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Scientific report

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Work title: *Refining the chronology of three archaeological sites in the Iberian Peninsula (Cuesta de la Bajada (Teruel), site of Pinilla del Valle (Community of Madrid) and site of Ambrona (Soria)), using cosmogenic nuclides dating.*

1. Introduction

The burial dating method is based on the radioactive decay two cosmogenic nuclides, 26Al and 10Be, produced within the quartz (SiO2) mineral fraction of rocks exposed at the Earth's surface (Granger and Smith, 2000). Over the last years burial dating have widely been applied in human evolution studies (Carbonell et al., 2008; Gibbon et al., 2009; Shen et al., 2009; Pappu et al., 2011, Lebatard et al., 2014). With the idea to refine the chronology of the three archaeological- paleontological sites in the Iberian Peninsula (Cuesta de la Bajada (Teruel), site of Pinilla del Valle (Community of Madrid) and site of Ambrona (Soria)).

The main objectives of this stay at Cosmogenic nuclides laboratory, CEREGE (Aix-en-Provence, France), was to work in collaboration with Régis Braucher (RB), researcher at CNRS, to proceed the aforementioned samples (treated at the CLNC lab) for 26Al and 10Be separation in the LN2C (Laboratoire National des Nucléides Cosmogéniques) high qualified laboratory, measured them in the 5 MV AMS ASTER facilities CEREGE (Aix-en-Provence, France) and to compare with data from the processed samples in the new CLNC laboratory. Following, to refine the chronology of the sites and finally to compare with the diverse results obtained from different absolute dating methods.

2. Regional settings of the sampling areas

The three Pleistocene archaeological- paleontological sites there are located in different geological frames of the Iberian Peninsula (Figure 1).

- Ambrona site (Soria, Spain)

Systematic and extensive excavations were conducted at the Lower Paleolithic site of Ambrona, since 1960s until present days. The sedimentary settings of the Ambrona site corresponding to fluvial-lacustrine deposits, in which six stratigraphic units were recognized, from AS1 at the base to AS6 at the surface. In these units were found an abundant fauna associated with Acheulian artefacts. The most abundant species were elephant, horse, deer and aurochs. Other species like carnivores occur in small numbers only. The lithic tools assemblage consists in bifaces, choppers and flakes distributed throughout levels AS1 to AS5. The fauna and the lithic industry document human presence at Ambrona during the Middle Pleistocene (Falgueres et al., 2006). In order to verify and refine the presumed antiquity of the Ambrona deposits several samples collected from the AS1 and AS2 units. The AS1 and AS2 units are alluvial fan deposits consisted by cobbles, sands and clays.

- Cuesta de la Bajada site (Teruel)

The Cuesta de la Bajada site contains an early Middle Paleolithic assemblage similar to other European early Middle Paleolithic industries. This site was formed around a pond not far from a river and contains remains of large macrofauna other than equids and cervids. Taphonomic analysis highlights the abundance of cut marks on bones, and supports the hypothesis of selective hunting by hominids. The numerical ages derived from the combination of ESR, OSL and AAR dating methods indicate that the archaeological site was very likely formed around the MIS 8-MIS 9. Cuesta de la Bajada site is located about 18 m above the known base of the T4 terrace fluvial sequence. At the Cuesta de la Bajada site area, the T4 terrace have been subjected to synsedimentary subsidence and reach up to 55 m of thicknesses. At Cuesta de la Bajada the archaeological levels are associated with a small deformation depression located between a cyclic sequence of gravel bars and floodplain muds (Santonja et al., 2014). Two samples from the Cuesta de la Bajada site for burial dating.

- Pinilla del Valle site (Community of Madrid, Spain)

The karstic system of Pinilla del Valle del Calvero de la Higuera formed in Late Cretaceous limestones and dolomites at the Upper Lozoya valley pop down located in the Eastern part of the Spanish Central System at the Guadarrama mountain range. The archaeological evidences during the excavation campaigns since 2002 revealed the presence of a Quaternary mountain multilevel karst modeled by lithological-structural controls and the local base lowering. Know days the subhorizontal cavities are dismantled as result of bed rock weathering and surface processes, and are totally infilled by Middle-Late Pleistocene alluvial sediments, debris and colluvium deposits. The systematic fieldwork shown Middle-Late Pleistocene human activity and carnivores inhabitants at the complex karstic system composed by Buena Pinta cave, Camino cave, Des-Cubierta cave and Navalmaillo rock shelter. Camino and Buena Pinta sites were identified like carnivores inhabitants whereas at the Des-Cubierta cave Middle-Late Pleistocene human activity evidences are recorded. Finally the Navalmaillo rock shelter recognized like Neanderthals site with abundance artifact records (Karampaglidis et al., 2014). Two samples were collected for burial dating.

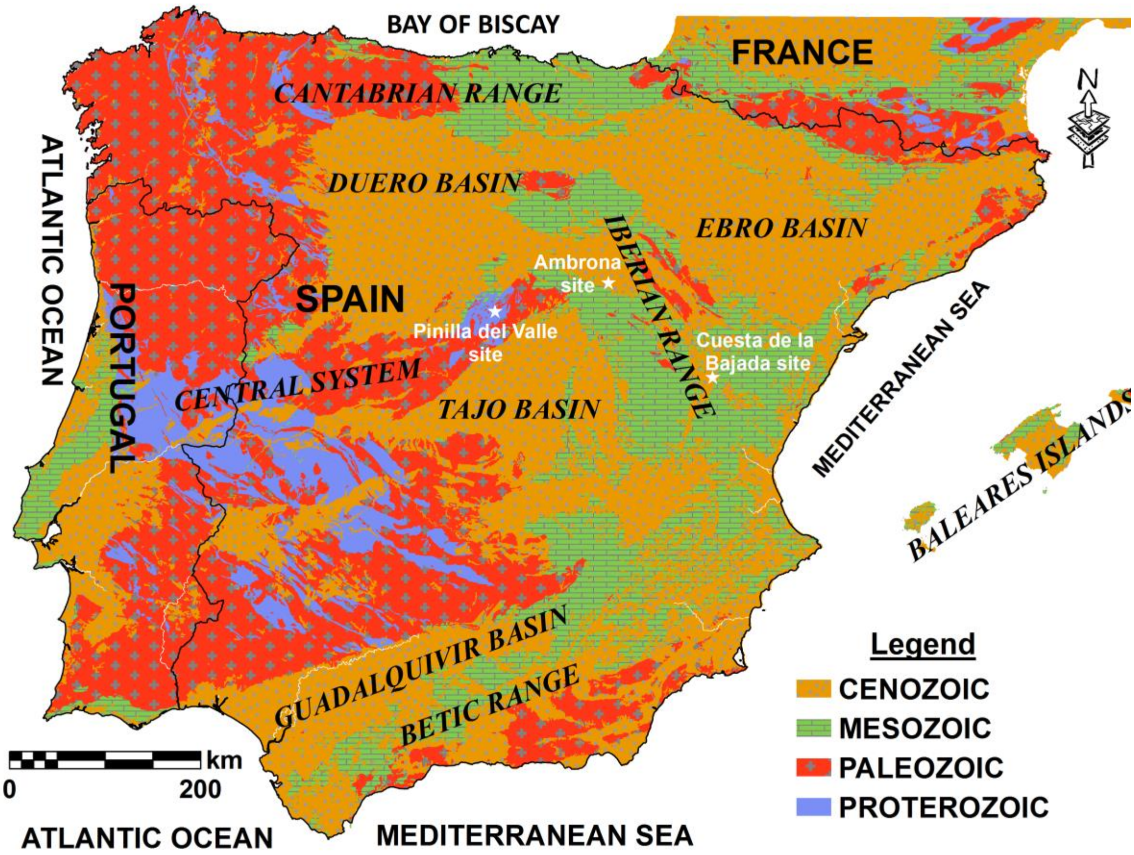

Figure 1. Location of the archaeological-paleontological sites.

3. Methods

3.1. Cosmogenic burial dating: basic principles

Burial dating with 10Be and 26Al nuclides only requires samples with quartz previously exposed at surface then buried and shielded from cosmic-ray bombardment. The surface spallogenic production rate ratio of 26Al:10Be in quartz is well-established on 6.61±0.50 (Rixhon et al., 2011; Pappu et al., 2011; Braucher et al., 2011). When the quartz samples are well shielded from the cosmic-ray flux, for example when they are deposited into caves or are buried by subsequent sediment sequence, the nuclide productions by spallation stop and the 10Be and 26Al concentrations, decrease by radioactive decay according to their respective half-lives (0.717±0.017 Ma for 26Al (Samworth et al., 1972; Granger, 2006) and 1.387±0.012 Ma for 10Be (Korschinek et al., 2010; Chmeleff et al., 2010).

There are significant advantages to apply this because both nuclides are produced in the same mineral (quartz), their production ratio is well known in quartz, largely independent from altitude-latitude and finally does not vary essentially with depth (Brown et al. 1992).

Two approaches cases have to be considered: (i) Simple, fast and complete burial Burial Dating and (ii) Slow and/or incomplete burial with variable inheritance.

3.1.1. Simple Burial Dating

One has to assume that the sample exposed at the surface was buried deeply enough (typically >10 m) that postburial production can be ignored. Simple burial dating is ideal for dating cave sediments or very thick terrace sediments (Granger et al., 1997; Granger and Muzikar, 2001; Gibbon et al., 2009)

3.1.2. Slow and/or incomplete burial with variable inheritance

There are diverse sampling and modelling strategies to deal with in situations with complex exposition history, variable inheritance and where burial is relatively slow and shallow so postburial production by muons needs to be considered (Granger and Muzikar 2001, Balco and Rovey 2008). One of them is to follow the model fully described in the SOM of Pappu et al., 2011 or sampling from depth profile (Granger and Smith 2000, Wolokowinsky and Granger 2004, Balco et al. 2005, Granger 2006, Balco and Rovey 2008) or to take multiple clasts from a single stratigraphic level (Balco and Rovey 2008; Erlanger et al., 2012).

4. Framework settings

4.1. Sampling

Several samples for Cosmogenic burial dating have been collected by Theodoros Karampaglidis (TK) in August 2014. Hence, TK collected 3 samples from the Middle Paleolithic site of Cuesta de la Bajada (Teruel, Spain), two samples from the Middle-Late Pleistocene archaeological site in the karstic system of Pinilla del Valle (Spanish Central System, Community of Madrid) and 5 samples from the Lower Paleolithic site of Ambrona, (Soria, Spain).

4.2. Previous work in the new CLNC laboratory

Grinding, sieving, magnetic separation and quartz cleaning for AMS analysis from pure quartz samples they have done during between of September and December 2014 in the new Cosmogenic nuclide laboratory (CLNC) CENIEH (National Research Centre on Human Evolution, Spain) facilities (Figure 2).

MUESTRA	AMB-1									
PROYECTO										
MASA TRATADA	117,219									
FRACCION	250-500 MICRAS									
ETAPA	NOTAS									
	% masa perdida después hexa						PÉRDIDA MUESTRA			
	% masa perdida respecto inicial						41,00			
	masa perdida						48,055			
	peso seco botella y muestr	322,585					274,53			
	botella	205,366					205,366			
	muestra seca	117,219					69,164			
LIMPIEZA	SPT	☑								
FRACC.MAG	SEPARADOR MAGNÉTICO	☑								
			lavado finos							
Hexa/ HCl	Hexa: HCl (86,475 : 43,237)			☑						
	Hexa: HCl (90: 45)				☑	rinse 2L pH=7				
	Hexa: HCl (:)									
	Hexa: HCl (:)									
HF	HF (500 mL, %) (250: 28)							☑	rinse 1L	
	HF (500 mL, %) (249:25)								☑	rinse 1L
	HF (500 mL, %) (249:25)									☑
	FECHA	día1(27/10/2014)	día2(27/10/2014)	día3(28/10/2014)	-29/10/2014	03/11/2014	12/11/2014	19/11/2014	21/11/2014	24/11/2014
		notas	☑ (1º etching)	HF 1350						
			☑ (2º etching)	HF 1350						
			☑ (3º etching)	HF 1400						
				test aluminio						
			☑ (4º etching)	?						

Figure 2. Sample tracking during the quartz cleaning in the new Cosmogenic nuclide laboratory (CLNC) CENIEH (National Research Centre on Human Evolution, Spain).

4.3. Results and description of the work carried out during the visit

Practically, the program of the research divided into 2 main phases. First, all samples with a blank, followed the chemical protocol of the LN2C (Braucher et al., 2011: elimination of the meteoric 10Be, total dissolution of the pure decontaminated quartz, Be and Al extractions). Elimination of meteoric 10Be made it with sequential partial dissolutions with HF. Next, in each sample added 9Be spike (~100 µl of a $3 \cdot 10^{-3}$ $at \cdot g^{-1}$ solution of 9Be), allowed to handle a ponderable amount and to fix the 10Be/9Be ratio for the AMS measurements. Following, total dissolution of the cleaned quartz achieved using HF. After the HF evaporation and Be extraction, was taken an aliquot of 500µL of the homogenize solution. Aliquots were collected to determine the 27Al total amount by inductively coupled plasma optical emission spectrometry (ICP-OES) measurements (Figure3).

Sample ID	Sample weig	tube weig	Sol + Tube	Mass of S	Mass of A	Mass of s	Fraction o	Aliquot fo	Final sol f	Dilution
	[g]	[g]	[g]	[g]	[g]	[g]		[g]	[g]	
AMB4	21,6049	12,9343	34,0023	21,068	0,4995	20,5685	0,976291	0.2059	10,725	52,08839
AMB3	20,7201	13,0085	24,5186	11,5101	0,5764	10,9337	0,949922	0.2062	10,3277	50,08584
AMB2	23,7537	12,9121	58,8516	45,9395	0,5085	45,431	0,988931	0.2013	9,7445	48,40785
AMB1-2	19,5403	13,0295	36,8866	23,8571	0,5112	23,3459	0,978572	0.2051	10,0226	48,86689
AMB1	21,7317	12,9529	38,9332	25,9803	0,5059	25,4744	0,980528	0.2048	10,0039	48,84717
TER3	22,4932	13,0435	32,2169	19,1734	0,5075	18,6659	0,973531	0.2203	10,0286	45,52247
TER2	22,1144	12,9738	45,2761	32,3023	0,5006	31,8017	0,984503	0.1939	9,9885	51,51367
SG1-2	18,7094	13,0536	43,4933	30,4397	0,5073	29,9324	0,983334	0.2089	9,9743	47,74677
NV1	23,0308	12,8719	32,5156	19,6437	0,5087	19,135	0,974104	0.2010	10,009	528,0515
BLKN	0	13,0006	23,7926	10,792	0,5191	10,2729	0,9519	0.2088	9,9772	47,78352

Sample ID	ICP	%	27Al natur	27Al spike	27Al spike	Total 27Al	R aster	%	26Al	26Al	Uncertainty 26Al	
	[ppm]		at in sol a	[g]	at after ali	at in sol after aliquot			at ap aliq	at/g ap ali	at/g	
AMB4	3,978255		9,51E+19		0	9,51E+19						
AMB3	7,328689		8,96E+19		0	8,96E+19						
AMB2	1,466199		7,2E+19		0	7,2E+19						
AMB1-2	2,684146		6,83E+19		0	6,83E+19						
AMB1	2,431512		6,75E+19		0	6,75E+19						
TER3	3,324428		6,3E+19		0	6,3E+19						
TER2	2,116198		7,74E+19		0	7,74E+19						
SG1-2	3,13371		1E+20		0	1E+20						
NV1	4,52591		1,02E+21		0	1,02E+21						
BLKN	0,033707		3,69E+17		0	3,69E+17						

Figure 3. Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements.

No further 27Al were added in the samples. Natural content of aluminium was determined by ICP-OES to fix the 26Al/27Al ratio for the AMS measurements. Upcoming, Beryllium and aluminium were subsequently separated from the solution by successive anionic and cationic resin extraction (DOWEX 1X8 then 50WX8) and precipitation. This process allows to separate Be-Al from other trace elements and to obtain them in their hydroxide form. The elimination of metallic cations and anions performed by separation on ion exchange resins. Cation exchange resins utilized for the B, Be and Al separation. All samples final precipitates were dried and oxidized at 800 ºC for 1 hour to obtain BeO and Al2O3.

All samples were prepared for AMS measurements with mixing and pressing of the cathodes. The Be samples were mixed with Nb powder whereas the Al samples with Ag powder.

The second phase, all measurements (Figure 4) performed at the French AMS National Facility, ASTER, located at the CEREGE in Aix-en-Provence. Beryllium data were calibrated directly against the National Institute of Standards and Technology (NIST) beryllium standard reference material 4325 by using an assigned value of (2.79 +/- 0.03)$\cdot 10^{-11}$. This standardization is equivalent to 07KNSTD within rounding error. Aluminium measurements will be performed against an in-house standard called SM-Al-12, with 26Al/27Al = (7.401 +/- 0.064)$\cdot 10^{-12}$. This has been cross-calibrated against the primary standards and certified by a round-robin exercise (S3) using a 26Al half-life of (7.17 +/- 0.17)·105 years (S4). 27Al concentrations, naturally present in the samples, were measured at the CEREGE by ICPOES. Analytical uncertainties (reported as 1 sigma) include uncertainties associated with AMS counting statistics, AMS external error (0.5%), chemical blank measurement and, in the case of 26Al, 27Al measurements. Long term measurements of chemically processed blanks yield ratios in the order of (3.0 +/- 1.5)·10–15 for 10Be and (2.2 +/- 2.0).10–15 for 26Al (S5).

Nom d'ecl	Descriptio	Be10/Be9	Total cou	Incertitud	N cath/ O	Dates	Position	Be10/Be9 machine
BeO Blan	-- Blanc m	7,47E-16	4	50,01502	AHDB	* 19/02/2015	12	3,59E-16
AMB-4	Theo-RB	2,88E-14	734	3,889201	BLTP	* 19/02/2015	24	1,39E-14
AMB-3	Theo-RB	2,35E-14	550	5,042803	BLTQ	* 19/02/2015	25	1,13E-14
AMB-2	Theo-RB	3,01E-14	873	3,599536	BLTR	* 19/02/2015	26	1,45E-14
AMB-1-2	Theo-RB	2,7E-14	1008	3,690124	BLTS	* 19/02/2015	27	1,3E-14
AMB-1	Theo-RB	2,83E-14	1181	3,245206	BLTT	* 19/02/2015	28	1,36E-14
TER-2	Theo-RB	2,64E-14	470	4,898486	BLTU	* 19/02/2015	29	1,27E-14
TER-3	Theo-RB	3,4E-14	1307	3,025395	BLTV	* 19/02/2015	30	1,64E-14
SG-1	Theo-RB	1,45E-14	275	6,615928	BLTW	* 20/02/2015	31	6,99E-15
NV-1	Theo-RB	3,81E-14	889	3,570784	BLTX	* 20/02/2015	32	1,83E-14
Blxn	Theo-RB -	9,6E-16	6	40,84322	BLTY	* 20/02/2015	33	4,62E-16

Figure 4. Be AMS measurements.

Al measurements will be probably performed at the second half of March according the local lab schedule. Also, during these measurements, is planned to measure the Be-Al blanks which will be used during the future sample preparation for AMS measurements of 10Be and 26Al at the CLNC laboratory. Cosmogenic 10Be and 26Al chemistry will be completed at the CLNC laboratory for interlaboratory data comparison with the LN2C after the Be-Al blanks measurements. The data reduction and interpretation will be performed after Al measurements.

5. Future collaboration with host institution and projected publications / articles resulting or to result from the grant (ESF must be acknowledged in publications resulting from the grantee's work in relation with the grant)

Close collaboration will be carry on with the host institute. It is expected to continue the sample preparation at the CLNC laboratory for AMS measurements at the French AMS National Facility, ASTER, located at the CEREGE in Aix-en-Provence. It is scheduled to write a manuscript based on these results during 2015. This manuscript will be submitted to an international journal where the ESF support will be acknowledged.

6. References

Balco, G. and Rovey, C. W., 2008. An isochron method for cosmogenic nuclide dating of buried soils and sediments, Am. J. Sci., 308, 1083–1114.

Balco, G., Rovey, C.W. and Stone, J. O., 2005. The first glacial maximum in North America, Science, 307 222.

Braucher, R., Merchel, S., Borgomano, J., Bourlès, D.L., 2011. Production of cosmogenic radionuclides at great depth: A multi-element approach. Earth Planet. Sci. Lett., 309 (1), 1–9.

Brown, R. T., Brook, E. J., Raisbeck, G. M., Yiou, F. and Kurz, M. D., 1992. Effective attenuation length of cosmic rays producing 10Be and 26Al in quartz: implications for exposure dating, Geophys. Res. Lett., 19, 369–372.
Carbonell, E., Bermúdez de Castro, J. M., Parés, J. M., Pérez-González, A., Cuenca-Bescós, G., Ollé, A., Mosquera, M., Huguet, R., vander Made, J., Rosas, A., Sala, R., Vallverdú, J., García, N., Granger, D.E., Martinón-Torres, M., Rodríguez, X.P., Stock, G.M., Vergès, J.M., Allué, E., Burjachs, F., Cáceres, I., Canals, A. ,Benito, A., Díez, C., Lozano, M., Mateos, A., Navazo, M., Rodríguez, J., Rosell, J., Arsuaga, J.L., 2008. The first hominin of Europe. Nature, 452, 465–470.
Chmeleff, J., von Blanckenburg, F., Kossert, K., Jackob, D., 2010. Determination of the 10Be half-life by multicollector ICP-MS and liquids cintillation counting. Nucl. Instrum. Methods Phys. Res., Sect.B, BeamInteract. Mater. Atoms, 268, 192–199.
Dunai, T. J., 2010. Cosmogenic nuclides principies. Concepts and applications in the Earth Sciences. New York, Cambridge University Press.
Erlanger, E., Granger, D., and Gibbon, R., 2012. Rock uplift rates in South Africa from isochron burial dating of fluvial and marine terraces. Geology, 40; 1019-1022.
Gibbon, R.J., Granger, D.E., Kuman, K., and Partridge, T.C., 2009, Early Acheulean technology in the Rietputs Formation, South Africa, dated with cosmogenic nuclides: Journal of Human Evolution, 56, 152–160.
Falgueres, C., Bahain, J., Perez-Gonzalez, A., Mercier, N., Santonja, M. and Dolo, J., 2006. The Lower Acheulian site of Ambrona, Soria (Spain): ages derived from a combined ESR/U-series model. Journal of Archaeological Science, 33, 149-157.
Granger, D. E. and Muzikar, P. F., 2001. Dating sediment burial with in-situ produced cosmogenic nuclides: theory, techniques, and limitations, Earth Planet. Sci. Lett., 1888 269–281.
Granger, D. E. and Smith, A. L., 2000. Dating buried sediments using radioactive decay and muogenic production of 26Al and 10Be, Nucl. Instr. Meth. Phys. Res. B, 172, 822–826.
Granger, D. E., Kirchner, J. W. and Finkel, R. C., 1997. Quaternary downcutting rate of the New River, Virginia, measured from differential decay of cosmogenic 26Al and 10Be in cave-deposited alluvium, Geology, 25, 107–110.
Granger, D., 2006. A review of burial dating methods using 26Al and 10Be. In: L. Siame, D. L. Bourles and E. T. Brown, (Eds) In Situ-Produced Cosmogenic Nuclides and Quantification of Geological Surfaces Special paper 415, Boulder: The Geological Society of America, pp. 1–16.
Hellborg, R. and Skog, G., 2008. Accelerator mass spectrometry, Mass Spec. Rev., 27, 398–427.
Theodoros Karampaglidis; Ana-Isabel Ortega; Alfredo Perez Gonzalez; Sergio Barez; Jose-Ignacio Alonso; Laura Sanchez Romero; Juan Luis Arsuaga; Enrique Baquedano. Middle-Late Pleistocene mountain human occupations in the karst of Pinilla del Valle (Spanish Central System). Uispp XVII World Congress. Burgos, Castile and León, Spain, 01-07/09/2014. Accepted to publish at the journal of Quaternary International.
Klein, J., Giegengack, R., Middleton, R., Sharma, P., Underwood, J. R. and Weeks, W. A., 1986. Revealing histories of exposure using in-situ produced 26Al and 10Be in Libyan desert glass, Radiocarbon, 28, 547–555.
Korschinek, G., Bergmaier, A., Faestermann, T., Gerstmann, U.C., Knie, K., Rugel, G., Wallner, A., Dillmann, I., Dollinger, G., Lierse von Gostomski, Ch., Kossert, K., Maiti, M., Poutivtsev, M., Remmert, A., 2010. A new value for the1 0Be half-life by Heavy-Ion Elastic Recoil detection and liquid scintillation counting.Nucl.Instrum. Methods Phys .Res., Sect.B, BeamInteract. Mater. Atoms, 268, 187–191.

Lal, D., 1991. Cosmic ray labeling of erosion surfaces: in situ nuclide production rates and erosion models, Earth Planet. Sci. Lett., 104, 424–439.
Lebatard, A.E., Alçiçekb, C., Rochette, P., Khatib, S., Vialet, A., Boulbes, N., Bourlès, D., Demory, F., Guipert, G., Mayda, S., Titov, V., Vidal, L., and Lumley, H., 2014. Dating the Homo erectus bearing travertine from Kocabas (Denizli, Turkey) at least 1.1Ma. Earth and Planetary Science Letters, 390, 8–18.
Nishiizumi, K., Winterer, E. L., Kohl, C. P., Klein, J., Middleton, R., Lal, D. and Arnold, J. R., 1989. Cosmic ray production rates of 10Be and 26Al in quartz from glacially polished rocks, J. Geophys. Res., 94, 17907–17915.
Pappu, S., Gunell, Y., Akhilesh, K., Braucher, R., Taieb, M., Demory, F., Thouveny, N., 2011. Early Pleistocene presence of Acheulian hominins in South India. Science, 33, 1596–1599.
Rixhon, G., Braucher, R., Bourlès, D., Siame, L., Bovy, B., Demoulin, A., 2011. Quaternary river incision in NE Ardennes (Belgium)–Insights from 10Be/26Al dating of river terraces. Quat. Geochronol., 6(2), 273–284.
Samworth, E.A., Warburton, E.K., Engelbertink, G.A.P., 1972. Beta decay of the 26Al ground state. Phys. Rev., C5, 138–142.
Santonja, M., Perez-Gonzalez, A., Domínguez-Rodrigo, M., Panera, J., Rubio-Jara, S., Sese, C., Soto, E., Arnold, L., Duval, M., Demuro, M., Ortiz, J., Torres, T., Mercier, N., Barba, R. and Yravedra, J. (2014). The Middle Paleolithic site of Cuesta de la Bajada (Teruel, Spain): a perspective on the Acheulean and Middle Paleolithic technocomplexes in Europe. Journal of Archaeological Science, 49, 556-571.
Shen, G., Gao, X., Gao, B., Granger, D.E., 2009. Age of Zhoukoudian Homo erectus determined with 26Al/10Be burial dating.Nature, 458, 198–200.
Wolokowinsky, F. L. and Granger, D. E., 2004. Early Pleistocene incision of the San Juan River, Utah, dated with 26Al and 10Be, Geology, 32, 749–752.