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ISOLEUCINE EPIMERIZATION AGES OF QUATERNARY MAMMALS FROM SICILY

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ABSTRACT - *Isoleucine Epimerization Ages of Quaternary Mammals from Sicily* - Il Quaternario, 4(1a),1991, p. 49-54 - Isoleucine epimerization ages of 48 fossil mammal samples taken from cave, coastal plain and marine deposits in three areas in Sicily fall in two significantly different relative age groups, *i.e.* about 455±90 and 200±40 Ka, respectively. The D-alloisoleucine/L-isoleucine (alle/ile) ratio was measured in the tooth enamel of *Elephas* cfr. *antiquus*, *E. mnaidriensis* Adams, *E. falconeri* Busck, *Hippopotamus pentlandi* Meyer, *Cervus Siciliae* Pohlig and *Praemegaceros carburangelensis* (De Gregorio), and come from the best known sites of mammal fossils in Sicily, *i.e.* the Peloritani-Nebrodi chain, the Iblean Plateau, and the Palermo mountains. *E. falconeri*, which has been considered as the youngest Sicilian elephant since the time when Vaufrey studied this dwarf species (Vaufrey 1929), falls actually in the older relative age group. The epimerization ratios for the medium-sized species of the *Elephas* genus (*E. mnaidriensis*) fall in both the two relative age groups. Conversely, the ratios obtained for the *Hippopotamus pentlandi* samples fit only to the younger group. *E. mnaidriensis* from the older group is associated with *E. falconeri* and with other typically endemic species. The *E. mnaidriensis* samples from the younger group, are associated with hippos as well as with cervids, bovids and carnivores. The obtained epimerization ratios support the assumption that Sicily experienced at least two elephant immigrations in Pleistocene times, and also suggest that a very thorough review of the remains of *E. mnaidriensis* may lead to a discrimination of separate species of this medium-sized elephant in each of the two relative-age groups.

RIASSUNTO - *Isoleucine Epimerization Ages of Quaternary Mammals from Sicily* - Il Quaternario, 4(1a), 1991, p. 49-54 - Vengono descritti i risultati di un'indagine cronologica, effettuata con il metodo basato sulla epimerizzazione della isoleucina, di reperti fossili di mammiferi provenienti da depositi di grotta, di pianura costiera e marini delle tre aree della Sicilia in cui i resti di Mammiferi sono più diffusi e meglio conosciuti(Catena dei Peloritani-Nebrodi, Plateau Ibleo, Monti di Palermo). Il rapporto D-alloisoleucina/L-isoleucina (alle/ile) é stato misurato nello smalto di denti di: *Elephas* cfr. *antiquus*, *E. mnaidriensis* Adams, E. falconeri Busck, *Hippopotamus pentlandi* Meyer, *Cervus siciliae* Pohlig e *Praemegaceros carburangelensis* (De Gregorio). I 48 valori di età ottenuti risultano compresi nelle 2 fasce cronologiche, significativamente ben distinte, di circa 455±90 anni e 200±40 Ka. L' *E. falconeri*, che rappresenta la forma di taglia più ridotta, e fin dai tempi di Vaufrey (1929) ritenuto il più recente elefante siciliano, risulta appartenere alla fascia di età più antica. I valori di età ottenuti per la specie del genere di taglia intermedia (*Elephas mnaidriensis*), ricadono in entrambe le fasce cronologiche, mentre quelli relativi a *Hippopotamus pentlandi* sono compresi solo nella fascia di età più recente. *E. mnaidriensis* della fascia più antica è associato a *E. falconeri* e ad altre specie tipicamente endemiche, mentre quello dell'intervallo più recente è associato all'Ippopotamo, a Cervidi, Bovidi, e Carnivori. I risultati del lavoro da una parte avvalorano l'ipotesi secondo la quale, durante il Pleistocene, sarebbero arrivate in Sicilia almeno due ondate migratorie comprendenti Elefanti e dall'altra indicano la possibilità che, attraverso una revisione dei resti, possano venire distinte due specie di elefanti di taglia intermedia appartenenti, rispettivamente, alla prima ed alla seconda fascia cronologica.

Key-words: Pleistocene mammals, racemization-epimerization reactions, amino-acid age determination, Sicily
Parole chiave: Mammiferi pleistocenici, racemizzazione-epimerizzazione, datazione con amino-acidi, Sicilia

1. INTRODUCTION

Several studies (Vaufrey, 1929; Accordi, 1962, 1963; Azzaroli, 1971; Thaler, 1973; Kotsakis, 1978; Ambrosetti *et al.*, 1980; Caloi & Palombo, 1983; Capasso Barbato & Petronio, 1983; Palombo, 1985; Esu *et al.*, 1986; Caloi *et al.*, 1986; Bonfiglio & Kotsakis, 1987; Brugal, 1987; Burgio & Cani, 1988; Caloi *et al.*, in press) based on various biostratigraphic assumptions have proposed various schemes of chronological sequence of the Quaternary mammalian fauna in Sicily. Newly acquired stratigraphic data, however, do not support some of the assumptions.

Recent studies (Bonfiglio, 1983, 1986, 1987, 1989a, 1989b) suggest, for instance, that the faunal associations in each deposit may depend on ecological factors, and that a faunal association in a cave deposit may be different from that which can be found in the areas facing the falaise on which the cave has been carved.

Current field studies on large mammal-bearing deposits in Sicily have shown the need of new and very detailed stratigraphic data. As a matter of fact no information has so far been given .on the facies of

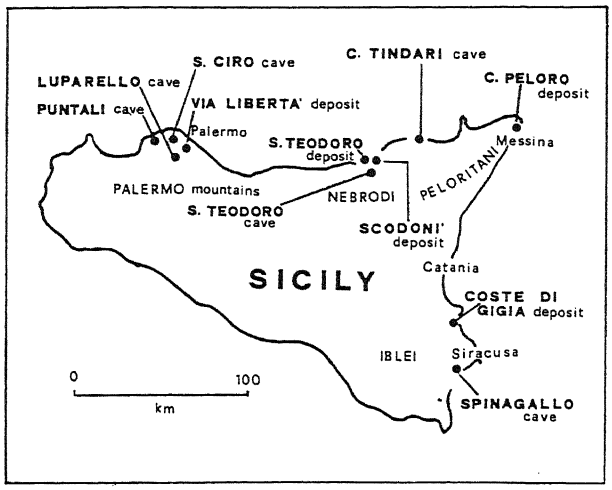

Fig. 1 - Sampled sites
Siti campionati

the sediments where the remains are contained (whether a lacustrine or a marine deposit, or a paleosol, etc.) and on the site where the deposit is found, *i.e.* whether a cave or a coastal plain, etc.). Moreover, no discrimination has been made among the three areas with the largest number of mammal-bearing deposits in Sicily, namely: the Peloritani-Nebrodi range; the Iblean Plateau; and the Palermo mountains (Fig. 1). The three areas are lithologically and morphologically very different from one another, and their pleistocenic tectonic evolution is also very different. Therefore, the respective paleogegraphic conditions must have been varied, each of the paleogeographic environment having a varied influence on the modes and times of settlement of mammalian fauna.

One of the authors (see, Belluomini and Bada, 1985) used the D-alloisoleucine/L-isoleucine ratio in order to date several samples of tooth enamel from *Elephas falconeri Busk* which was thought to be the youngest pleistocenic elephant (Vaufrey, 1929), and the age obtained is 550,000 yr.

Consequently, it was decided to carry on a chronological study on as many samples as possible of mammals from various sites of the three above-mentioned geographic areas in order to complement stratigraphic data and give a scheme of the distribution of mammalian fauna in time.

The method of dating fossil samples using the amino-acid racemization has been developed in the last twenty years (Bada, 1972, 1985; Schröeder and Bada, 1976). It has an effective age determination range from a few 1,000 yr B.P. to several 100,000 yr B.P. (Pleistocene; in some cases, it may also be useful for the entire Pliocene), the actual range being dependent upon the general temperature of the area where the sample was found. Only a few grams (about 5 g) of fossil material are needed for a racemization analysis. Thus, the method offers the possibility of dating even very precious and/or rare samples.

Racemization dating is based on the fact that amino-acid molecules in active living tissues are of the left-handed, or L-isomer, variety — namely, the only form used by the animal enzyme systems. When an animal dies, or the tissues cease to be metabolically active (*e.g.*, tooth enamel), amino-acid molecules begin to change into the right-handed, or D-isomer, variety. The process ends when the ratio of the two isomers is 1:1.

Racemization is a chemical reaction which occurs very slowly at a well-known rate for each amino-acid. Because racemization is a chemical reaction it is temperature-dependent, and to determine the age of a fossil with this method requires that the average temperature to which the fossil has been exposed is carefully evaluated. Temperature evaluation may be attained using the procedure in which the *in situ* rate of amino-acid racemization for a particular area is calculated by measuring the extent of racemization in a sample which was dated with another method. After this "calibration" has been made, other samples from the entire area can be dated based on their extent of amino-acid racemization.

Amino acid racemization reaction has important application in anthropology, paleontology and geochronology.

This paper gives the results of amino acid racemization age determinations on tooth enamel obtained from fossil samples from several sites in Sicily. We assumed that all the samples — all of them having been taken at a depth from 1 to 2 m — although coming from three different areas (see Fig. 1), have probably experienced the same thermal history because it is reasonable to consider Sicily in its whole as a single climatic area.

Calibration of isoleucine epimerization reaction in tooth enamel for Sicily has been obtained by using the tooth enamel of a normal-sized continental elephant — *Elephas (P.) antiquus* — which had been taken from the well-dated middle Pleistocene site of Isernia La Pineta (central Italy) (see Table 1). For Sicily, which, as mentioned, has been considered as a single climatic area, the obtained K_{iso} is equal to $4.7 \cdot 10^{-7}$ yr^{-1} (see Belluomini and Bada, 1985, on how K_{iso} value was calculated).

2. LIST OF THE STUDY SITES AND SAMPLES WITH BASIC INFORMATION

Site: *The Puntali Cave*
Analysed species: *Elephas mnaidriensis* and *Hippopotamus pentlandi*
Type of site or environment: cave
References: Fabiani (1928); Pohlig (1893); Schweinfurth (1907); Vaufrey (1929); Burgio *et al.*

Table 1 - Isoleucine epimerization ages of fossil tooth enamel from Sicily (Italy)
Età calcolata dall'epimerizzazione dell'isoleucina dello smalto di denti fossili provenienti dalla Sicilia

Site[a]	Sample	Alle/ile[b] average	Group average	Alle/ile[d] age (x10^{3}yr)
S.Teodoro Cave	*Elephas mnaidriensis* (A)	0.21 (3)		
Spinagallo Cave	*Elephas falconeri*	0.26 (7)[f]		
Luparello Cave	*Elephas falconeri*	0.21 (3)	0.216±0.013[c]	455±90[e]
Ghiaie di Messina (Capo Peloro)	*Elephas mnaidriensis*	0.18 (4)		
Via Libertà Deposit	*Elephas (cfr) antiquus*	0.22 (4)		
Coste di Gigia Deposit.	*Hippopotamus pentlandi*	0.11 (6)		
Puntali Cave	*Elephas mnaidriensis*	0.08 (2)[f]		
	Hippopotamus pentlandi	0.11 (1)[g]		
Capo Tindari Cave	*Cervus siciliae*	0.08 (2)[g]		
	Praemegaceros carburangelensis	0.09 (4)[g]	0.094±0.004	200±40
S.Ciro Cave	*Hippopotamus pentlandi*	0.09 (3)		
S.Teodoro Deposit. (Acquedolci)	*Hippopotamus pentlandi* (B)	0.08 (3)		
Scodonì Deposit	*Hippopotamus pentlandi* (C)	0.09 (2)		
	Hippopotamuspentlandi	0.11(5)		

a See Figure 1 for site locations
b Number of samples analyzed in parentheses; all the samples were taken from a depth between 1 and 2 m
c Standard deviation
d Calculated from

$$\text{Age} = \frac{\ln Q}{1.8\ K_{iso}} \quad [1], \qquad \text{where } Q = \frac{1 + \text{alle/ile}}{1 - 0.8\ \text{alle/ile}} \quad [2]$$

Ages were calculated by using the Isernia-La Pineta Deposit (Central Italy) for rate calibration (K_{iso}= 2.1 · 10^{-7} yr-1 for Isernia). For Sicily, considered as a single climatic area, the following value was obtained: K_{iso} = 4.7 · 10^{-7} yr-1 (see Belluomini & Bada for a discussion on how the K_{iso} value was obtained).
e The error on the data was computed using the equation of error propagation
d From Belluomini & Bada (1985)
g From Belluomini (1985)
A - From San Teodoro cave; B - From the base of the palaeofalaise; C - From a marine terrace

(1983); Brugal (1987); Petronio (in press); Masini *et al.* (in press); Belluomini (1985); Belluomini and Bada (1985).

Site: *The Luparello Cave*
Analysed species: *Elephas falconeri*
Type of site or environment: cave
References: Vaufrey (1929); Imbesi (1956).

Site: *The San Ciro Cave*
Analysed species: *Hippopotamus pentlandi*
Type of site or environment: cave
References: Scinà (1831); Falconer (1860); Fabiani (1928); Bonfiglio and Di Patti (in press).

Site: *Palermo, Via Libertà*
Analysed species: *Elephas cfr. antiquus*
Type of site or environment: coastal plain (?)
References: Fabiani (1932); Aguirre (1968-1969).

Site: *The San Teodoro Cave*
Analysed species: *Elephas mnaidriensis*
Type of site or environment: cave
References: Anca (1860); Vaufrey (1929); Graziosi & Maviglia (1946).

Site: *Acquedolci* (at the base of the palaeofalaise where San Teodoro cave has been carved)
Analysed species: *Hippopotamus pentlandi*
Type of site or environment: lacustrine deposit
References: Bonfiglio (1983; 1986; 1989a; 1989b).

Site: *Acquedolci* (marine terrace younger than the lacustrine deposit, see above)
Analysed species: *Hippopotamus pentlandi*
Type of site or environment: coastal plain
References: Bonfiglio (1989b).

Site: *Rocca Scodonì*
Analysed species: *Hippopotamus pentlandi*
Type of site or environment: coastal plain
References: Bonfiglio (1987).

Site: *Capo Tindari*
Analysed species: *Praemegaceros carburangelensis, Cervus siciliae*
Type of site or environment: cave
References: Malatesta (1958); Gliozzi & Malatesta (1982); Belluomini (1985).

Site: *Capo Peloro (Messina)*
Analysed species: *Elephas mnaidriensis*
Type of site or environment: fluvio-marine littoral gravel
References: Bonfiglio & Berdar (1979; 1986); Bonfiglio & Violanti (1983); Barrier (1984); Hearty *et al.* (1986).

Site: *Coste di Gigia*
Analysed species: *Hippopotamus pentlandi*
Type of site or environment: karstic cavity and coastal plain
References: Accordi (1957); Bonfiglio (in press).

Site: *The Spinagallo Cave*
Analysed species: *Elephas falconeri*
Type of site or environment: karstic cavity
References: Accordi & Colacicchi (1962); Ambrosetti (1968); Belluomini & Bada (1985).

3. RESULTS AND CONCLUSIONS

The main results obtained from this study are (see also Table 1):

1) The alle/ile ratios obtained from the set of examined samples fall within two relative age groups, the older having an age of 455±90 Ka and the younger of 200±40 Ka.
2) The older age group includes only elephants.
3) Hippos and cervids fall within the younger age group.
4) The alle/ile ratio we obtained for the dwarf elephant species from the Luparello Cave matches very well the relative age of 500,000 years obtained by Belluomini & Bada (1985) for the *Elephas falconeri Busk* from the Spinagallo cave, a result that was much discussed at the time obtaining a large interest and that can now be fully confirmed.
5) The relative age of the elephant-hippo association was determined only from samples from the Puntali Cave, because the samples of elephant remains from Coste di Gigia and S.Ciro Cave we had at disposal were unique specimens from private collections which we were not allowed to damage. Nevertheless, stratigraphical data on Coste di Gigia (Accordi, 1957; Bonfiglio, in press) and S.Ciro cave (Scinà, 1831) deposits leave no doubt that the elephant and hippo remains from the two deposits are coeval.
6) In the Messina Gravel deposit the only samples suitable to be used for age determinations were remains of the medium-sized elephant, *i.e. E. mnaidriensis*. Because of reworking, the mammal remains within the deposit (Bonfiglio & Berdar,1979) cannot surely be regarded as coeval with *E. falconeri*, hippos and deers, such as can be inferred for the Coste di Gigia and S.Ciro Cave associations.
7) Even if we analysed a large number (48) of samples, none of them has given relative age values falling in the wide interval between the two aforesaid relative age groups (≅ 500,000 and ≅ 200,000 years). This fact cannot be regarded as casual, and it has to be further investigated because it may indicate two well discriminated environmental conditions in Sicily.

On the basis of these results, and from the current knowledge on the stratigraphy of the sampling sites, we can conclude that:

1) The *E. mnaidriensis* remains giving relative age values in the older group are associated with *E. falconeri* and other typically endemic species.
2) The *E. mnaidriensis* remains giving relative age values in the younger group are associated with hippos, cervids, bovids and carnivores. In some of the sites (Coste di Gigia; San Ciro cave) hippos are the dominant species, whereas in other sites (Puntali Cave) elephants prevail.
3) *E. falconeri* has resulted to be associated with hippos only in the Messina Gravel deposit where, however, its remains are reworked.
4) Studies still in progress (Burgio & Cani, in press) would show that there are significant morphological differences between elephant remains which have up to now been ascribed to the same species even if coming from different deposits
   A review of these remains in the light of the results we have obtained in this study might lead to a discrimination between the populations of *E. mnaidriensis*, assigning them to either of the two age groups we have discriminated.
5) The results of age determinations we carried out and the conclusions reached support the assumption that Sicily experienced at least two elephant immigrations in Pleistocene times (Belluomini & Bada, 1985). There are still too few data, however, to define which species composed the membership of the two faunal immigrations. This should be obtained through: – a review of the Sicilian mammalian fauna in Pleistocene with special reference to their origin; and – a detailed stratigraphic analysis of a number of settings as large as possible.

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