[14]C AGES OF BONE FRACTIONS FROM ARMENIAN PREHISTORIC SITES

Alexander Cherkinsky

CAIS, University of Georgia, 120 Riverbend Road, Athens, Georgia 30602, USA. Corresponding author.
Email: acherkin@uga.edu.

Christine Chataigner

Maison de l'Orient et de la Mediterranee, CNRS, University Lyon 2, 7 rue Raulin, Lyon 69007, France.

ABSTRACT. Prehistoric cultures in Armenia are still poorly known; thus, accelerator mass spectrometry (AMS) radiocarbon dates are invaluable in constructing an accurate chronology. Bone samples have been collected from sites representing the Middle Paleolithic, Chalcolithic, and Early Bronze periods. Most of the bone samples are poorly preserved. We describe the separation technique for the extraction of both the bioapatite and collagen fractions. In many cases where the bone had very low organic material content, the collagen fractions yielded a younger age, although the ages of bioapatite fractions were found to be in good agreement with associated archaeological artifacts. In cases where bone was well preserved, both fractions exhibited ages in good agreement with the artifacts. The accuracy of ^{14}C dating of bone material always depends on its degree of preservation, and each case should be carefully evaluated to determine which fraction is less contaminated in order to accurately date a burial event.

INTRODUCTION

The dating of bone has been problematic since the early days of radiocarbon dating due to frequent discrepancies between bones and associated charcoal or wood dates and/or between different fractions isolated from a single bone. Recently published studies show that these problems still exist (Nielsen-Marsh et al. 2000; Collins et al. 2002; Ambrose and Krigbaum 2003; Smith et al. 2007).

Today, most methods of bone preparation for ^{14}C dating are designed to extract and purify a fraction of the organic residue. In general, the goal of these methods is to isolate collagen or some individual compounds such as protein or amino acids (Hüls et al. 2009) However, for badly preserved bones, the problem becomes acute, as the bones often do not contain enough collagen even for accelerator mass spectrometry (AMS) dating. We discuss alternative techniques for preparation of the mineral carbon fraction from bioapatite of bone.

More than 20 years ago, it was suggested that carbon of bioapatite from fossil bone should provide reliable dietary and environmental information (Sullivan and Krueger 1981). The validity of such information depends on the lack of alteration of the isotopic composition of the carbon in bioapatite by exchange with carbonates in soil, groundwater, or atmospheric carbon dioxide. The validity also depends upon the ability of the sample preparer to remove any deposits of secondary or diagenetic carbonates that may be present in the bone.

The mineral fraction does not usually undergo microbiological decomposition but may be exposed to isotopic exchange with environmental carbonates (Lee-Thorp 2000). The problem thus becomes one of separating the diagenetic carbonates without significantly destroying the bioapatite content. Lee-Thorp (2000) was one of the first to use the mineral fraction of bone and teeth in stable isotope dietary and climate reconstruction studies. Minerals in bones and teeth usually survive much better than the organic fractions of collagen and lipids. Collagen tends to undergo microbiological decomposition, hydrolysis, dissolution, and denaturing over archaeological and geological timescales, so that only in exceptional conditions, such as burial in permafrost, is collagen found to survive without significant changes into Pleistocene. Survival is usually far shorter for the bones buried in warmer regions. In contrast, the mineral fraction of bones and teeth could be preserved quite well or it could

alter and stabilize, thus recording the changes of fossilization. We offer here a technique for removing the secondary diagenetic carbonates by treatment with diluted acetic acid in vacuum.

MATERIALS AND METHODS

Procedures for the preparation of bone samples for isotopic analysis are critical for obtaining reliable data (Koch et al. 1997). In general, it must be assumed that bone samples have undergone some alteration or contamination in their natural environment, and also that the excavation process may have added modern contaminations as a result of handling and/or preservation procedures.

The carbonates in fossil bone may be contaminated by secondary carbonates, precipitated in the process of burial either as pore-filling cements or as bicarbonates absorbed to the surface of crystals. To remove these diagenetic carbon compounds, the bone is soaked overnight in 1N acetic acid (Cherkinsky 2009). The samples are then washed free of acetic acid by repeated decantation. Loose or extraneous material is discarded and the bone sample is dried at ~70 °C. After drying, a sample of 1–3 g is selected for further preparation. The bone is gently crushed to small fragments <1 mm, but not to a fine powder, for further cleaning. The bone fragments are again reacted with 1N acetic acid in a 250-mL Erlenmeyer flask. The flask is periodically evacuated to remove air and/or CO_2 from the micropores, after which the flask is returned to atmospheric pressure to force fresh acid into microspaces of the sample. The first evacuation may be fairly violent since both absorbed air and external diagenetic carbonates will be removed. The nature of this reaction is a qualitative indication of $CaCO_3$ contamination. This process of evacuation and repressuring is continued at ~20-min intervals until no substantial release of gas as fine foamy bubbles occurs, even at the vapor pressure of water. The process of evacuation and repressurization to atmospheric pressure should be repeated at least 4–5 times, the last reaction being overnight (20+ hr). Large bubbles will always form, but they are primarily water vapors at such low pressures.

The reaction of acetic acid and bone should not be allowed to stand much more than 72 hr, since the bioapatite will slowly react with acetic acid and the legitimate bioapatite carbon may be depleted or lost altogether (Krueger 1991). Once the evolution of fine gas bubbles has ceased (virtually an end point of the reaction), it can be assumed that all secondary or surface exchanged carbonates have been removed. The completely cleaned bone sample is then washed free of acetic acid by repeated soaking and decantation with demineralized water and then vacuum-dried. The sample is now ready for isotopic analysis of carbon in bioapatite and for collagen extraction.

For analysis of carbon isotopes in bioapatite, approximately 100–500 mg of the cleaned bone powder is transferred to a vacuum flask and evacuated to remove air. The bone is then reacted under vacuum with ~10 mL of degassed 1N HCl. The reaction is usually completed within 20 min or less and can be monitored to determine whether or not collagen pseudomorphs have sunk to the bottom. If the bone is suspected of being highly altered, this reaction should be performed at 0 °C in an ice bath to improve collagen recovery.

The released CO_2 is cryogenically purified and collected in sealing tubes for AMS and stable isotope analyses. Bioapatite should have a carbon content of about 0.4–0.7%. If the yields are much higher, it is probable that diagenetic carbonates were not completely removed.

Koch et al. (1997) tested the effect of treatment with oxidizers, such as NaOCl and H_2O_2, followed by acid treatment, but they did not find any improvement versus the acid treatment only. Step heating of tooth enamel and bone material (Surovell 2000) did not show simple results; however, the first fraction separated at low temperature (500–600 °C) always yielded the youngest ages due to

contamination by secondary carbonates. The ^{14}C age of the high temperature fractions increased with increasing temperature, but only in 1 case did tooth enamel sample reach the estimated age based on the charcoal date.

For AMS analysis, the cleaned carbon dioxide was catalytically converted to graphite using the method of Vogel et. al. (1984). Graphite ^{14}C/^{13}C ratios were measured using a 0.5MV Pelletron AMS instrument. The sample ratios were compared to the ratio measured from oxalic acid standard OXI to calculate the ^{14}C age.

RESULTS AND DISCUSSION

Several prehistoric sites in the Lesser Caucasus of Armenia (Figure 1) have been studied. Due to its particular geographic position, the Caucasus isthmus, being a mountainous region lying between Europe and Asia, was both a zone of passage as well as one of refuge for prehistoric populations. And although the regions which border it (SE Europe and Mesopotamia) have for decades been the subjects of intense research, our knowledge of the Caucasus, especially in Armenian territory, has remained much more fragmentary.
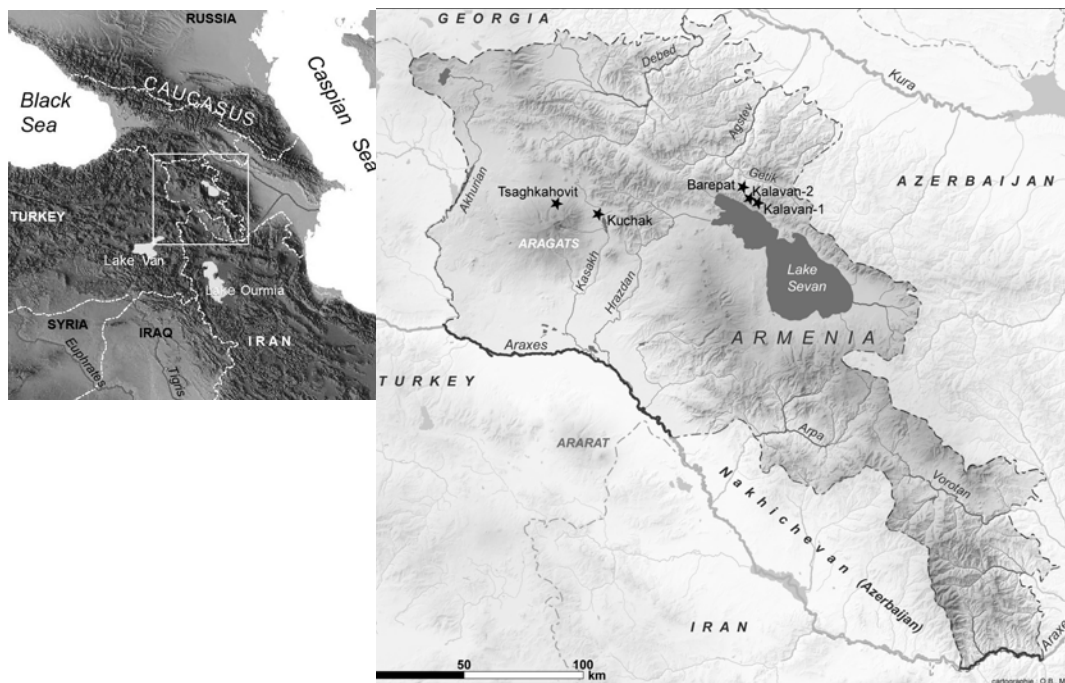

Figure 1 Map of Armenia

For this reason, a French-Armenian archaeological mission has recently undertaken surveys in Armenia, from the Lesser Caucasus to the Araxes Valley, in order to uncover prehistoric sites. As the sequence from the Paleolithic to the beginning of the Bronze Age has few ^{14}C dates, AMS dates are invaluable in constructing an accurate chronological framework.

Kalavan-2 (Late Middle Paleolithic)

In the Southern Caucasus, the transition between the Late Middle Paleolithic (Neanderthal populations) and Early Upper Paleolithic (anatomically modern humans), generally dated between 40,000 and 25,000 BP, is very controversial (Adler 2002; Pinhasi et al. 2008). According to one theory, the Caucasus may have seen a very late survival of Middle Paleolithic transitions and their long coexistence with the Upper Paleolithic (Cohen and Stepanchuk 1999; Nioradze and Otte 2000; Golovanova and Doronichev 2003). A second theory, based on reexcavations at Ortvale Klde in Georgia, argues that a distinct archaeological, stratigraphic, and temporal break existed between the Late Middle Paleolithic and the Early Upper Paleolithic (Adler and Tushabramishvili 2004; Bar-Yosef et al. 2006).

The open-air site of Kalavan-2 was discovered during a survey in 2005 in the mountains dominating the northern bank of Lake Sevan. This site is located in a forested region, at an altitude 1600 m, on a triangular plateau at the confluence of 2 streams that are part of the drainage basin of the Kura River. Excavations have revealed a stratigraphic sequence with several phases of occupation attributed to the Late Middle Paleolithic (Colonge et al. 2007).

The main excavation area is situated on the longitudinal axis of the spur, near its northern extremity. The stratigraphy has provided 20 levels (Figure 2), which represent several main sedimentary cycles. The upper part of the sequence (layers 2 to 13) has a thickness of 1.80 m and is affected by fissures caused by freezing, which present secondary carbonation related to an intense circulation of water.

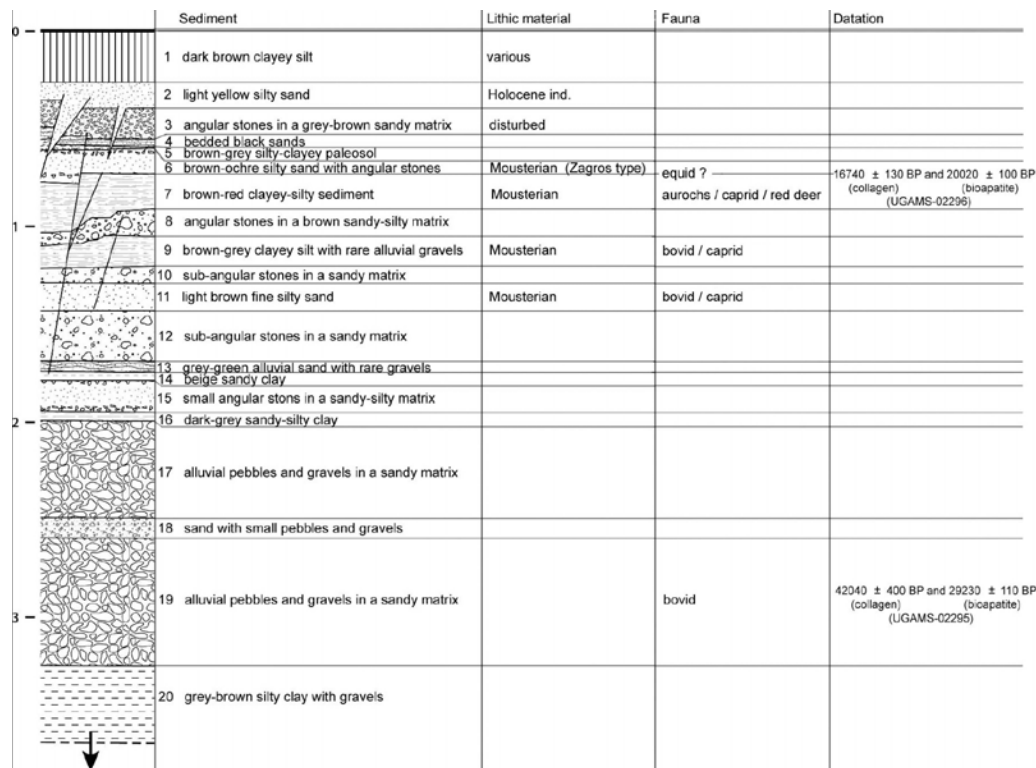|	Sediment	Lithic material	Fauna	Datation
1	dark brown clayey silt	various		
2	light yellow silty sand	Holocene ind.		
3	angular stones in a grey-brown sandy matrix	disturbed		
4	bedded black sands			
5	brown-grey silty-clayey paleosol			
6	brown-ochre silty sand with angular stones	Mousterian (Zagros type)	equid ?	16740 ± 130 BP and 20020 ± 100 BP (collagen) (bioapatite) (UGAMS-02296)
7	brown-red clayey-silty sediment	Mousterian	aurochs / caprid / red deer	
8	angular stones in a brown sandy-silty matrix			
9	brown-grey clayey silt with rare alluvial gravels	Mousterian	bovid / caprid	
10	sub-angular stones in a sandy matrix			
11	light brown fine silty sand	Mousterian	bovid / caprid	
12	sub-angular stones in a sandy matrix			
13	grey-green alluvial sand with rare gravels			
14	beige sandy clay			
15	small angular stons in a sandy-silty matrix			
16	dark-grey sandy-silty clay			
17	alluvial pebbles and gravels in a sandy matrix			
18	sand with small pebbles and gravels			
19	alluvial pebbles and gravels in a sandy matrix		bovid	42040 ± 400 BP and 29230 ± 110 BP (collagen) (bicapatite) (UGAMS-02295)
20	grey-brown silty clay with gravels			

Figure 2 Kalavan-2 stratigraphy

The lithic material consists mainly of obsidian, which is exogenous to the Barepat Valley, and of sedimentary rocks present in the alluvial deposits of the rivers bordering the site. Most of the archaeological material comes from layers 6 and 7. The lithic material of layer 6 is characterized by a high percentage of convergent scrapers and by typotechnological features (basal thinning, truncating-faceting technique), which are linked to the Zagros-Taurus Mousterian (Baumler and Speth 1993). A similar assemblage has been found in layers 7–5 of the Georgian cave Ortvale Klde, which have been dated to 42,000–35,000 BP (Adler and Tushabramishvili 2004).

A Kalavan-2 bone sample from level 6 (UGAMS-2296) was poorly preserved and yielded a collagen date more than 3000 ^{14}C yr younger than the bioapatite (Table 1). Both dates were much younger than expected. The secondary carbonation of the fissures, which have literally cut layers 2 to 7 into "blocks," indicates the presence of dissolved younger carbon in the water and, thus, the possibility of isotopic exchange with bioapatite carbon, as well as chemical hydrolysis of the organic fraction.

Table 1 ^{14}C age of the bone fractions from Armenian sites.[a]

UGAMS #	Sample ID	Collagen			Bioapatite		
		δ^{13}C ‰	^{14}C age, yr BP	Calendar age BC, 2 σ	δ^{13}C ‰	^{14}C age, yr BP	Calendar age BC, 2 σ
Tsaghkahovit site							
2822	Tsa.07.F14.247	−22.1	4150 ± 40	2879–2620	−9.2	5370 ± 40	4331–4055
2823	Tsa.07.G14.290	−24.3	2470 ± 40	764–414	−11.5	5530 ± 40	4455–4330
2824	Tsa.07.G14.305	−19.7	5210 ± 40	4226–3954	−9.8	5450 ± 40	4360–4236
2825	Tsa.07.G14.310	−20.6	4530 ± 40	3364–3098	−9.5	5540 ± 40	4455–4335
Kalavan-1 site							
2294	Kal 1_UF5_78	−19.1	4080 ± 40	2862–2547	−11.4	4160 ± 50	2886–2619
Kalavan-2 site							
2295	Kal 2_L22_82	−19.9	42,040 ± 400	44,112–42,776	−9.0	29,230 ± 110	32,565–31,455
2296	Kal 2_L20_15	−21.5	16,740 ± 130	18,312–17,596	−11.8	20,020 ± 100	22,374–21,723
Kuchak site							
2817	Kuc.07.019.c2	−20.4	170 ± 40	AD 1655–1953	−11.6	190 ± 40	AD 1645–1953
2818	Kuc.07.022.c2	−21.9	3420 ± 40	1877–1622	−10.9	5030 ± 40	3947–3712
Barepat site							
2819	Bar.07.son2.185	−18.9	5360 ± 40	4328–4053	−9.3	5360 ± 40	4328–4053

[a]Calibration after Reimer et al. (2009).

Layer 19, dated in the same profile (UGAMS-2295), has shown the opposite the date distribution. The collagen fraction gave a much older ^{14}C age than the bioapatite. The stratigraphy for this layer is also completely different from layer 6. Layer 19 is underlain by dense silty clay with very little gravel inclusions and it actually is a water table for the layer. Thus, this layer could possibly lead to isotope exchange between bone bioapatite and groundwater dissolved inorganic carbon compounds. As a result, the date for bioapatite is significantly younger than the date for collagen, which is coherent with the material of this Late Middle Paleolithic site.

The importance of carrying out dating based on both the organic and mineral fractions for each sample is demonstrated here, as the inconsistencies observed necessitate identifying the contamination present and permit evaluation of whether one of the fractions or both are affected by the problem.

Tsaghkahovit, Kuchak, Barepat (Chalcolithic)

The Chalcolithic period is still poorly understood in the Armenian region; only 1 site has been excavated and published until now (Torosyan 1976). Among the sites uncovered by our archaeological mission, the most interesting is Tsaghkahovit (Table 1). This site is situated on the northern foothills of the Aragats Massif at ~2000 m asl (Figure 1). It has yielded only 1 level of occupation, 20–35 cm thick. The site itself is located at the foot of a huge basalt block. The archaeological material consists of chipped stone (obsidian and dacite), pottery, and bone remains. Among the obsidian artifacts, geometric microliths and transverse arrowheads are numerous. Based on to the lithic material and the bone remains (mainly wild horse) recovered, it is believed to have been a hunting camp. The lithic material and the pottery find their closest parallels in the Late Neolithic and Chalcolithic cultures of western Georgia (Nebieridze 1972; Gogitidze 1977), but the sites belonging to these cultures were excavated in the 1960s–1970s and no ^{14}C dates are known.

Therefore, at Tsaghkahovit, the bioapatite data is much more consistent with the archaeological data, because the 4 dates are within the 2-σ range and belong to the same level of occupation, and also because these dates correspond to the end of the 5th millennium cal BC (Table 1), well within the Chalcolithic period. The collagen data were unexpectedly "heterogeneous" (from 5210 to 2470 BP), and most of these results were much younger than the artifacts, in particular the microliths, which are characteristic of the Late Neolithic and Chalcolithic periods and disappear in the Early Bronze Age.

The faunal remains were buried at a shallow depth (20–40 cm) on a pronounced slope prone to the rapid flow of water; the bones were in a very poor state of preservation due to the harsh climate at that altitude (alternating gel/thaw, hot/cold), which resulted in their cracking and alteration. We suggest that the organic fraction of most of these samples was very badly preserved and as a result the data was rejuvenated by microbiological processes during the burial. On the other hand, the mineral fraction of bone was not treated by microbiological and chemical processes and preserved the original carbon isotope composition.

Kuchak is a small open-air site (1820 m asl) on an upper terrace of the Kasakh River, northeast of the Aragats Massif. The 2 samples come from the lower layer at ~30 cm depth. According to the ^{14}C dating results, this layer is "mixed" with relatively modern material. The young bone (UGAMS-2817) gave very close results for both fractions. For the bone sample from the Chalcolithic period (UGAMS-2818), we see the same relation between fractions as in Tsaghkahovit site: rejuvenation of the organic fraction by microbiological processes and preservation of the mineral fraction in a non-carbonate environment.

The Barepat site is a small cave (1700 m asl) in the mountains north of Lake Sevan, not far from Kalavan. A trench was excavated on the terrace in front of the cave. The first artifacts (obsidian, pottery) were discovered at a depth of ~1.8 m mixed with bone remains. The analyzed bone fragment (UGAMS-2819) was in good condition and the bioapatite date of 5360 ± 40 yr BP is equivalent to the collagen date of 5360 ± 40 yr PB, and agrees with the dates of the artifacts.

Kalavan-1 Tombs (Early Bronze Age)

During the Early Bronze Age (about 3500–2200 cal BC), the Southern Caucasus area became closely tied into a regional "ecumene," termed the Kura-Araxes culture or the Early Transcaucasian culture (Smith 2005). However, the periodization and chronology of Kura-Araxes sites have long been a matter of contention and the ^{14}C dates are invaluable in providing a precise chronology.

The forested mountains of the Lesser Caucasus, north of Lake Sevan, were rarely studied and few sites have been uncovered in this region until now. Kalavan-1 is located at 1600 m altitude, on the right bank of the Barepat River, a couple hundred meters away from the Paleolithic open-air site Kalavan-2. Two phases of occupation have been uncovered (Liagre et al. 2006) (see Figure 3):

a) An Epipaleolithic layer (layer 7) with a lot of lithic material and bones, belonging exclusively to ovi-caprines, so this occupation was presumably a hunting camp site;

b) Early Bronze Age tombs, which have been dug in the layers 4 to 6, just overlying the Epipaleolithic layer; these tombs are marked by a pile of big stones. The bodies are generally lying on the right side and sometimes the skulls are missing. Some vessels lay close to the body. The funerary ritual and the pottery are characteristic of the second phase of the Kuro-Araxes culture (Le Mort 2007). The bones, buried 1–2 m deep in mostly loamy sand deposits, were in a very good state of preservation. In this case, both fractions of the analyzed bone, collagen and bioapatite, yielded the same ^{14}C age within the 2-σ standard deviation (UGAMS-2294 in Table 1).

① Modern humus, very dark brown
② Soil including clay, sand and limited gravel, dark greyish-brown
②b Soil including clay, sand and limited gravel, including limited amount of charcoal, dark greyish-brown
③a Clay including limited sand and gravel, yellowish-brown
③b Clay including limited sand, gravel and debris, yellowish-brown
④ Loam including limited sand and gravel, light yellowish-brown   EARLY BRONZE AGE
⑤ Loamy sand with domination of gravel and debris, yellowish-brown
⑥ Loamy sand including limited debris, with domination of big blocks, yellowish-brown
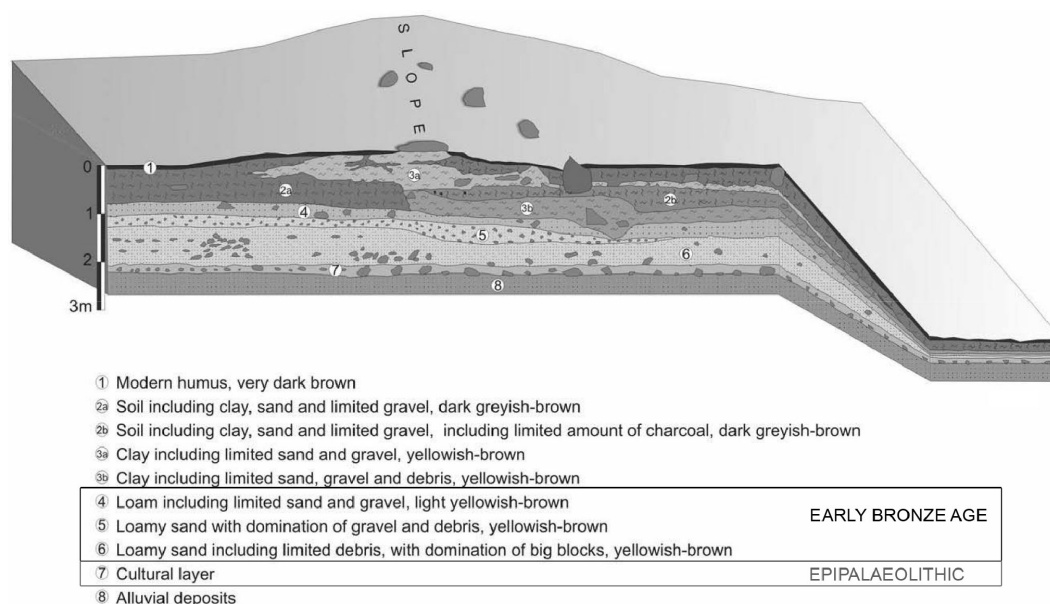⑦ Cultural layer   EPIPALAEOLITHIC
⑧ Alluvial deposits

Figure 3 Kalavan-1 stratigraphy

CONCLUSIONS

The proper pretreatment of bone samples permits the separation of diagenetic, secondary carbonates from bioapatite carbonates if their structure has not been degraded completely and exposed to isotope exchange in the environment. Tooth bioapatite usually is better preserved than bone bioapatite, with larger and more stable crystals of bioapatite.

In the case of samples derived from environments with groundwater and soil solution saturation, it is very likely that isotope exchange occurring in wet conditions could affect the carbon isotope composition and rejuvenate the ^{14}C age as shown in the case of Kalavan-2, layers 19 and 6. Or if old carbonate material present is leaching from the deposits, the samples may seem older as a result of exchange with old, "dead" carbonates. However, the reaction of isotope exchange between bioapatite and water solution of inorganic carbon compound is extremely slow and most Holocene samples

exhibit reliable ^{14}C ages on the bioapatite fraction. Thus, at Tsaghkahovit, only the bioapatite gave results that were coherent with the archaeological context (occupation of short duration and material characteristic of the 6th and 5th millennia), while the collagen gave heterogeneous results, most of the dates being later and incompatible with the material.

The ^{14}C dating accuracy of bone material always depends on its degree of preservation, and each case should be carefully evaluated to determine which fraction is less contaminated in order to date the burial event.

The dating of the bioapatite fraction can also be used for museum collection samples that were preserved using natural and/or synthetic glues. If casein was used for bone preservation, the bone cannot be dated using the collagen fraction, as the glue and collagen have an almost identical organic structure and it is extremely difficult to distinguish these chronologically different organic phases. In such cases, only the bioapatite fraction can be used for ^{14}C dating.

ACKNOWLEDGMENTS

REFERENCES

Adler DS. 2002. Late Middle Paleolithic patterns of lithic reduction, mobility, and land use in the southern Caucasus [PhD dissertation]. Cambridge: Harvard University.

Adler DS, Tushabramishvili N. 2004. Middle Paleolithic patterns of settlement and subsistence in the Southern Caucasus. In: Conard NJ, editor. *Middle Paleolithic Settlement Dynamics*. Tübingen: Kerns Verlag. p 91–132.

Ambrose SH, Krigbaum J. 2003. Bone chemistry and bioarchaeology. *Journal of Anthropological Archaeology* 22(3):193–9.

Bar-Yosef O, Belfer-Cohen A, Adler DS. 2006. The implications of the Middle-Upper Paleolithic chronological boundary in the Caucasus to Eurasian prehistory. *Anthropologie* 44(1):49–60.

Baumler M, Speth J. 1993. A Middle Paleolithic assemblage from Kunji Cave, Iran. In: Olszewski D, Dibble H, editors. *The Paleolithic Prehistory of the Zagros-Taurus*. Philadelphia: University of Pennsylvania Museum of Archaeology and Anthropology. p 1–74.

Cherkinsky A. 2009. Can we get a good radiocarbon age from "bad bone"? Determining the reliability of radiocarbon age from bioapatite. *Radiocarbon* 51(2):647–56.

Cohen V, Stepanchuk VM. 1999. Late Middle and Early Upper Paleolithic evidence from the East European plain and Caucasus: a new look at variability, interactions and transitions. *Journal of World Prehistory* 13(3):265–319.

Collins MJ, Nielsen-Marsh CM, Hiller J, Smith CI, Rob-

erts JP, Prigodich RV, Wess TJ, Csapò J, Millard AR, Turner-Walker G. 2002. The survival of organic matter in bone: a review. *Archaeometry* 44(3):383–94.

Colonge D, Nahapetyan S, Monchot H. 2007. Le gisement de Kalavan-2. In: Chataigner C, editor. *Rapport 2007 de la mission "Caucase."* Lyon. p 15–29.

Gogitidze S. 1977. *The Neolithic Culture of the Southeastern Black Sea Littoral*. Tbilisi: Metsniereba. In Georgian with Russian summary.

Golovanova LV, Doronichev VB. 2003. The Middle Paleolithic of the Caucasus. *Journal of World Prehistory* 17(1):71–140.

Hüls CM, Grootes PM, Nadeau M-J. 2009. Ultrafiltration: boon or bane? *Radiocarbon* 51(2):613–25.

Koch PL, Tuross N, Fogel ML. 1997. The effects of sample treatment and diagenesis on the isotopic integrity of carbonate in biogenic hydroxylapatite. *Journal of Archaeological Science* 24(5):417–29.

Krueger HW. 1991. Exchange Of Carbon With Biological Apatite. *Journal of Archaeological Science* 18(4):335–61.

Le Mort F. 2007. Kalavan-1: les sépultures du Bronze ancien. In: Chataigner C, editor. *Rapport 2007 de la mission "Caucase."* Lyon. p 41–5.

Lee-Thorp JA. 2000. Preservation of biogenic carbon isotope signals in Plio-Pleistocene bone and tooth mineral. In: Ambrose SH, Katzenberg KA, editors. *Biogeochemical Approaches to Paleodietary Analysis*. New York: Plenum Press. p 89–116.

Liagre J, Chataigner C, Gasparyan B, Nahapetyan S, Arakelyan D, Hovsepyan R. 2006. Kalavan-1, niveau

Paléolithique supérieur/Epipaléolithique. In: Chataigner C, editor. *Rapport 2006 de la mission "Caucase."* Lyon. p 20–34.

Nebieridze L. 1972. *The Neolithic Cultures of the Southwestern Caucasus*. Tbilisi: Metsniereba. In Georgian with Russian summary.

Nielsen-Marsh CM**,** Hedges REM, Mann T, Collins MJ. 2000. A preliminary investigation of the application of differential scanning calorimetry to the study of collagen degradation in archaeological bone. *Thermochimica Acta* 365(1–2):129–39.

Nioradze M, Otte M. 2000. Paléolithique Supérieur de Géorgie. *L'Anthropologie* 104:265–300.

Pinhasi R, Gasparian B, Wilkinson K, Bailey R, Bar-Oz G, Bruch A, Chataigner C, Hoffmann D, Hovsepyan R, Nahapetyan S, Pike AWG, Schreve D, Stephens M. 2008. Hovk 1 and the Middle and Upper Paleolithic of Armenia: a preliminary framework. *Journal of Human Evolution* 55(5):803–16.

Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Buck CE, Burr GS, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Hajdas I, Heaton TJ, Hogg AG, Hughen KA, Kaiser KF, Kromer B, McCormac FG, Manning SW, Reimer RW, Richards DA, Southon JR, Talamo S, Turney CSM, van der Plicht J, Weyhenmeyer CE. 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP. *Radiocarbon* 51(4): 1111–50.

Smith AT. 2005. Prometheus unbound: Southern Caucasia in prehistory. *Journal of World Prehistory* 19(4): 229–79.

Smith CI, Nielsen-Marsh CM, Jans MME, Collins MJ. 2007. Bone diagenesis in the European Holocene I: patterns and mechanisms. *Journal of Archaeological Science* 34(9):1485–93.

Sullivan CH, Krueger HW. 1981. Carbon isotope analysis of separate chemical phases in modern and fossil bone. *Nature* 292(5821):333–5.

Surovell TA. 2000. Radiocarbon dating of bone apatite by step heating. *Geoarchaeology* 15(6):591–608.

Torosyan R. 1976. *The Early Agricultural Settlement of Tekhut - IVth Millennium BC*. Yerevan: Publications of the Academy of Sciences. In Armenian with Russian summary.

Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research B* 5(2):289–93.