Omurov and Sazliika Rivers show relative homogenous ratios. In contrast, measurements of the Starata bed deposits are generally higher by a factor of two, but can be as low as the values reported from the Omurov and Sazliika Rivers. There are many possible reasons for this observed heterogeneity between rivers and within a river location:

a) Geochemical equilibrium between water and particles: The initial $^{10}Be/^{9}Be$ ratio in the authigenic mineral phase depends on the partitioning between water and particle phases (e.g., Aldahan et al., 1999). It is important to know if the contact between water and particles is long enough to reach geochemical equilibrium. If not, the measured $^{10}Be/^{9}Be$ ratio cannot be used as the initial ratio for age calculations.
b) Lithologies: Different lithologies show variable ^{9}Be concentrations (Staudigel et al., 1998). Whereas the ^{9}Be concentrations may be as low as ~0.5 ppm in carbonates, the concentration in granites may reach ~5 ppm. Depending on the lithologies exposed in the drainage area, the initial $^{10}Be/^{9}Be$ ratio may vary considerably between sample locations as observed in this study.
c) Mineral composition: Due to the denudation of different lithologies and different denudation processes (e.g., soil creep,

Table 4
Carrier-free authigenic $^{10}Be/^{9}Be$ measurements and ages of terrace sediments.

Sample	Cycle	$^{10}Be/^{9}Be$ authigenic[a]	$^{10}Be/^{9}Be$ authigenic[b]	Age[c]	Min. age[d]	Max. age[e]
		10^{-10}	10^{-10}	Ma	Ma	Ma
10AZM016/017	5	5.75 ± 0.20	5.75 ± 0.20	5.24 ± 0.41	4.45 ± 0.10	6.14 ± 0.12
10AZM019/020/021	5	7.35 ± 1.20				
10AZM019	5	13.4 ± 4.2				
10AZM020	5	5.77 ± 1.22	9.43 ± 0.66	4.25 ± 0.42	3.46 ± 0.15	5.15 ± 0.17
10AZM021	5	10.3 ± 0.6				
10AZM021B	5	10.3 ± 0.6				
10AZM013/014/015	4	3.05 ± 0.27				
10AZM013	4	3.89 ± 0.38				
10AZM014	4	3.60 ± 0.23	3.56 ± 0.12	6.20 ± 0.41	5.41 ± 0.10	7.1 ± 0.12
10AZM014B	4	3.47 ± 0.18				
10AZM015	4	3.45 ± 0.18				
10AZM031	3	1.07 ± 0.14				
10AZM032	3	0.772 ± 0.135	0.815 ± 0.148	9.15 ± 0.54	8.36 ± 0.38	10.1 ± 0.4
10AZM033	3	0.602 ± 0.125				
10AZM028	2	2.18 ± 0.31				
10AZM029	2	1.03 ± 0.17	1.83 ± 0.39	7.53 ± 0.59	6.74 ± 0.43	8.43 ± 0.44
10AZM030	2	2.27 ± 0.45				
10AZM034/035/036	2	4.22 ± 0.64				
10AZM034	2	3.43 ± 0.62				
10AZM035	2	5.82 ± 1.15	4.67 ± 0.55	5.66 ± 0.46	4.87 ± 0.24	6.56 ± 0.25
10AZM036	2	6.48 ± 0.48				
		Mean[f]	4.34 ± 1.26	5.80 ± 0.70		

[a] Measured values of mixed and individual samples.
[b] Average value of sample location used in age calculation. Individual samples are combined as an arithmetic average. Replicates are combined as an error-weighted average. Combination of replicate values and averaged individual sample values are error-weighted averages.
[c] Age calculation of sample location using the overall initial ratio and the decay constant of Chmeleff et al. (2010) and Korschinek et al. (2010).
[d] Minimum age calculation using the averaged value with the lowest measured initial ratio (Sample 10SAZ001/002/003) and the decay constant of Chmeleff et al. (2010) and Korschinek et al. (2010).
[e] Maximum age calculation using the averaged value with the highest measured initial ratio (Sample 10STA001/002/003) and the decay constant of Chmeleff et al. (2010) and Korschinek et al. (2010).
[f] Arithmetic mean of ratios of the six terrace locations, which is the basis for the age calculation of the entire terrace sequence using the mean initial ratio.

landslides), the collected sample may have a variable mineral composition.

d) Grain size distribution: Wittmann et al. (2012) showed that $^{10}Be/^{9}Be$ ratios do not vary considerably with grain size smaller than 0.125 mm. The grain size range sampled and analyzed in this study is < 2 mm. $^{10}Be/^{9}Be$ ratios may vary considerably in the larger grain size fractions. The sampled material might show a completely different grain size distribution and different mineral composition. Therefore, the

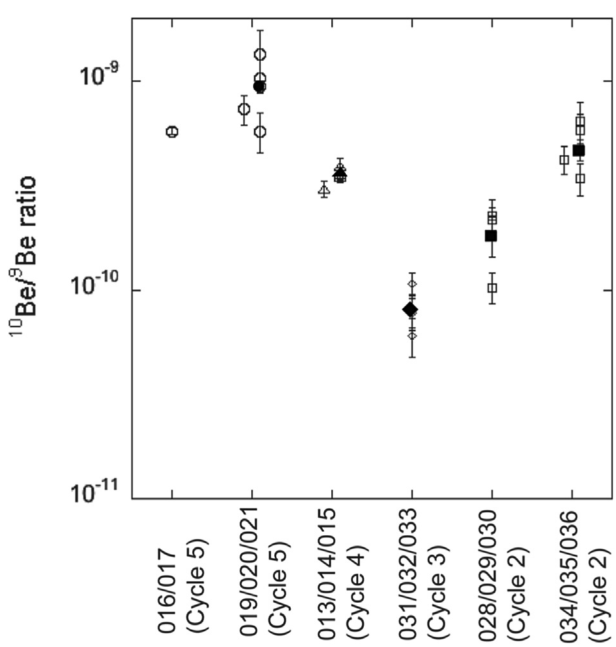

Fig. 5. Authigenic $^{10}Be/^{9}Be$ ratios of terrace samples from different cycles of the Ahmatovo Formation in the Azmaka Quarry. Ratios are measured for individual and mixed samples (from the same depth). The average of the individual samples (black symbols) are in agreement with the measured values of the mixed samples.

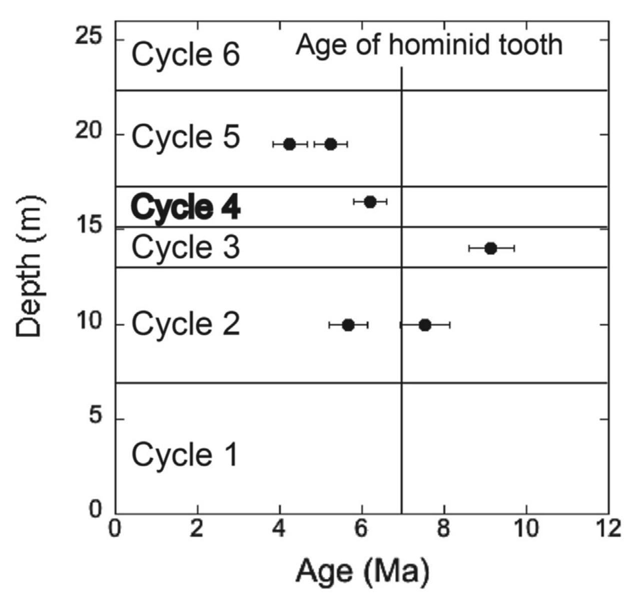

Fig. 6. Authigenic $^{10}Be/^{9}Be$ ages of terrace samples collected from different cycles observed in the stratigraphy of the Azmaka Quarry. Ages increase with depth to cycle 3 (13–15 m in profile depth). Ages from cycle 2 are younger again. Cycle 4, in which the hominid tooth (~7 Ma, Spassov et al., 2012) was found, has an authigenic age of 6.20 ± 0.41 Ma.

measured $^{10}Be/^{9}Be$ ratio may be variable from sample to sample.

e) Denudation rate and mechanism: $^{10}Be/^{9}Be$ ratios can vary considerably within soils (e.g., Barg et al., 1997). Depending on the denudation rate and mechanism (e.g., soil creep, landslides) different layers of soils are eroded. The resulting sediment transported in the river system may vary in the $^{10}Be/^{9}Be$ ratio.

f) Inhomogeneous sample preparation or analytical problems: Samples from the Starata river were generally measured with a high $^{10}Be/^{9}Be$ ratio (Table 3). Only the mixed sample 10STA004/005/006 reports a low ratio as observed in the Sazliika and Omurov rivers. A repetitive analysis of the same sample resulted in a high $^{10}Be/^{9}Be$ ratio comparable to the ratios determined for the individual analysis of this sample. Either the sample preparation is very inhomogeneous, the analytical procedure very sensitive, or a mistaken identity cannot be excluded.

Another problem in this study is the assumption that Be-ratios of the modern fluvial channel bed deposits at present are similar to the fluvial deposits at the time of terrace formation. Different lithologies might have been weathered and eroded at a different rate or with a different mechanism than today (e.g., human land use). Due to these different erosional mechanisms, the grain size fractions in the past and present may be different resulting in a non-systematic and non-quantifiable offset of the geochronologic clock. Furthermore, different conditions in the past and present (e.g., dry and wet climate) may cause a different distribution of Be between water and minerals (Aldahan et al., 1999).

For a better understanding of the observed heterogeneity in the analyzed modern fluvial channel bed deposits, further investigations are required and suggested: 1) Grain size distribution of modern fluvial channel bed deposits; 2) Mineral composition of modern fluvial channel bed deposits; 3) $^{10}Be/^{9}Be$ analysis of different grain sizes; 4) $^{10}Be/^{9}Be$ analysis in river water and suspended load; 5) pH of river water; 6) Sampling along a river; 7) Sampling of more rivers; 8) Sampling of soils and bedrock in river catchments.

5.2. Age determination

Age determination of fluvial terrace sediment is highly uncertain due to four main problems: 1) Inhomogeneity in the initial ratio (see discussion above) leading to an uncertain initial ratio for the geochronologic clock. Using the mean initial ratio based on the averaged ratios measured in fluvial channel bed deposits (Table 3) and a mean terrace ratio based on the average ratios measured in the terrace sediments (Table 4) results in a mean age of 5.80 ± 0.70 Ma. The age of cycle 4 is determined to be 6.20 ± 0.41 Ma. The use of the lowest and highest measured initial ratios imply a decrease and increase in ages of 0.79 Ma and 0.90 Ma, respectively. 2) Validity of the assumption that the initial ratio derived from modern fluvial bed deposits reflects the starting point of the geochronologic clock (see discussion above). 3) Inhomogeneous terrace sediments due to inhomogeneities in the deposited river material. Samples from the same depth of the terrace deposits can be substantially variable (Table 4). This variability may be caused by possible different grain size distribution and mineralogical compositions (see discussion 5.1 Initial $^{10}Be/^{9}Be$ ratio). 4) Open system behavior in the terrace sediments. Regardless of the uncertainties in the initial ratio, ages are increasing to a depth of 14 m in the stratigraphy (cycle 3) but then decrease with further depth in the stratigraphy (cycle 2) disturbing the expected general increase in age with stratigraphic depth. Furthermore, ages in the quarry section are highly variable (~4 Ma). These observations may be due to violation of the assumption of closed system behavior at insufficient present-day sampling depths.

The addition or removal of ^{10}Be or ^{9}Be after sediment deposition needs to be considered. In order to decrease the ratio and increase the calculated ages, ^{9}Be needs to be added or ^{10}Be might be lost after deposition. ^{9}Be might be added due to further mineral formation after deposition from material with a high ^{9}Be concentration. The loss of only ^{10}Be from the authigenic mineral and no ^{9}Be is not likely, as ^{9}Be would be extracted in a similar way as ^{10}Be (e.g., Wittmann et al., 2012). In order to increase the ratio and to decrease the calculated ages, ^{9}Be needs to be lost or ^{10}Be added after deposition. The loss of ^{9}Be without loss of ^{10}Be is not likely. However, the addition of ^{10}Be is easily possible by meteoric ^{10}Be incorporated into the authigenic mineral after sediment deposition. The post-depositional alteration is the most realistic scenario to explain the increased ratios and younger ages at greater depth in the stratigraphy. This post-depositional alteration may have happened shortly after deposition (e.g., during paleo-soil formation) or later due to surface denudation and shallow burial over time (e.g., Fig. 2 and Table 1).

In order to better understand the age inhomogeneity with stratigraphic depth, depth profiles at each sampling locations need to be collected and analyzed for grain size distribution, mineral composition, and $^{10}Be/^{9}Be$ ratios in the grain size fractions. The depth profile will give information about when the system could potentially be considered as a closed system. As previous studies have shown, depth profiles in soils formed on bedrock or terrace material can be highly variable with depth (e.g., Pavich et al., 1984, 1986). Ideally, the $^{10}Be/^{9}Be$ ratios in one soil unit are decreasing with depth (e.g., Pavich et al., 1985; West et al., 2013) as meteoric ^{10}Be penetrates into the system whereas ^{9}Be concentrations should be homogeneous with depth. If this is the case, the lowest measured $^{10}Be/^{9}Be$ ratio of a soil unit may reflect its deposition age.

5.3. The Ahmatovo Formation and the age of the hominid tooth

Based on biochronology of fossil mammals from various outcrops the Ahmatovo Formation is generally Late Miocene and younger and may be earliest Pleistocene in age (Kojumdgieva and Dragomanov, 1979; Dragomanov et al., 1981, 1984). From biochronology, the expected age of the Late Miocene deposits in the Azmaka Quarry are ~7 Ma (Spassov et al., 2012). The mammalian fossils from cycle 1 to cycle 6 in the 26 m thick Ahmatovo Formation in Azmaka show no significant biostratigraphic difference (Spassov et al., 2012). Therefore, a narrow age range is expected for the Ahmatovo Formation in the Azmaka Quarry. This expectation is not reflected by the authigenic $^{10}Be/^{9}Be$ ages reported in this study. The age scatter observed in the different cycles is considerable and the initial starting point of the geochronologic clock not well-constrained. However, given all the uncertainties the method encounters (e.g., heterogeneities in initial ratios and terrace sediments, closed system behavior of terrace sediments), the mean age of 5.80 ± 0.70 Ma as well as the age of 6.20 ± 0.41 Ma for cycle 4 are reasonably close to the expected value of ~7 Ma.

6. Conclusions

The method of authigenic $^{10}Be/^{9}Be$ ratios to determine continental sediment deposition ages (e.g., Lebatard et al., 2008, 2010) is applied to clastic sediments stored in river terraces.

1) The carrier-free method is a valuable technique to measure $^{10}Be/^{9}Be$ ratios in clastic sediments. The separate analysis of ^{9}Be concentrations required in the traditional method is not needed.

2) Initial $^{10}Be/^{9}Be$ ratios from modern fluvial bed deposits are heterogeneous and the initial ratio for the age calculation not well constrained. This heterogeneity needs better understanding (e.g., more rivers, further locations along rivers, different grain sizes).
3) A general increase of ages with stratigraphic depth is not observed and the age range reported from the different sedimentary cycles is large (~4 Ma). Closed system behavior is not guaranteed. To better understand this age range, depth profiles of the river terraces need to be analyzed (e.g., for $^{10}Be/^{9}Be$ concentrations, grain size distribution, mineralogical composition, pH).
4) The method of authigenic $^{10}Be/^{9}Be$ age determination may be a valuable tool for dating clastic sediments after investigating the systematics and the problems in more detail (e.g., $^{10}Be/^{9}Be$ analysis of more rivers and samples along a river section, bedrock in the sediment source area).

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References

Agusti, J., Sanz de Siria, A., Garees, M., 2003. Explaining the end of the hominoid experiment in Europe. J. Hum. Evol. 45, 145–153.
Aldahan, A., Haiping, Y., Possnert, G., 1999. Distribution of beryllium between solution and minerals (biotite and albite) under atmospheric conditions and variable pH. Chem. Geol. 156, 209–229.
Bacon, A.R., deB Richert, D., Bierman, P.R., Rood, D.H., 2012. Coupling meteoric ^{10}Be with pedogenic losses of ^{9}Be to improve soil residence time on an ancient North American interfluve. Geology 40, 847–850.
Barg, E., Lal, D., Pavich, M.J., Caffee, M.W., Southon, J.R., 1997. Beryllium geochemistry in soils: evaluation of $^{10}Be/^{9}Be$ ratios in authigenic minerals as a basis for age models. Chem. Geol. 140, 237–258.
Begun, D.R., Nargolwalla, M.C., Kordos, L., 2012. European miocene hominids and the origin of the African ape and human clade. Evol. Anthropol. 21, 10–23.
Bonitz, F., 2013. Geologic Mapping (Scale 1:10.000) North of Chirpan (Central Bulgaria). Unpublished report. University Tuebingen, 103 pp.
Bourlès, D., Raisbeck, G.M., Yiou, F., 1989. ^{10}Be and ^{9}Be in marine sediments and their potential for dating. Geochim. Cosmochim. Acta 53, 443–452.
Boyanov, I., Goranov, A., Shilyafova, S., Ruseva, M., Nenov, T., 1990. Geologic Map of Bulgaria 1:100.000, Chirpan Sheet. Department of Geophysical Prospecting and Geological Mapping, Sofia.
Chmeleff, J., von Blankenburg, F., Kossert, J., Jakob, D., 2010. Determination of the ^{10}Be half-life by multicollector ICP-MS and liquid scintillation counting. Nucl. Instrum. Methods Phys. Res. Sect. B 268, 192–199.
Christl, M., Maden, C., Kubik, P.W., Müller, A., Ivy-Ochs, S., Suter, M., Synal, A.-H., 2010. Carrier-free measurements of natural $^{10}Be/^{9}Be$ ratios at low energies. Nucl. Instrum. Methods Phys. Res. 268, 726–729.
Christl, M., Vockenhuber, C., Kubik, P.W., Wacker, L., Lachner, J., Alfimov, V., Synal, A.-H., 2012. The ETH Zuerich AMS facilities: performance parameters and reference materials. Nucl. Instrum. Methods Phys. Res. 294, 29–38.
Dragomanov, L., Kazarinov, V., Kojumdgieva, E., Nikolov, I., Enchev, E., Christoc, C., 1981. Palaeogeography of the Neogene in Plovdiv and Pazardzik districts. Palaeontology. Stratigr. Lithol. 14, 65–75 (in Bulgarian with French and English abstracts).
Graly, J.A., Bierman, P.R., Reusser, L.J., Pavich, M.J., 2010. Meteoric Be-10 in soil profiles – a global meta-analysis. Geochim. Cosmochim. Acta 74, 6814–6829.
Jungers, M.C., Bierman, P.R., Matmon, A., Nichols, K., Larsen, J., Finkel, R., 2009. Tracing hillslope sediment production and transport with in situ and meteoric ^{10}Be. J. Geophys. Res. Earth Surf. 114.
Kojumdgieva, E., Dragomanov, L., 1979. Lithostratigraphy of the Oligocene and Neogene sediments in Plovdiv and Pazardzik districts. Palaeontol. Stratigr. Lithol. 11, 49–61 (in Bulgarian with French and English abstracts).
Kopralev, I., 2002. Geography of Bulgaria. 2002. Inst. Of Geography, Bulg. Acad. Sci. For Kom Publ. House, Sofia, 760 pp.
Kopralev, I. (Ed.), 2010. Bulgaria Geographic Atlas. 2010. Inst. Of Geography, Bulg. Acad. Sci.. For Tangra TanNakRa Publ. House, Sofia, 219 pp.
Korschinek, G., Bergmaier, A., Faestermann, T., Gerstmann, U.C., Knie, K., et al., 2010. A new value for the half-life of ^{10}Be by heavy-ion elastic recoil detection and liquid scintillation counting. Nucl. Instrum. Methods Phys. Res. Sect. B 268, 187–191.
Koufos, G.D., 2003. Late Miocene mammal events and biostratigraphy in Eastern Mediterranean. Deinsea 10, 343–371.
Lachner, J., Christl, M., Synal, A.-H., Frank, M., Jakobsson, M., 2013. Carrier free $^{10}Be/^{9}Be$ measurements with low-energy AMS: determination of sedimentation rates in the Arctic Ocean. Nucl. Instrum. Methods Phys. Res. B 294, 67–71.
Lal, D., Barg, E., Pavich, M., 1991. Development of cosmogenic nuclear methods for the study of soil erosiono and formation rates. Curr. Sci. 61, 636–639.
Lebatard, A.-E., Bourles, D., Braucher, R., Arnold, M., Duringer, P., Jolivet, M., Abderamane, M., Deschamps, P., Roquin, C., Carcaillet, J., Schuster, M., Liboreau, F., Likius, A., Mackaye, H.T., Vignau, P., Brunet, N., 2010. Application of the authigenic $^{10}Be/^{9}Be$ dating method to continental sediments: reconstruction of the Mio-Pleistocene sedimentary sequence in the early hominid fossiliferous areas of the northern Chad Basin. Earth Planet. Sci. Lett. 297, 57–70.
Lebatard, A.-E., Bourlès, D., Duringer, P., Jolivet, M., Braucher, R., Carcaillet, J., Schuster, M., Arnaud, N., Monie, P., Liboreau, F., Likius, A., Mackaye, H.T., Vignau, P., Brunet, N., 2008. Cosmogenic nuclide dating of Sahelanthropus tchadensis and Australopithecus bahrelghazali: mio-Pliocene hominids from Chad. PNAS 105, 3226–3231.
Maejima, Y., Matsuzaki, H., Nakano, C., 2004. ^{10}Be concentrations of red soils in Southwest Japan and its possinility of dating. Nucl. Instrum. Methods Phys. Res. B 223–223, 596–600.
Monaghan, M.C., Krishnaswami, S., Thomas, J.H., 1983. ^{10}Be concentrations and the long-tern fate of particle-reactive nuclides in five soil profiles from California. Earth Planet. Sci. Lett. 65, 51–60.
Müller, A.M., Christl, M., Lachner, J., Suter, M., Synal, A.-H., 2010. Competitive ^{10}Be measurements below 1MeV with the upgraded ETH-Tandy AMS facility. Nucl. Instrum. Methods Phys. Res. 268, 2801–2807.
Nikolov, V., 2011. Neolithic pit sanctuaries. Arheologia 2011 (1), 7–24.
Pavich, M.J., Brown, L., Harden, J.W., Klein, J., Middleton, R., 1986. ^{10}Be distribution in soils from Merced River terraces, California. Geochim. Cosmochim. Acta 50, 1727–1735.
Pavich, M.J., Brown, L., Klein, J., Middleton, R., 1984. ^{10}Be accumulation in a soil chronosequence. Earth Planet. Sci. Lett. 68, 198–204.
Pavich, M.J., Brown, L., Valette-Silver, N.J., Klein, J., Middleton, R., 1985. ^{10}Be analysis of a Quaternary weathering profile in the Virginia Piedmont. Geology 13, 39–41.
Pavich, M., Vidic, N., 1993. Application of paleomagnetic and ^{10}Be analyses to chronostratigraphy of alpine glacio-fluvial terraces, Sava River Valleu, Slovenie. Geophys. Monogr. 78, 263–275.
Reusser, L.J., Bierman, P.R., 2010. Using meteoric ^{10}Be to track flvuial sand through the Waipaoa River basin, New Zealand. Geology 38, 47–50.
Rousseva, S., Lazarov, A., Tsvetkova, E., Marinov, I., Malinov, I., Kroumov, V., Stefanova, V., 2006. Bulgaria in soil erosion in Europe. In: Boardman, J., Poesen, J. (Eds.). Wiley, London, pp. 167–182.
Spassov, N., Geraads, D., Hristova, L., Markov, G.N., Merceron, G., Tzankov, T., Stoyanov, K., Böhme, M., Dimitrova, A., 2012. A hominid tooth from Bulgaria: the last pre-human hominid of continental Europe. J. Hum. Evol. 62.
Staudigel, H., Albarède, F., Blichert-Toft, J., Edmond, J., McDonough, B., et al., 1998. Geochemical Earth Reference Model (GERM): description of the initiative. Chem. Geol. 145, 153–161.
von Blanckenburg, F., Bouchez, J., Wittmann, H., 2012. Earth surface erosion and weathering from the 10Be (meteoric)/9Be ratio. Earth Planet. Sci. Lett. 351-352 (0), 295–305.
West, N., Kirby, E., Bierman, P., Clarke, B.A., 2014. Aspect-dependent variations in regolith creep revealed by meteoric ^{10}Be. Geology 42, 507–510.
West, N., Kirby, E., Bierman, P., Slingerland, R., Ma, L., et al., 2013. Regolith production and transport at the Susquehanna Shale Hills critical zone observatory, Part 2: insights from meteoric ^{10}Be. J. Geophys. Res. Earth Surf. 118, 1877–1896.
Wittmann, H., von Blanckenburg, F., Bouchez, J., Dannhaus, N., Neumann, R., Christl, M., Gaillardet, J., 2012. The dependence of meteoric ^{10}Be concentrations on particle size in Amazon River bed sediment and the extraction of reactive $^{10}Be/^{9}Be$ ratios. Chem. Geol. 318–319, 126–138.