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Age and significance of the Quaternary cemented deposits of the Duje Valley (Picos de Europa, Northern Spain)

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ABSTRACT

Cemented calcareous breccias appear in the Picos de Europa (Cantabrian Mountains, Spain) resting on glacially abraded surfaces and covered by moraines. U/Th dating of the calcite coating the clasts was successful in two samples, the oldest one indicating that the breccias accumulated during or prior to Marine Isotope Stage (MIS) 11, and the youngest indicating later cementation during MIS 8. The former introduces a limit for the age of the glaciation preceding the breccias, which cannot correspond to an event younger than MIS 12. This is the oldest absolute age so far obtained for intercalated glacial/interglacial deposits of the Iberian Peninsula.

Introduction

The Picos de Europa massifs (Cantabrian Mountains, northern Spain) constitute a rugged relief rising 2600 m above sea level. Rocks exposed here correspond almost exclusively to Carboniferous limestones, representing one of the largest outcrops of calcareous strata of this age in the world.

The proximity of the Bay of Biscay coast, only ~20 km north of the highest summit, is responsible for the incision caused by rivers, which have excavated narrow and deep gorges in the carbonate rocks. Such gorges, along with the abundant glacial erosive forms and the karstic sculpture, are the main geomorphological characteristics of these mountains.

Evidence of glacial features was already recognized by pioneer studies such as those of Penck (1897) and, especially, Obermaier (1914), the latter establishing that at least two glacial phases can be recognized in the headwaters of the Duje River. Among later authors, some supported Obermaier's inference (e.g., Flor and Baylon-Misioné, 1989) whereas others (Castañón and Frochoso, 1996) suggested that only one glaciation can be inferred from geomorphologic evidence. An interesting approach is that of Gale and Hoare (1997), who estimated that erosional forms preserved in the relief indicate at least five glacial phases. These same authors, using rates of entrenchment determined by Smart (1986), calculated that the oldest phase cannot be younger than early Quaternary.

Recent absolute dating of lacustrine sequences in the Western Massif (Moreno et al., 2010) and in the Puertos de Áliva (Serrano et al., 2012) showed that the last maximum glacial extent was prior to 35 cal ka BP. However, dating the age of erosive and sedimentary forms corresponding to older phases constitutes a more difficult objective, because of the limits in ^{14}C chronology and the tendency of glaciers to erode prior deposits. A promising source of data, however, may emerge from the study of cemented Quaternary deposits (calcareous breccias) that occur in discontinuous and scarce patches throughout the Picos de Europa massifs, being particularly noticeable and well-preserved in the upper part of the Duje Valley (Fig. 1).

The Duje Valley

Karstic conditions of Picos de Europa have favored underground water circulation so that few perennial rivers run across these massifs (Fig. 1A). One of them is the Cares River, which has carved a long and deep gorge. In contrast, the intermittent Duje River runs at high altitude with most of its course having extensive subterranean drainage into the Cares Valley, local base level in this sector, a fact demonstrated by dye tracer studies (e.g., Ogando, 2007). As a result of this karstic transference of water, the Duje River only maintains a permanent flow near its confluence with the Cares River, where the bottom valley rapidly deepens (Fig. 1B).

The absence of an intensive fluvial incision in the upper part of the valley allowed the preservation there of an extensive cover of Quaternary calcareous breccias (Fig. 2). These, in contrast, have been nearly removed from the other areas of Picos de Europa where rivers have

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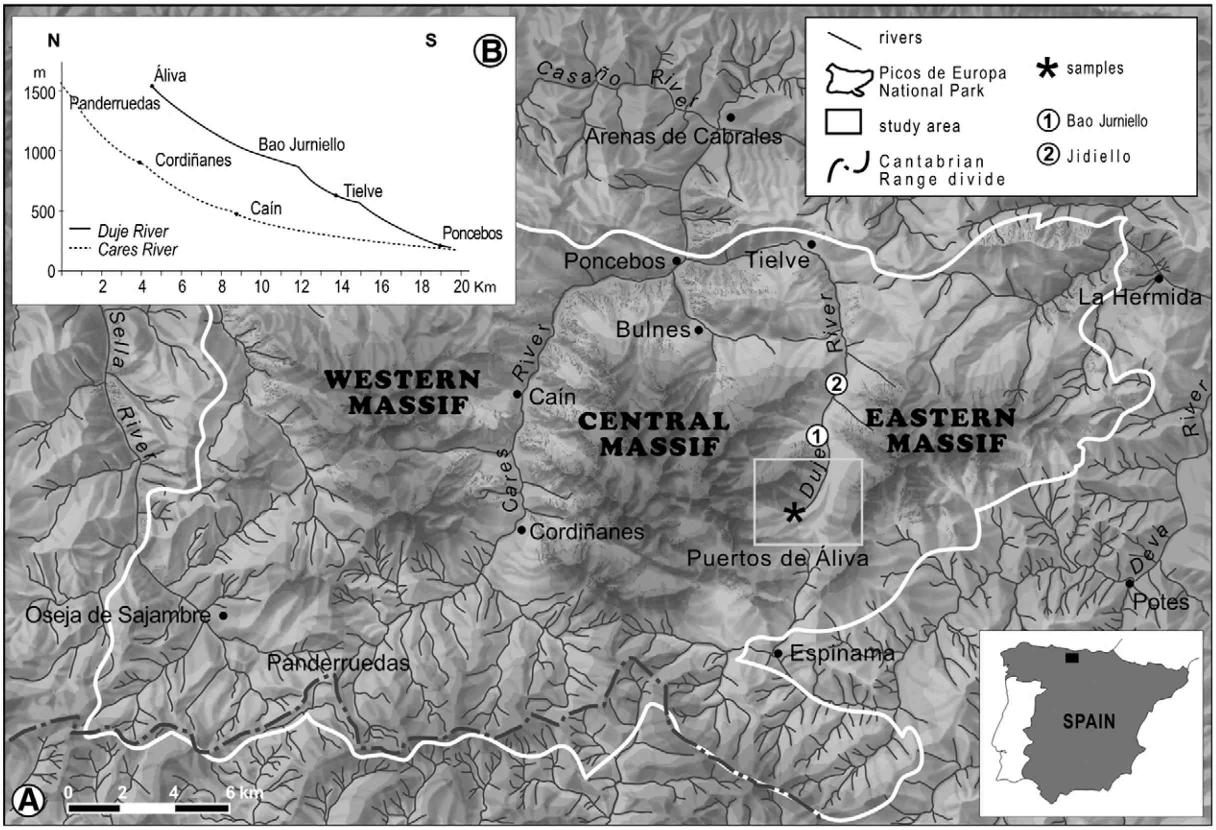

Figure 1. A) Scheme showing the course of the main rivers in Picos de Europa. B) Simplified longitudinal profiles of the Duje and Cares rivers. Note that the Duje River is constantly running at an altitude higher than the Cares Valley.

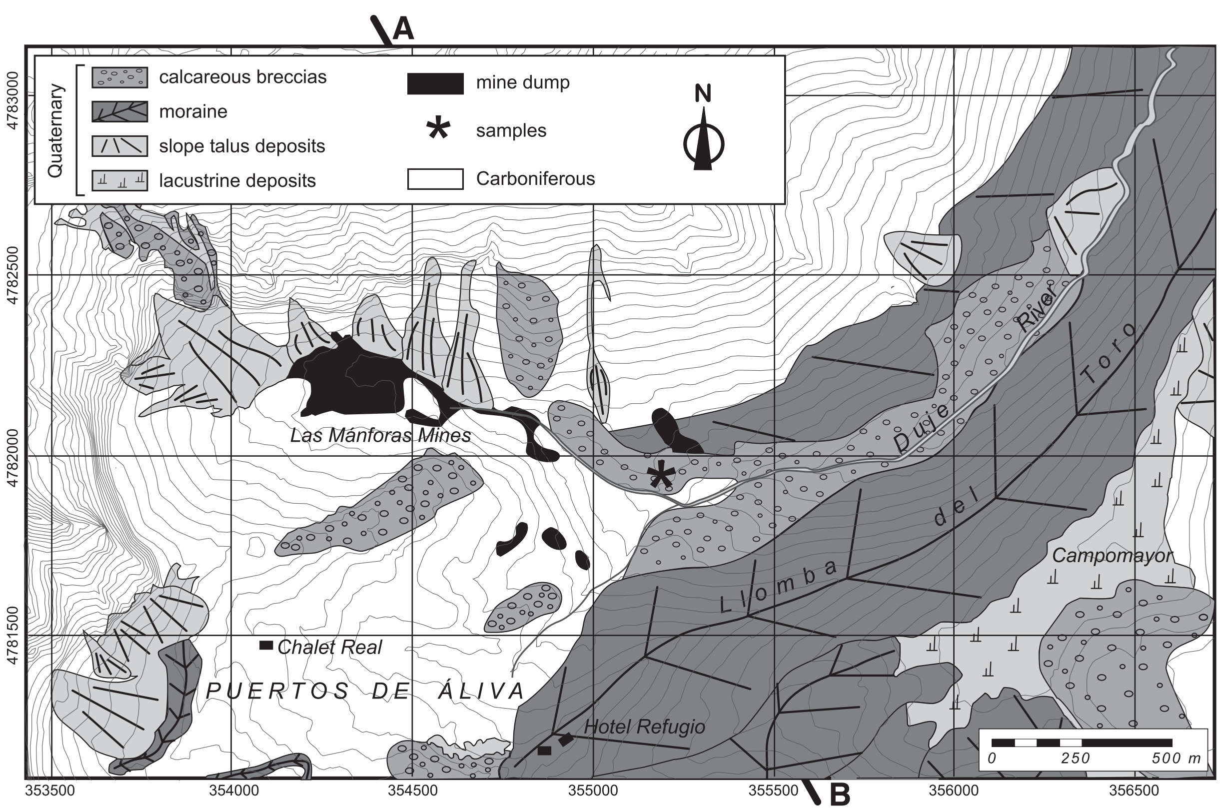

Figure 2. Geomorphological sketch showing the distribution of the Quaternary breccias in the Duje Valley and location of some relevant localities (A–B, cross-section in Fig. 3).

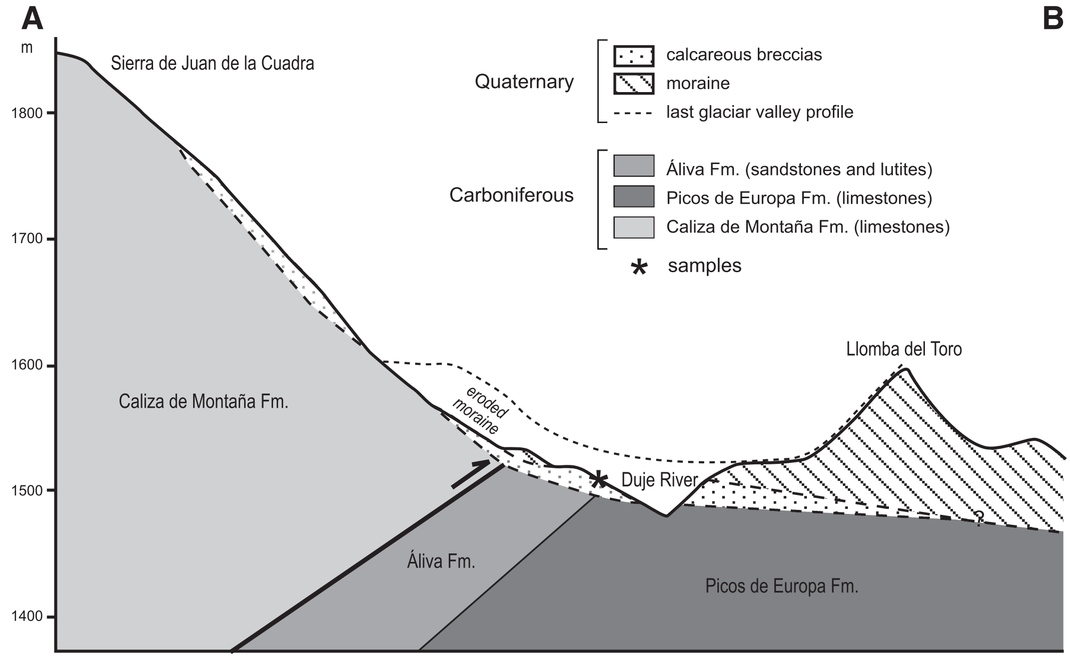

Figure 3. Cross-section of the Quaternary deposits observed in the upper part of the Duje Valley.

excavated deep valleys whose oversteepened slopes induced intensive mass-wasting processes.

The Quaternary calcareous breccias of the Duje Valley

The Quaternary calcareous breccias of the Duje Valley were already noticed by Obermaier (1914), who gave them the name of *gonfolitas*, a classical term for carbonate conglomerates. The main characteristics of these deposits can be summarized as follows: 1) they correspond to calcareous breccias embedded in a fine matrix, also of calcareous composition; calcitic cement may occur locally. 2) Pebbles are usually somewhat rounded, although accumulations of angular clasts or boulders occur locally. 3) Characteristics of these deposits may change both laterally and vertically. 4) In some localities, the deposits are clearly layered, showing beds with different granulometry. 5) Maximum thickness preserved (Bao Jurniello and Canal de Jidiello localities, Fig. 5) is up to 25–30 m.

Figure 4. Outcrop in the Duje Valley exposing bedded and cemented Quaternary breccias. Note the moraine resting on top of these calcareous deposits.

These features suggest that the Duje breccias were accumulated through a number of mass-wasting processes, from individual rock fall to debris flows. Vertical variations could be a consequence of changes in pluviometry, which would modify the role of water during transport. Lateral variations were probably linked to different transport distances from the cliff scarps that sourced the clasts.

The accumulation of breccias had to occur during a warmer interval, when the mountains were free of glacial ice. The formation of the carbonate cements requires the presence of soils that elevate the pCO_2 and promote dissolution and subsequent oversaturation with $CaCO_3$. Seasonal high evaporation may also favor the precipitation of cements, analogous to caliche formation in semi-arid to arid regions. In either case, the formation of cements requires climatic conditions conducive to formation of soils at the high elevation of the Picos. It is worth noting that high-elevation groundwater draining into the modern Lake Enol in the Picos de Europa Western Massif, an area without soil development today, is currently undersaturated with $CaCO_3$ but was oversaturated with $CaCO_3$ during the peak summer insolation of the early to mid-Holocene (Moreno et al., 2010). If analogous to Lake Enol groundwater, therefore, the development of cements may require conditions warmer than the present day. Considering the thickness of the breccias deposits still preserved after subsequent erosion, which involved at least an important glacial interval, that warmer period had to have been remarkably long.

An important aspect concerning the breccias is their relation with glacial features. Obermaier observed that in the Duje Valley (Fig. 1A) these deposits rest on a polished glacial surface and are, in turn, eroded by a later ice flow. These observations allowed him to establish that at least two different glacial phases existed during the Quaternary. Subsequent papers dealing with these deposits have essentially maintained two different opinions. Castañón and Frochoso (1996) considered that only one glaciation, with several advances and retreats, is recorded in the area; whereas others, as Flor and Baylon-Misioné (1989), supported Obermaier's idea of two glacial phases.

Our survey of the Quaternary breccias of the Duje Valley confirmed their position between the two glacial phases, since they appear clearly resting on a wide U-shaped valley of older age in the Puertos de Áliva (valley head) (Figs. 2–3) as well as in the locality mentioned by Obermaier (Fig. 5B). In addition, remarkable moraine deposits are resting on the calcareous breccias, as is the case for the long lateral moraines

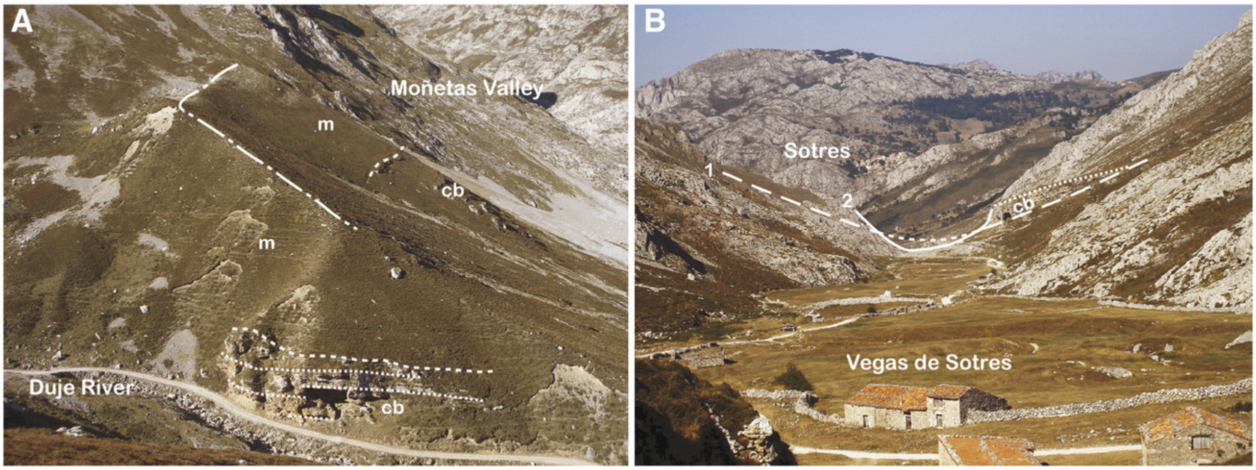

Figure 5. Position of the cemented deposits with respect to glacial features. A) Moraine (m) resting on calcareous breccias (cb) at Bao Jurniello. B) View of the Jidiello locality from the south; the Quaternary breccias (cb) rest there on a glacially abraded valley (1) and are cut by a later ice flow (2).

of Puertos de Áliva (the right one is the most prominent moraine preserved in the area) (Figs. 2–3) and for the moraine that rests on the cemented deposits at Bao Jurniello locality (Fig. 5B). All of these glacial deposits prove a younger glacial phase, which could be responsible for the minor U-shaped profile carving the calcareous breccias at the Jidiello locality.

Age and significance of the calcareous breccias in a global context

The importance of the consolidated calcareous breccias of the Duje Valley is the suggestion that they were formed during a distinct and extended interglacial episode. What is the age of this event? A first attempt to U/Th dating has been made by Castañón and Frochoso (1996) in two localities of the Duje Valley. In the Canal del Jierro section (Bao Jurniello in this paper), they analyzed two samples and obtained ages of 20 ka (+1.1/−1.0) for the lower, and 55.4 ka (+3.0/−3.0) for the upper. In the nearby Jidiello section, three samples were analyzed and their ages were 192.7 ka (+31.9/−23.3), 17.5 ka (+7.3/−6.6), and 79.1 ka (+7.3/−6.6) from base to top, respectively. Castañón and Frochoso (1996) assigned these ages to diverse periglacial stages stating that, although the oldest could correspond to the Riss, an early Wurm is more problable. They concluded that, from the available geomorphological and stratigraphic evidences, only one glacial stage could be established.

A new attempt has been made now for dating the calcite cementing the limestone pebbles of the Quaternary breccias. Eight samples were collected and treated in the lab to extract the calcite. Much care was taken to avoid contamination with the limestone from the clasts, which would bias the result to an older age. Of the samples processed, two of them collected from the same section in the Puertos de Áliva (Fig. 4) exhibited the pure calcitic cement required for radiometric analysis. U/Th dating was completed at the University of Minnesota as described in Moreno et al. (2010), and results provided the ages shown in Table 1. Large uncertainties result from the presence of detrital Th in the calcite, as well as counting uncertainties due to the relatively low U content and old age of the samples. Duje-2 corresponds to the calcite coating a clast that probably is part of the infilling of a karstic cavity in the breccias, whereas Duje-5 comes from a breccias bed close to the base of these deposits. It must be noticed that the sample collected from the probable karstic infilling yielded an age considerably younger than the sample from the breccias bed.

Sample Duje-5 bears most significance since it is the oldest date so far obtained from the calcareous breccias. Calcite cement in this sample coincides with MIS 11, an unusually warm interglacial (Prokopenko et al., 2010; Vaks et al., 2011), which was also unusually long due to the phasing of Milankovitch cycles (Laskar et al., 2004). Such anomalous length of the warmer MIS 11 interval accounts for the importance and extension of the ancient cemented debris of Picos de Europa, which almost completely covered the substrate at the mountain's base in the Duje Valley. Later erosion related to younger glacial phases was not able to wholly remove this cover, and scarcity of running water (due to karstic infiltration) in the subsequent warm intervals favored its preservation.

The younger age of sample Duje-2 indicates a subsequent episode of cementation that probably also took place during a period of mild climate. This younger age encompasses MIS 8, which although a glacial period was the weakest one of the last 800 ka, characterized by unusually warm sea-surface temperatures in the mid-latitude North Atlantic

Table 1
Uranium and thorium isotopic compositions and ^{230}Th ages for samples analyzed by ICP-MS.

Sample	Weight	^{238}U	^{232}Th	$d^{234}U$	$[^{230}Th/^{238}U]$	$[^{230}Th/^{232}Th]$	Age	Age	$d^{234}U_{initial}$
ID	g	ppb	ppt	Measured[a]	Activity[c]	ppm[d]	Uncorrected (yr)	Corrected[c,e] (yr)	Corrected[b]
DUJE-2	0.3356	39 ± 0	11,588 ± 100	106.6 ± 4.9	1.05419 ± 0.01910	59.2 ± 1,2	283.470 ± 24012	**276.319 ± 22826**	232.4 ± 20,0
DUJE-5	0.3946	38 ± 0	4575 ± 30	80.1 ± 4.6	1.08016 ± 0.01355	147.6 ± 2.0	396.999 ± 52058	**394.140 ± 50674**	243.6 ± 46.9

Analytical errors are 2 s of the mean.
Those are the values for a material at secular equilibrium, with the crustal $^{232}Th/^{238}U$ value of 3.8. The errors are arbitrarily assumed to be 50%.
Decay constants are $9.1705 \times 10^{-6} yr^{-1}$ for ^{230}Th, $2.8221 \times 10^{-6} yr^{-1}$ for ^{234}U, and $1.55125 \times 10^{-10} yr^{-1}$ for ^{238}U.
[a] $d^{234}U = ([^{234}U/^{238}U]_{activity} - 1) \times 1000$.
[b] $d^{234}U_{initial}$ corrected was calculated based on ^{230}Th age (T), i.e., $d^{234}U_{initial} = d^{234}U_{measured} \times e^{l234*T}$, and T is the corrected age.
[c] $[^{230}Th/^{238}U]_{activity} = 1 - e^{-l230*T} + (d^{234}U_{measured}/1000)[l_{230}/(l_{230} - l_{234})](1 - e^{-(l230 - l234)T})$, where T is the age.
[d] The degree of detrital ^{230}Th contamination is indicated by the $[^{230}Th/^{232}Th]$ atomic ratio instead of the activity ratio.
[e] Age corrections were calculated using an average crustal $^{230}Th/^{232}Th$ atomic ratio of $4.4 \times 10^{-6} \pm 2.2 \times 10^{-6}$.

(Lang and Wolff, 2011). These conditions may have favored continuous formation of calcite cement under humid and temperate conditions. In this respect, the range of the U/Th ages obtained by Castañón and Frochoso (1996) clearly shows the long and complex history of successive cementations recorded in the calcareous breccias.

The oldest age obtained (Duje-5) is of particular interest because it indirectly assigns an age to the glacial phases postulated by Obermaier (1914) and Flor and Baylon-Misioné (1989) that would be, respectively, older and younger than MIS 11. The great width and length of the glacial valley fossilized by the calcareous breccias, which cannot be younger than 430 ka, strongly suggest that this glacial erosion took place during MIS 12, when the most extreme glacial period of the last 1 million years occurred from 460 to 430 ka (Voelker et al., 2010).

Absolute ages dating glacial phases are very scarce in the Iberian Peninsula and most of them refer to the last glacial maximum (LGM). Vidal Romaní et al. (1999), through the study of cosmogenic isotopes from two samples of ice-abraded granite surfaces in Sierra de Xurés-Gêrez (Spain–Portugal boundary), obtained absolute ages indicating 130.7 and 238.3 ka, which they interpreted as belonging to glacial phases older than the LGM. Data now obtained in the Duje Valley correspond to climatic intervals older than those from Xurés-Gêrez, making Duje-5 the oldest date so far obtained in the Iberian Peninsula on intercalated glacial/interglacial deposits.

A more extensive study of these calcareous breccias of Picos de Europa may shed light on the timing and extent of mid-Pleistocene climatic events in southern Europe. In this respect, it is worth noting that the age of the maximum glacial advance observed in the Duje Valley is in accordance with the results provided by in-depth studies carried out in several mountain areas of the Balkans by Hughes et al. (2006, 2010, 2011). These authors, based on geomorphological evidences, soil profile analysis, and U/Th series, established several glacial phases of which the earliest and most extensive recorded glaciation, characterized by large valley glaciers and ice fields, occurred during the mid-Pleistocene during an interval that they correlated with MIS 12.

Concluding remarks

- Calcite cementing the clasts of the extensive Quaternary calcareous breccias exposed in the Duje Valley (Picos de Europa, Cantabrian Mountains) has been dated through the U/Th method. The age obtained indicates that these breccias accumulated during or prior to the anomalously long and warmer climatic period of MIS 11.
- Another sample collected in these same deposits has yielded an age suggesting an additional younger cementation phase during MIS 8.
- Geomorphologic evidence observed in the Duje Valley shows that the calcareous breccias are separating two older and younger glacial phases.
- The older (and major) glacial phase, which is fossilized by the breccias, probably corresponds to MIS 12, the most extreme glacial period of the last 1 million years.
- The age of the maximum glacial advance recorded in the Duje Valley seems to be similar to the age of the maximum glacial advance observed in mountain areas of the Balkans Peninsula.

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