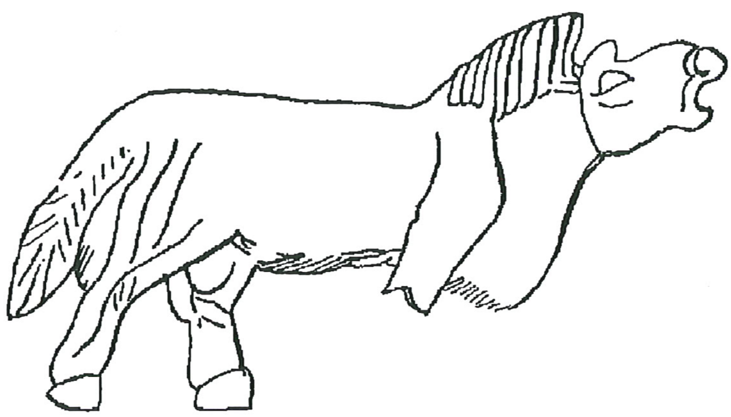
ICAZ

ARCHAEOZOOLOGY OF THE NEAR EAST IV B

Proceedings of the fourth international symposium on the archaeozoology of southwestern Asia and adjacent areas

edited by

M. Mashkour, A.M. Choyke, H. Buitenhuis and F. Poplin



ARC - Publicatie 32
Groningen, The Netherlands, 2000

Cover illustration:
Przewalski from Susa (nacre – mother of pearl)
Dated to 2500 – 2000 BC, identified by F. Poplin

Printing: RCG -Groningen

Information: Centre for Archeological Research and Consultancy
Poststraat 6, 9712 ER Groningen, The Netherlands

ISBN 90 – 367 – 1243 - 2
NUGI 644 - 134

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VOLUME B

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VOLUME A

PALAEOENVIRONMENTAL AND ARCHAEOLOGICAL IMPLICATIONS OF BONE AND TOOTH ISOTOPIC BIOGEOCHEMISTRY (^{13}C, ^{15}N) IN SOUTHWESTERN ASIA

Hervé Bocherens[1], Daniel Billiou[1], Vincent Charpentier[2] and Marjan Mashkour[3]

Abstract

Preliminary isotopic investigations of modern and archaeological skeletal remains from Southwestern Asia have been undertaken on sites spread geographically from the Caspian Sea shores in the North to the southern part of the Arabian Peninsula in the South. The time period considered ranges from Neolithic (sixth millennium BC) to recent times. Carbon and nitrogen isotopic compositions of modern herbivores demonstrate great variability according to local environmental conditions. Such high variability emphasizes the need for calibration of the food webs on a local scale. The preservation of collagen appeared very good in sites from cold and dry areas (Northern Iran) but very poor at sites in hot and dry regions (Arabian Peninsula). In the latter case, the inorganic (bioapatite) phase of mineralized vertebrate tissues may be a potential support for carbon isotopic signatures, especially in enamel which is extremely stable under burial conditions.

Résumé

Des recherches isotopiques préliminaires ont été entreprises sur des éléments squelettiques modernes et archéologiques du sud-ouest de l'Asie s'étendant géographiquement du sud de la mer Caspienne à l'extrême nord et à l'est de la Péninsule arabique. La période considérée s'échelonne du Néolithique (ca 6000 BC) à la période actuelle. Les compositions isotopiques en carbone et en nitrogène d'herbivores modernes montrent une grande variabilité suivant les conditions environnementales locales. Ces écarts importants soulignent la nécessité d'un calibrage des réseaux trophiques à l'échelle locale. La conservation du collagène s'est montrée très satisfaisante dans les sites appartenant à des environnements froids et secs (nord de l'Iran) mais très mauvaise dans les sites de régions chaudes et sèches (Péninsule arabique). Dans ce dernier cas, la phase inorganique (bioapatite) des tissus minéralisés de vertébrés est un support potentiel pour la signature isotopique du carbone, spécialement dans l'émail qui demeure extrêmement stable dans des conditions d'enfouissement.

Key Words: Bioapatit, Carbon-13, Collagen, Nitrogen-15, Palaeoenvironment

Mots Clés: Bioapatite, Carbon-13, Collagène, Nitrogen-15, Paléoenvironnement

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Introduction

Isotope biogeochemistry of bone and tooth has become a widespread approach in archaeozoology and palaeoanthropology, increasing greatly the amount of information that can be retrieved from osteological remains. Such studies were first carried in tropical areas, i.e. Africa and America (e.g. Vogel and van der Merwe 1977; Burleigh and Brothwell 1978; van der Merwe and Vogel 1983; Ambrose and DeNiro 1986) and later spread to other places, such as Europe (e.g. Tauber 1981, 1986; Noe-Nyggard 1988; Bocherens *et al.* 1991), Asia (Roksandic *et al.* 1988) and Australia (Hobson and Collier 1984). However, Southwestern Asia remains rather neglected as far as this approach is concerned. Applications of carbon and nitrogen isotope biogeochemistry in archaeological bone and tooth is linked to the isotopic heterogeneity of the environment and to the preservation of biogenic isotopic signatures in vertebrate mineralized tissues, namely in their organic (collagen) and mineral (carbonate

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hydroxylapatite) fractions. Isotopic heterogeneity is best in tropical environments, especially between grassland and forested areas, where plants clearly exhibit different carbon isotopic signatures, and between coastal and terrestrial environments, where carbon and nitrogen isotopic signatures are different. Several decades of radiocarbon dating have exemplified the fact that the preservation of collagen is much better in archaeological skeletal fragments from cold compared to warm environments. When collagen is not sufficiently well preserved, carbon isotopic signatures can potentially be retrieved from the carbonate fraction of these fragments.

In this paper, we will focus on the potentialities of carbon and nitrogen isotopic geochemistry of archaeozoological remains from the Southwestern Asian area, with emphasis on ecological particularities as compared to more thoroughly investigated regions. The state of preservation of collagen will also be investigated through case studies. Most results are new but already published values have been added when necessary. Finally some applications carried out in this region and perspectives will be briefly presented.

Principles of isotopic geochemistry of archaeozoological remains with emphasis on southwestern Asian ecosystems

Carbon-13

Carbon isotopic compositions (expressed as $\delta^{13}C$[4] values) in ecosystems primarily reflect the photosynthetic pathways and environmental parameters of the plants forming the basis of the food webs. In terrestrial plants, the two major photosynthetic pathways, i.e. the so-called "C_3" and "C_4" pathways, lead to clearly different isotopic discriminations. Both types of plants are ^{13}C-depleted relative to their source of inorganic carbon, atmospheric CO_2 with a $\delta^{13}C$ value around -8 ‰, but C_4-plants are much less depleted than C_3-plants ($\delta^{13}C$ = -27.1 ± 2.0 ‰ and $\delta^{13}C$ = -13.1 ± 1.2 ‰ for C_3 and C_4-plants respectively; O' Leary 1981). On a worldwide scale, most C_4-plants are grasses from warm areas, distributed in regions where the growing season is the warm one (monsoon system), on the other hand, C_3-plants are represented by all the trees as well as herbaceous plants, under any climatic condition, from temperate and cold areas, where the growing season is cool. In Southwestern Asia and adjacent areas, the zone of monsoon rainfall is represented by the Saharo-Arabian and the Sudanian regions (Fig. 1). The boundary of this zone is not so sharp and progressive changes in the relative abundance of C_4 versus C_3-grasses is observed, for instance along the Nile valley in Egypt (Batanouny *et al.* 1988). Less important in biomass but locally significant are some C_4 species which are halophytes adapted to saline environments in the Irano-Turanian region (Fig. 1: Winter 1981; Frey and Kürschner 1983). In the Euro-Siberian and Mediterranean regions, the last phytogeographical areas represented in Southwestern Asia, C_4-plants are extremely scarce (Mateu Andrès 1993). Thus, Southwestern Asia can be roughly divided into three zones as far as the proportion and ecological role of C_4-plants is concerned (Fig. 1): the Euro-Siberian and Mediterranean regions, where C_4-plants are negligable; the Irano-Turanian region, where C_4-plants can locally be ecologically important in saline environments, mainly as Chenopodiaceae; and the Saharo-Arabian and Sudanian regions, where C_4-plants are very widespread as grass. Among C_3-plants, some environmental conditions lead to different carbon isotopic compositions. In closed forested environments, where the CO_2 available to understorey plants is ^{13}C-depleted relative to the general atmosphere due to the contribution of CO_2 generated by respiration and organic matter decomposition and where light intensity is lower, plants exhibit $\delta^{13}C$ values as low as or lower than -30 ‰. On the other hand, water and saline stress environments lead to less isotopic fractionation of carbon in C_3-plants, which thus have $\delta^{13}C$ values as high as -20 ‰ (Guy *et al.* 1980). It is noteworthy that the carbon I sotopic composition of atmospheric CO_2 has

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[4] Isotopic abundances are expressed as δ (delta) values as follows: $\delta^{E}X = (R_{sample}/R_{standard} - 1)x1000$ (‰), where X stands for C or N, E stands for 13 or 15 respectively, and R stands for the isotopic ratios $^{13}C/^{12}C$ and $^{15}N/^{14}N$ respectively. The internationally defined standard is a marine carbonate (PDB) for carbon and atmospheric nitrogen (AIR) for nitrogen

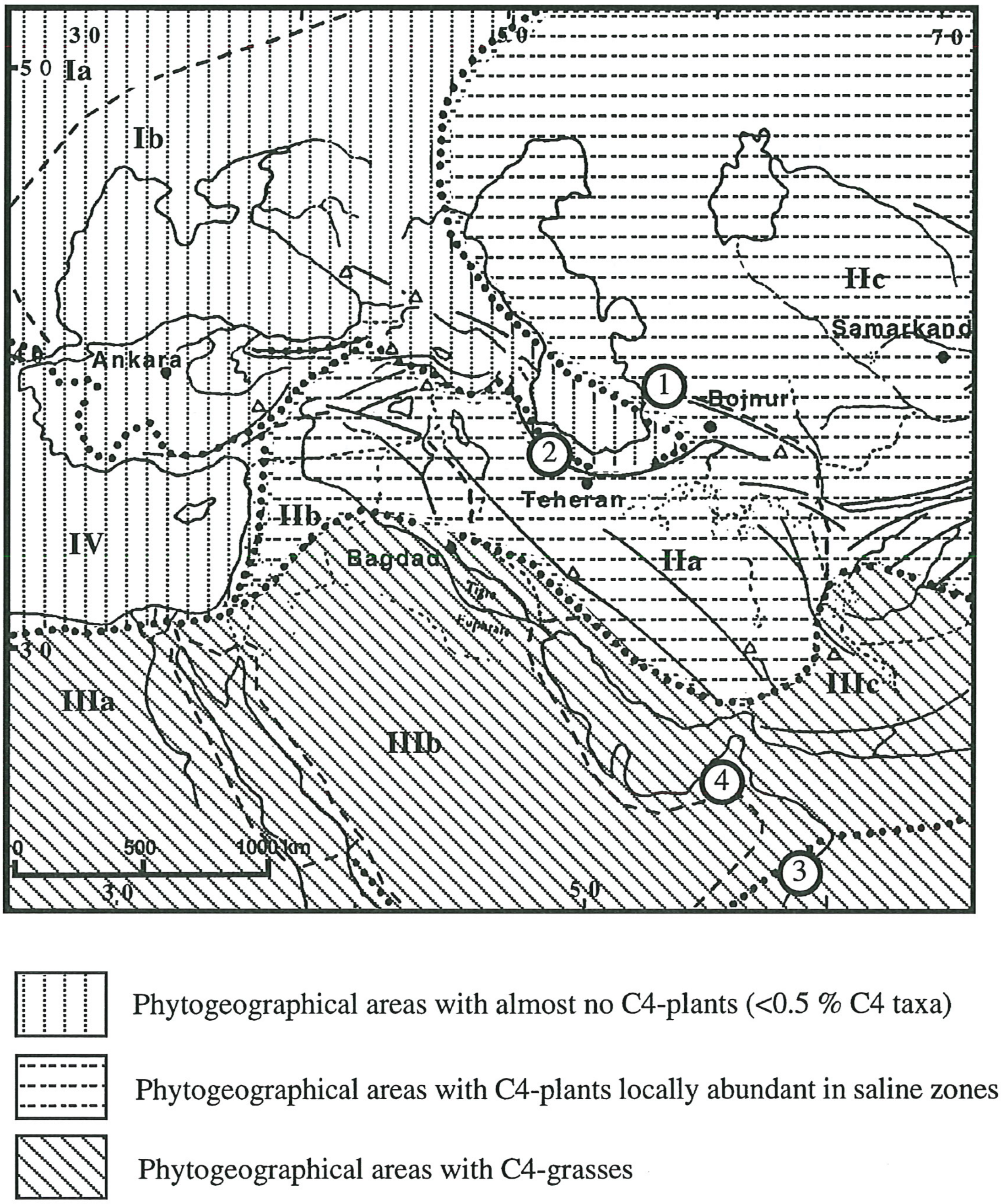

Fig. 1: Main phytogeographical areas in southwestern Asia and site location (1 = Dehistan Plain; 2 = Qavzin Plain; 3 = Ras Al-Junayz area; 4 = Mleiha). The phytogeographical areas have been separated according to the proportions and ecological distribution of C4-plants. Map after Klein (1994, modified). I: Euro-Siberian region : Ia = Medio-European sub-region; Ib: Pontic sub-region; II: Irano-Turanian region : IIa = Irano-Anatolian sub-region; IIb = Mesopotamian sub-region; IIc = Medio-Asiatic sub-region; III: Sindian region; IIIa = Saharian sub-region; IIIb = Arabic sub-region; IIIc = Nubo-Sindian sub-region; IV: Mediteranean region

changed since the Industrial Revolution, about 150 years ago. The addition of CO_2 resulting from fossil fuel combustion and deforestation with low $\delta^{13}C$ values led the $\delta^{13}C$ values of atmospheric CO_2 to decrease from around -6.5 ‰ in 1850 to -8 ‰ nowadays (Marino and McElroy 1991). This isotopic shift will have to be considered when attemps are made to compare $\delta^{13}C$ values measured in archaeological versus modern specimens.

The carbon isotopic compositions of plants are reflected in the tissues of their consumers, with an isotopic shift which is mainly linked to the analysed tissue (DeNiro and Epstein 1978). The average $\delta^{13}C$ value in an organism's body is similar to that of its average diet, but its different biochemical fractions consistently present different carbon isotopic compositions due to fractionation during the metabolic pathways (Deines 1980). For instance, carbohydrates globally present a similar $\delta^{13}C$ value compared to the body as a whole, whereas lipids are depleted (around 4 ‰) and proteins are enriched (around 2 ‰) relative to the whole body (DeNiro and Epstein 1978). The tissues of interest for the archaeozoologist are collagen in bone and dentine, the carbonate fraction of bioapatite present in bone, as well as dentine and enamel, due to their potentials for long-term preservation. Soft tissues may also be exceptionally preserved in very dry environments, for instance in mummies. However, such occurences are very limited and will not be considered in the present work. The actual value of the isotopic shift between the carbon isotopic composition of diet and that of the analysed tissue, collagen or carbonate, is crucial for interpreting the measured values. It has been investigated through laboratory experiments (e.g. DeNiro and Epstein 1978; Hare *et al.* 1991; Ambrose and Norr 1993;

Table 1. List of modern specimens considered in the present study with their isotopic composition. Abbreviation: av = average; sd = standarddeviation; [1] = Bocherens (1992)

Number	Species		Body part	yield mg/g	C %	N %	C/N	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	ref
Dehistan Plain (Southwestern Turkmenistan)										
GD100	sheep	*Ovis aries*	mandible	182.7	44.1	15.4	3.3	-19.5	11.2	
GD200	sheep	*Ovis aries*	mandible	174.5	44.1	15.3	3.3	-19.9	12.5	
GD900	cattle	*Bos taurus*	phalanx I	242.8	42.8	15.5	3.2	-18.8	12.6	
GD70000	donkey	*Equus asinus*	mandible	182.1	43.8	15.8	3.2	-17.2	12.0	
GD1400	camel	*Camelus dromaderius*	mandible	165.0	43.9	15.5	3.3	-14.2	12.0	
							av.	-17.9	12.0	
							sd	2.1	0.5	
Qavzin Plain (Northern Iran)										
IR300	caprine	*Ovis/Capra*	skull	242.4	42.6	15.3	3.2	-19.5	8.7	
IR400	goat	*Capra*	radius/ulna	232.5	42.6	16.1	3.1	-19.1	9.6	
IR500	caprine	*Ovis/Capra*	mandible	171.9	42.7	15.5	3.2	-17.1	11.6	
IR600	donkey	*Equus asinus*	radius/ulna	200.9	43.3	15.9	3.2	-17.2	10.8	
IR700	donkey	*Equus asinus*	mandible	236.4	43.2	16.2	3.1	-15.9	10.3	
							av.	-17.7	10.2	
							sd	1.3	1.0	
Oman										
OM100	equid	*Equus*	mandible	118.3	40.8	14.9	3.2	-10.5	6.3	
OM200	donkey	*Equus asinus*	metapodium	217.0	42.3	15.5	3.2	-9.5	7.9	
OM300	bovid	*Bos*	vertebra	173.3	40.8	15.1	3.2	-10.8	6.7	
							av.	-10.3	7.0	
							sd	0.6	0.7	
Turkey										
40601	horse	*Equus caballus*	skull	212.0				-20.1	4.7	[1]
2201	camel	*Camelus dromedarius*	rib	156.0				-20.6	7.7	[1]
Northern Greece										
34701	sheep	*Ovis aries*	skull	219.6				-20.7	6.4	[1]
34501	horse	*Equus caballus*	mandible	170.6				-18.8	4.4	[1]
							av.	-20.1	5.8	
							sd	0.8	1.3	

Tiezsen and Fagre 1993) as well as in the field (e.g. Vogel 1978; Van der Merwe 1982; Lee-Thorp *et al.* 1989; Bocherens and Mariotti 1992). Recently some very well controlled dietary experiments on rodents have yielded key results regarding the relationship between dietary and measured carbon isotopic compositions (Ambrose and Norr 1993; Tieszen and Frage 1993). Both studies have clearly demonstrated that collagen presents $\delta^{13}C$ values directly linked to those of the protein fraction of the diet, whereas carbonate presents $\delta^{13}C$ values directly linked to those of the whole diet. In cases where all the biochemical fractions, i.e. lipids, carbohydrates and proteins, come from an isotopically homogeneous source, collagen is enriched around 5 ‰ relative to the average diet whereas carbonate apatite is enriched around 9 ‰ relative to the average diet. There seems to be a special case for large herbivores, such as ruminants and equids, using digestion assisted by microbial fermentation where the shift between dietary and carbonate $\delta^{13}C$ values is larger (around 12-14 ‰: Lee-Thorp *et al.* 1989; Bocherens and Mariotti 1992). This effect has been interpreted as a consequence of methane production during such digestive processes (Hedges and van Klinken, in press). Another special case occurs when the protein fraction of the diet presents a different $\delta^{13}C$ value than that of the carbohydrates and lipids. This might occur in the case of omnivorous species, such as humans, where the protein rich dietary fraction, such as fish meat, may be isotopically distinct from the rest of the diet (plants). In such a case, a large range of values can be obtained (Ambrose 1998).

Nitrogen-15

As opposed to carbon, a significant enrichment occurs between an organism's diet and its body, leading to $\delta^{15}N$ values around 3 to 4 ‰ higher in the body than in the average diet (Minagawa and Wada 1984). This trophic isotopic effect leads to higher $\delta^{15}N$ values in carnivore collagen relative to that of their prey. Independantly from dietary factors, a relationship has been found between herbivore $\delta^{15}N$ values and annual rainfall: collagen $\delta^{15}N$ values increase with aridity (Heaton *et al.* 1986; Sealy *et al.* 1987; Gröcke *et al.* 1997). Thus, collagen $\delta^{15}N$ cannot be used as an absolute proxy for diet. However, knowledge of individual diet allows $\delta^{15}N$ variations to be interpreted in terms of aridity level (Gröcke *et al.* 1997). Local conditions such as soil acidity or salinity can also change plant $\delta^{15}N$ values (Mariotti *et al.* 1980; Page 1995), thus shifting the whole food web isotopically (Rodière *et al.* 1996).

Material

Modern samples

Skeletal fragments from modern domestic herbivores found during archaeological excavations have been collected from Iran, Turkmenistan and Oman (Table 1). The samples come from the following species: cattle (*Bos taurus*), sheep (*Ovis aries*), goat (*Capra hircus*), camel (*Camelus dromaderius*), horse (*Equus caballus*) and donkey (*Equus asinus*). The collection area in Iran is the

Table 2. Amount of nitrogen in archaeological bones from Iran and the Arabian Peninsula. Values for Iranian samples are from Bocherens *et al.* (in press) while values for Mleiha are from Bocherens and Mashkour (1999)

Site	Age	% N bone				
		min.	max.	av.	sd	n
Zagheh (Iran)	~4,700 cal BC	0.5	3.4	2.0	1.0	14
Qabrestan (Iran)	~3,500 cal BC	0.2	3.5	2.2	0.9	18
Sagzabad (Iran)	~1,000 cal BC	1.0	3.4	2.5	0.9	12
Mleiha (Trucidal States)	AD 225 – 325	0.2	0.6	0.4	0.1	18
Ra's Al-Jins	2,000 BC	0.1	0.6	0.3	0.2	9

Qavzin Plain, located in Zanjan Province 140 km north-west of Tehran, approximately 1200 m above sea level. It is delimited by the two most important mountains in Iran: Elburz on the east and north-east which also separates the plain from the Caspian shores, and the eastern slopes of the Zagros Mountains on its western part (Mashkour, in preparation). Samples from Turkmenistan have been collected from the Dehistan plain, located on the eastern shores of the Caspian Sea (Mashkour 1998). Samples from Oman come from the Ras Al-Junayz region, a desert area close to the sea on the eastern coast of Oman, where annual rainfall is extremely low (Büttiker and Krupp 1989; Bökönyi 1998). Only equids and cattle samples have been investigated since goat, sheep and camels are frequently fed with dried fish in this area (Munton 1988; Charpentier 1996), which means that their collagen isotopic compositions do not reflect the local vegetation cover.

Table 3. Amount of nitrogen in archaeological bones from Ra's Al Jins (2,200 BC)

Species	Number	%N bone
equid (*Equus* sp.)	OM900	0.1
equid (*Equus* sp.)	OM1000	0.2
goat (*Capra ibex)*	OM1100	0.1
goat (*Capra ibex)*	OM1200	0.2
goat (*Capra ibex)*	OM1300	0.6
goat (*Capra ibex)*	OM1400	0.2
dog (*Canis familiaris)*	OM1500	0.2
wolf (*Canis lupus)*	OM1600	0.6
human (*Homo sapiens)*	OM1700	0.2

Archaeological samples

Bone material from two sets of sites have been investigated for collagen preservation (Table 2), one set from northern Iran where arid, cold climatic conditions prevail and one set from the southeastern Arabian Peninsula where the climate is arid and warm.

Three Iranian sites located in the Qazvin plain and ranging in age from around 5000 to 1000 cal BC have been studied. Zagheh dates back to the sixth millennium BC (Neolithic), Qabrestan to the fourth millenium BC (Bronze Age) and Sagdabad to end of the second millenium BC (Mashkour *et al.* in press).

Two sites from Oman (Ra's Al-Jins) and the Trucid States (Mleiha) have been investigated. Ra's Al-Jins dates back to the third millenium (Chalcolithic). The bone material comes from domestic herbivores, i.e. equids and goats, as well as dog, wolf and humans (Table 3). Mleiha is located south of the modern city of Dhayd, in the western Piedmont of the Oman Mountains. The occupation period of the site extends from the 3rd century BC to the 1st-2nd centuries AD (Mouton 1992). The studied material comes from the CW harbour area and dates from AD 225 to AD 325. The bones come from herbivorous herbivores (ovicaprines, camelids), wild herbivores (gazella) and fish (Bocherens and Mashkour 1999).

Methods

Measurement of nitrogen amounts in whole bone

In order to estimate the amount of collagen potentially preserved in archaeological bone, whole bone nitrogen was measured using an EA-IRMS elemental analyser calibrated with standard products (Bocherens *et al.* 1997).

Collagen purification and isotopic analysis

Collagen was extracted according to the protocole published in Bocherens *et al.* (1991). Briefly, about 200 to 500 mg of powdered bone or dentine were decalcified in 1 M HCl for 20 minutes at about 20°C. After filtering, the insoluble residue containing collagen, was treated at room temperature with 0.125 N NaOH for 20 hours. The collagen was then filtered again, rinsed with distilled water and solubilised in 0.01 M HCl (pH=2) in closed tubes at 100°C for 17 hours. After centrifugation, the supernatant containing solubilised collagen was freeze dried. Extraction yield (mg/g) is expressed as the ratio of the freeze dried organic matter to the dry weight of the bone or tooth sample. Collagen was analyzed for the isotopic composition of nitrogen and carbon by means of an EA-IRMS elemental analyser connected to an VG Optima isotopic ratio mass spectrometer which also allowed the calculation of the %C, %N and C/N ratios (Iacumin *et al.* 1996). Isotopic results are calibrated against a well-known product analysed in the same way as the samples, used as an internal reference. Isotopic abundances measured in this way are relative abundances: enrichment or depletion of heavy isotopic varieties (^{13}C, ^{15}N) are expressed versus international standards. The isotope ratios are expressed for carbon as $\delta^{13}C$ *versus* PDB-1 (a marine carbonate) and for nitrogen as $\delta^{15}N$ *versus* AIR (atmospheric N_2): $\delta X = (R_{sample}/R_{standard} - 1)x1000$, where X stands for ^{13}C or ^{15}N and R stands for $^{13}C/^{12}C$ or $^{15}N/^{14}N$, respectively. The precision is 0.1 ‰ for $\delta^{13}C$ and 0.2 ‰ for $\delta^{15}N$.

Results and Discussion

Notes on the isotopic ecology of Southwestern Asia

It appears that the isotopic compositions of the modern herbivore collagen analysed in this study vary greatly according to their places of origin (Table 1). The Turkmenistan specimens yielded collagen with $\delta^{13}C$ values ranging from -19.9 to -14.2 ‰ (average = -17.9 ± 2.1 ‰) and $\delta^{15}N$ values ranging from 11.2 to 12.6 ‰ (average = 12.0 ± 0.5 ‰). The range of $\delta^{13}C$ values is quite similar for Iranian specimens (-19.5 to -15.9; average = -17.7 ± 1.3 ‰), but their $\delta^{15}N$ values are lower, ranging from 8.7 to 11.6 ‰ (average = 10.2 ± 1.0 ‰), the ranges barely overlapping. The Omanian specimens exhibit much higher $\delta^{13}C$ values, ranging from -10.8 to -9.5 ‰, whereas their $\delta^{15}N$ values are much lower than those of Iranian and Turkmenistan specimens, ranging from 6.3 to 7.9 ‰. Isotopic compositions from Turkish and Greek specimens examined by Bocherens (1992) have been referred to here for comparison and their $\delta^{13}C$ values are the lowest, ranging from -20.7 to -18.8 ‰, whereas their $\delta^{15}N$ values are low and range from 4.4 to 7.7 ‰ (Table 1 and Fig. 2).

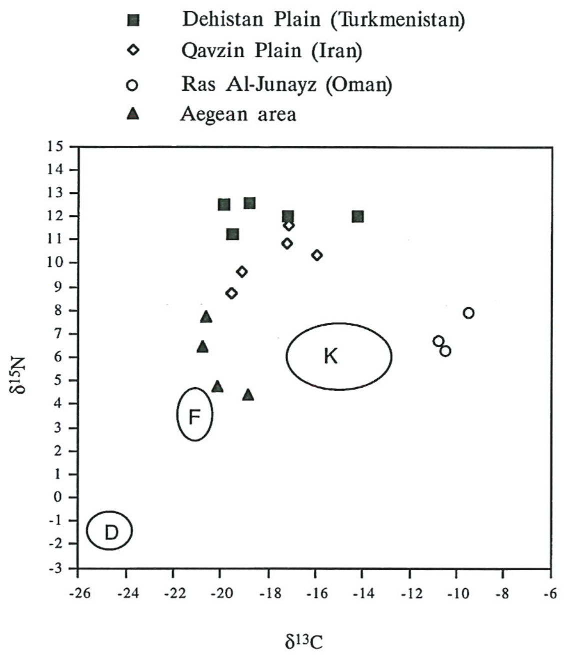

Fig. 2. Carbon and nitrogen isotopic compositions of modern herbivorous mammals bone collagen from different geographical areas. Keys for abbreviations are as follows: Ellipses are centered on the respective average δ values of three modern populations outside the study area, with their diameters equal to the standard-deviations of $\delta^{13}C$ and $\delta^{15}N$ values. D stands for Dourdan forest roe-deers (Rodière *et al.*, 1996), F stands for France (Bocherens *et al.*, 1994) and K stands for Kerma (Iacumin *et al.*, 1998).

As expected from the botanical composition of their respective areas of origin, the $\delta^{13}C$ values of the studied herbivores tend to increase when the proportion of C_4-plants increases. Almost no evidence of C_4-plant consumption is seen in herbivores from the Aegean area, as deduced from the comparison with the average composition of herbivores from France (Fig. 2). Slightly less negative $\delta^{13}C$ values from the Aegean specimen, relative to the French specimens, might reflect a more open environment in the former area. The samples from Oman present $\delta^{13}C$ values indicating an almost pure C_4 diet (Fig. 2). In this area, herbaceous plants are predominantly C_4. Indeed, grasses such as *Cenchrus ciliaris*, *Panicum turgidum* and *Pennisetum divisum*, which are the dominant species in the area according to Cope (1988), are C_4-plants (Batanouny *et al.* 1988). In Iran and Turkmenistan, herbivore $\delta^{13}C$ values indicate a significant contribution of C_4-plants in the diet, although C_3-plants seem to be predominant. In these areas, C_4-plants are mainly halophyte species adapted to saline environments rather than grasses (Winter 1981).

The nitrogen isotopic compositions taken altogether present a wide range of variation, from 4.4 to 12.5 ‰. The $\delta^{15}N$ values appear to be clustered relative to the geographical origin of the studied specimens. The average $\delta^{15}N$ value is highest for herbivores from Turkmenistan ($\delta^{15}N = 12.0 \pm 0.5$ ‰), lower for herbivores from Iran ($\delta^{15}N = 10.2 \pm 1.0$ ‰), still lower for specimens from Oman ($\delta^{15}N = 7.0 \pm 0.7$ ‰) and lowest for specimens from the Aegean area ($\delta^{15}N = 5.8 \pm 1.3$ ‰). These results clearly illustrate the variability of herbivore $\delta^{15}N$ values, independently from their diet. Herbivores can present clearly different $\delta^{15}N$ values even when they lived in rather nearby geographical zones, such as the Qavzin and Dehistan Plains, both on the edges of the Caspian Sea. Although these results are still few and preliminary, it is noteworthy that the highest $\delta^{15}N$ values are measured for herbivores from dry areas (the Dehistan and Qavzin Plains), and in such cases, there seems to be a correlation between high $\delta^{15}N$ and high $\delta^{13}C$ values (Fig. 2). This is not surprising since in the study area C_4-plants (with high $\delta^{13}C$ values: Guy *et al.* 1980) are related to saline environments, where plants present high $\delta^{15}N$ values (Page 1995). When compared to $\delta^{15}N$ values measured on herbivores from adjacent regions, the range of values for herbivores around the Caspian Sea seem rather high (Fig. 2). Such high $\delta^{15}N$ values are similar to those usually measured in freshwater ecosystems (Dufour *et al.*, in press) and thus confusion may occur if a palaeodietary study involving such terrestrial herbivores and freshwater food resources is carried out. These results demonstrate the necessity of calibrating the isotopic values of food resources on a local basis, as within any other region in the world, but the heterogeneity of Southwestern Asia in this matter makes this calibration all the more crucial. Moreover, due to environmental changes through time, the calibration of the isotopic values of local food resources must be performed on samples collected from the same time horizon as the studied population.

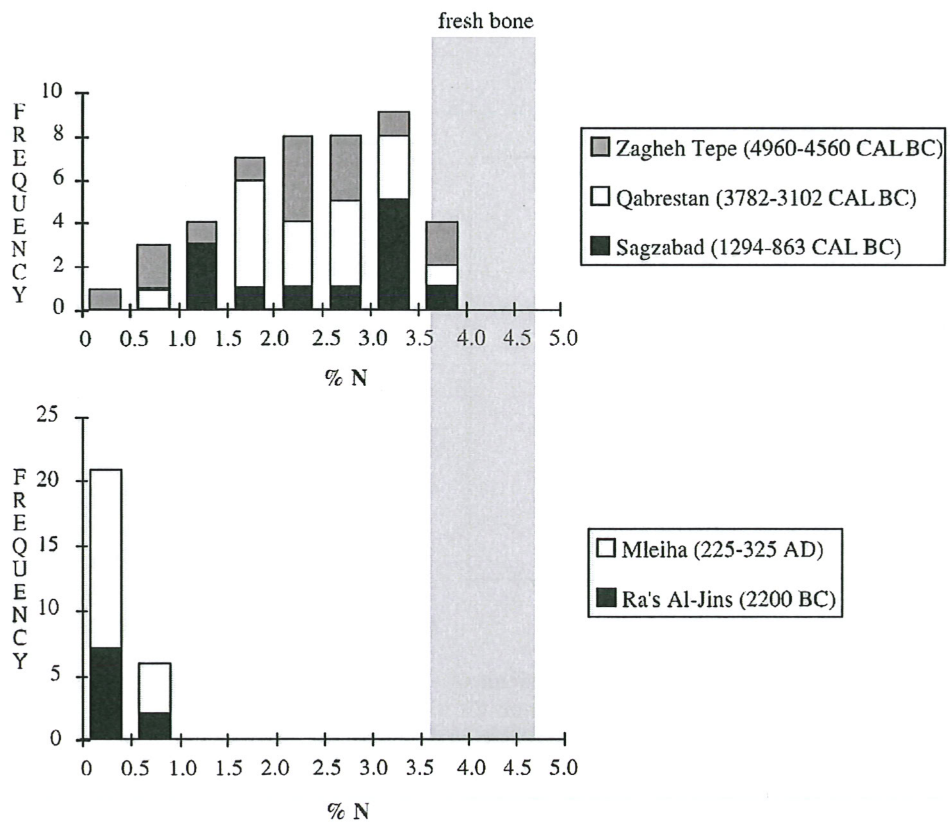

Fig. 3. Percentage (%) N in whole bones from archaeological sites in Iran (above) and in the Arabian Peninsula (below). The grey area stands for the range of % N measured in fresh bones

Notes on collagen preservation

The amount of nitrogen ranges from 0.2 to 3.5 % in samples from three archaeological sites from Iran (Table 2 and Fig. 3). The average and standard-deviation values are very similar at the different sites (Table 2), between 2.0 and 2.5 %, independently of their respective ages. On the contrary, samples from the Arabian Peninsula present nitrogen amounts ranging from 0.1 to 0.6 %, with very low average values (0.4 and 0.3 % for Mleiha and Ra's al-Jins: Table 2). It thus appears clearly that skeletal material from the northern sites yielded much more collagen than those from the southern warm sites, although many of the latter samples are younger in age than the former ones. Other studies had evidenced the negative impact of warm and dry climates on collagen preservation. For instance, bones dated around 700 BC to 400 AD from Egypt showed very poor collagen preservation (Grupe 1995), and bones from Kerma (Sudan, around 2,000 years BC) also presented bad collagen preservation (Iacumin *et al.* 1998). On the other hand, numerous sites, many thousand years old, from temperate Europe have yielded well preserved collagen (e.g. Bocherens *et al.* 1991; 1997; Ambrose 1998). Some obvious implications for archaeozoology in southwestern Asia are that sites located in cold environments will be more promising for studies in isotopic biogeochemistry of ancient collagen, whereas bones from sites located in arid and warm areas will have little chance to contain sufficiently well-preserved collagen. In such cases, even when whole bone nitrogen amounts are high enough and when insoluble residues can be extracted from the bones, the chemical quality of such residues is frequently altered. Their C/N ratios fall outside the 2.9 - 3.6 range which characterizes unaltered collagen (DeNiro 1985), such as for the samples from Ra's Al Jins and Kerma (Fig. 4). Such samples are thus useless for palaeobiological applications of isotopic biogeochemistry. In such cases, an alternative is to use isotopic biogeochemistry in the mineral phase of fossil samples, i.e. the carbonate hydroxylapatite, which isotopic signature is usually preserved in enamel, but may be altered in bone or dentine even a few thousand years old (Koch *et al.* 1997).

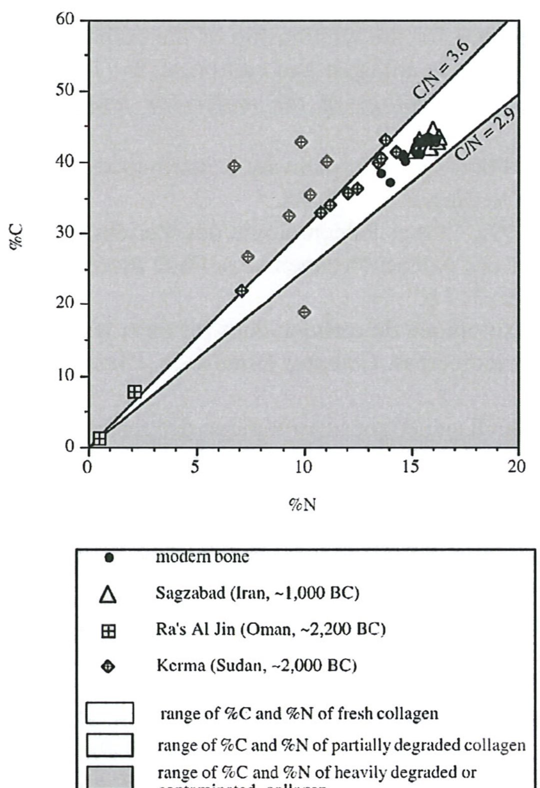

Fig. 4. %N and %C of collagen extracted from modern and archaeological bones from different sites. Kerma values are from Iacumin *et al.* (1998) and Sagzabad values are from Bocherens *et al.* (in press)

Archaeological implications

At sites where collagen is sufficiently well preserved, it will be possible to use both carbon and nitrogen isotopic signatures to investigate palaeodietary and palaeoenvironmental questions. For instance, one application of nitrogen isotopic variations in ancient collagen is the investigation of possible changes in aridity and salinity around the Caspian Sea (Bocherens *et al.*, submitted). Also amounts of ^{15}N in coastal areas can be used to investigate fish consumption, which is an important issue in Southwestern Asian archaeology (e.g. Grupe and Schutkowski 1989; Littleton and Frohlich 1989; Bökönyi 1998; Cleuziou and Tosi 1998). However, such applications may be limited by very poor collagen preservation in the sites containing the relevant bones, especially in the Arabian Peninsula, unless exceptional conditions of preservation prevailed.

In the cases where collagen is not preserved, which may be the rule in dry and warm sites, carbon isotopic compositions from tooth enamel will provide valuable information on the ancient plant cover, and thus, indirectly, on palaeoenvironmental conditions. This is especially appropriate in areas where C_3 and C_4-plants coexist (Fig. 1). The possible shifts in the boundaries between phytogeographical zones through time may be investigated, as well as the occurrence of individuals coming from foreign phytogeographical zones (one example has been presented in Iacumin *et al.* 1996). High amounts of ^{13}C in archaeological ovicaprine enamel from Mleiha indicate a heavy consumption of C_4-plants, not found close to the site, and suggest that the herds were kept at some distance from the town (Bocherens and Mashkour 1999). A promising perspective is the use of intra-tooth carbon isotopic variations, which may allow dietary changes to be identified during a given individual's lifetime (Wiedemann *et al.* 1999).

Conclusions

The results presented here are still preliminary and further isotopic studies will probably reveal more interesting cases where biogeochemistry will prove useful in Southwestern Asia. However, some tendencies can already be seen. First, collagen preservation is likely to be poor in hot and dry sites, even when their age is rather young. Except when preservation conditions are exceptional (such as mummification and sealed burial conditions), only bioapatite will be available and the information will thus be limited, but nonetheless useful.

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