DILEMMA POSED BY URANIUM-SERIES DATES ON ARCHAEOLOGICALLY SIGNIFICANT BONES FROM VALSEQUILLO, PUEBLA, MEXICO *

Barney J.SZABO, Harold E.MALDE

U.S. Geological Survey, Federal Center, Denver, Colorado 80225, USA

and

Cynthia IRWIN-WILLIAMS

Paleo-Indian Institute, Eastern New Mexico University, Portales, New Mexico 88130, USA

Received 25 June 1969

In an attempt to date stone artifacts of Early Man excavated from several sites at the Valsequillo Reservoir, a few kilometers south of Puebla, Mexico, Szabo applied the uranium-series method on bone samples known to be either from the same geologic formation as the sites or in direct association with the artifacts. The geologic context of the bones was studied by Malde, and the archaeological sites were excavated by Irwin-Williams. A date determined for bone associated with an artifact (Caulapan sample M-B-6, see below) agrees with a radiocarbon date for fossil mollusks in the same bed and indicates man's presence more than 20 000 years ago. However, some of these bone dates exceed 200 000 years. Because such dates for man in North America conflict with all prior archaeological evidence here and abroad, we are confronted by a dilemma – either to defend the dates against an onslaught of archaeological thought, or to abandon the uranium method in this application as being so much wasted effort. Faced with these equally undesirable alternatives, and unable to decide where the onus fairly lies (if a choice must be made), we give the uranium-series dates as a possible stimulus for further mutual work in isotopic dating of archaeological material. A sample from the Lindenmeier archaeological site north of Fort Collins and another from a Pleistocene terrace along the Arkansas River, both in Colorado, were also dated.

Bones of an extinct vertebrate fauna were known at Valsequillo as early as about 1900 [1], but it was not until about 1950 that the possible presence of artifacts was suspected as the result of assiduous collecting by the Mexican prehistorian, Juan Armenta Camacho [2]. In 1962, Irwin-Williams and Armenta found and excavated four sites in which artifacts were clearly associated with the vertebrate fossils. In 1964 and 1966 they excavated additional assemblages of artifacts and bones [3]. These sites are on the north shore of the Valsequillo Reservoir in the lower part of

a dissected alluvial formation about 30 m thick known as the Valsequillo Gravels (fig. 1). According to unpublished geologic mapping by Malde, the Valsequillo Gravels at the reservoir are equivalent to similar alluvial deposits in tributary barrancas (deep ravines) to the north where the Valsequillo vertebrate fauna is also found. Molluscan fossils in the lowest beds at three of the barranca alluvial sections are beyond the reliable range of radiocarbon dating (> 35 000 years, fig. 1), but higher beds in one section, Barranca de Caulapan, yield finite dates (fig. 2). Our choice of bone samples for uraniumseries dating was governed by the radiocarbon dates and by knowledge about the archaeology. That is, we

^{*} Publication authorized by the Director, U.S. Geological Survey.

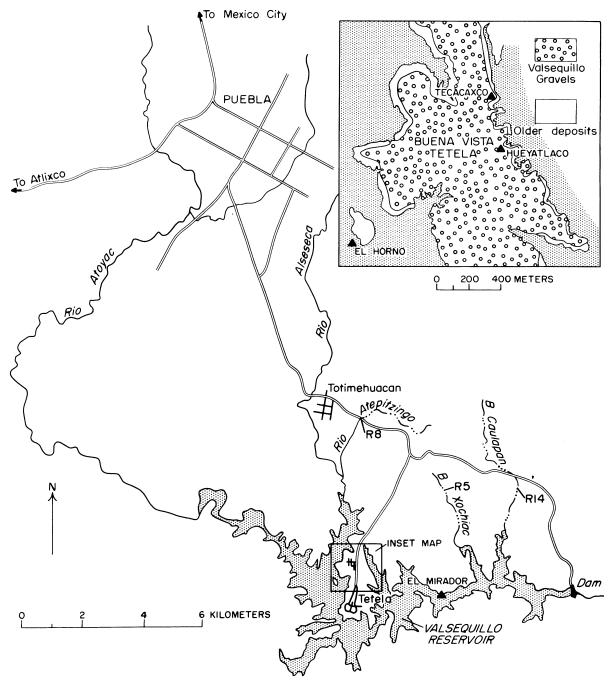


Fig. 1. Index map of Valsequillo area south of Puebla, Mexico. Inset map shows north part of Tetela peninsula and position of the archaeological sites of El Horno (2040 m), Tecacaxco (2055 m), and Hueyatlaco (2056 m). Most of the Tetela peninsula consists of Valsequillo Gravels; the top of the Valsequillo Gravels is at an altitude of 2070 m. The Valsequillo Gravels are also preserved as terrace remnants north of the reservoir along Barranca de Caulapan, Barranca de Xochiac, Rio Atepitzingo, and the Rio Alseseca. Molluscan shells in the lowest beds in these tributary deposits, localities R-8, R-5, and R-14, have all been dated as more than 35000 years old (radiocarbon samples W-1899, W-1901, and W-1898, respectively). For other radiocarbon dates on shells at locality R-14, see fig. 2.

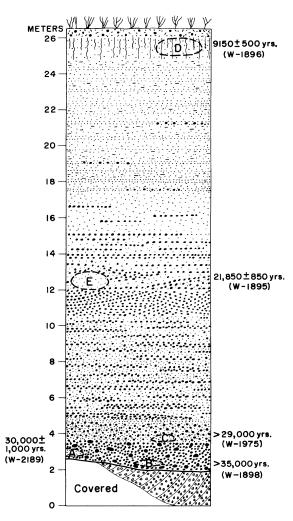


Fig. 2. Schematic section of Valsequillo Gravels at locality R-14 in Barranca de Caulapan, showing position of molluscan fossils (lettered sites) dated by radiocarbon. Uranium-series dates on bone samples from site E and possibly from a lower bed are discussed in the text.

tried to test the uranium method against other facts.

Dates by the uranium-series method are derived from measurements of uranium isotopes and their long-lived decay products, ²³⁰Th and ²³¹Pa. If a sample to be dated initially had some uranium but no thorium or protactinium, and if uranium and its decay products did not demonstrably migrate either in or out of the sample (thus, a "closed" system), then dates for samples up to about 180 000 years old, as calculated from the measured activity ratios (²³⁰Th/²³⁴U

and ²³¹Pa/²³⁵U), are concordant, within limits of experimental error. The method has been applied most successfully to dating of corals and shells [4]. Most of the early measurements determined only the ²³⁰Th/²³⁴U activity ratio, from which the ²³⁰Th closed system date was calculated. However, it was shown that ²³⁰Th and ²³¹Pa dates on some corals and most shells can be discordant [5]. An "open" system model, in which uranium is assumed to move through the sample, has therefore been applied recently for dating shells that deviate from the ideal closed system requirements [6]. Uranium-series dating of bones from archaeological sites has been applied previously by assuming a closed model [7], but the measurements reported here are the first on bones for which all the pertinent isotope ratios have been determined.

The bone samples for this study were cleaned by scraping and by thorough ultrasonic scrubbing. The samples were then crushed to a fine powder and homogenized in a mechanical shaker. The abundances of uranium and thorium were determined on a solidsource mass spectrometer by isotope dilution techniques, using enriched ²³⁵U and ²³⁰Th spikes. Thorium 230 and the ²³⁴U/²³⁸U activity ratio were measured by alpha-counting of electroplated thin sources after chemical separation by a combined method of anion exchange, coprecipitation, and solvent extraction [6, 8]. Protactinium 231 was determined by thermal neutron activation. Using a total flux of from 2 to 3×10^{19} neutrons/cm², the ²³¹Pa was partly transformed to ²³²U, and the ²³²U/²³⁵U activity ratio was then measured by alpha spectrometry after the separated uranium isotopes were electroplated on a platinum disc [9]. X-ray diffraction analysis indicated that the bones are apatite with minor calcite as open-space filling.

The abundances of uranium and thorium are given in table 1, together with the sample data. All the samples have a high content of uranium. The measured isotopic activity ratios and the calculated dates are listed in table 2. The ²³⁰Th/²³²Th activity ratio was greater than 30 in all samples — high enough to indicate that no significant amount of thorium from the environment has been added. Of the seven samples, M-B-6, M-B-5, and L-B-1 give results consistent with the closed model. M-B-3 and M-B-8, which give ²³⁰Th dates older than 165 000 years, have ²³¹Pa/

Sample No.	Field No.	Material	Location	U (ppm)	Th (ppm)
M-B-6 (a)	66-R-14, 86(E)	Proboscidean vertebra	Middle part of Caulapan (E in fig. 2)	77.3 ± 0.8	0.085 ± 0.008
M-B-5 (a)	64-R-14, 5-25	Proboscidean tusk	Lower part of Caulapan	78.6 ± 0.8	0.057 ± 0.006
M-B-3 (a)	66-1, 5-5, 10	Camel pelvis	Hueyatlaco site, Tetela (unit C in fig. 3)	86.5 ± 0.9	0.060 ± 0.006
M-B-8 (a)	62-3-B3/A	Mastodon cheek tooth	El Horno site, Tetela	150 ± 1.5	0.024 ± 0.002
M-B-4 (a)	64-R-8, 6-11	Horse metapodial	Atepitzingo	58.6 ± 0.6	0.23 ± 0.01
L-B-1 (b)	93	Bison astragalus	Lindenmeier site, Colorado	46.2 ± 0.5	0.20 ± 0.01
C-B-9 (c)	D-720	Giant bison, skull and horn pieces	Arkansas River terrace, Fremont County, Colorado (Sec. 26, T. 18 S., R. 70 W.)	91.2 ± 0.9	0.061 ± 0.006

Table 1
Uranium and thorium in fossil bones from Valsequillo (Puebla, Mexico), from Lindenmeier Site (Colorado), and from Fremont County (Colorado).

- (a) Collected by associates of C.E.Ray, U.S. National Museum, from Valsequillo area.
- (b) Collected by F.H.H.Roberts, Jr., and submitted by E.N.Wilmsen, U.S. National Museum.
- (c) Donated to the U.S.Geological Survey by the Canon City Municipal Museum, Colorado, and identified by G.E.Lewis, U.S. Geological Survey, as Bison (Gigantobison) latifrons (Harlen).

²³⁵U activity ratios of unity (within experimental error), which circumstance indicates that these two samples each formed a closed system during at least the last 165 000 years. The remaining samples, M-B-4 and C-B-9, give finite ²³⁰Th dates but have ²³¹Pa/ ²³⁵U activity ratios larger than unity (thus not conforming with a closed system), and these two samples are therefore dated by the open model [6].

Bone sample M-B-6 from Barranca de Caulapan was directly associated with fossil mollusks and with a solitary artifact (flake scraper, see fig. 3). The ²³⁰Th, ²³¹Pa, and ¹⁴C dates agree remarkably well. Sample M-B-5, which dates by ²³⁰Th and ²³¹Pa about the same as M-B-6, was assigned to lower beds at Caulapan where three nearby collections of fossil mollusks are dated by ¹⁴C as 30 000 years or older (fig. 2). The apparent disagreement between the bone and shell dates may stem from an uncertainty about the provenience of the bone; it was picked from the "surface" and does not represent an excavated specimen. Sample M-B-3 was one of many articulated skeletons recovered during controlled excavation of

the upper part of Hueyatlaco, the youngest known Early Man site at the Valsequillo Reservoir (fig. 3), and there is no doubt whatever about its association with artifacts. Sample M-B-8 was a tooth fragment from a butchered mastodon at El Horno, the oldest known site, and was therefore itself an artifact. Sample M-B-4 was obtained with a large and diverse collection representative of the Valsequillo fauna in a single bed along the Rio Atepitzingo. Fossil mollusks older than the range of ¹⁴C dating (> 35 000 years, W-1899) were simultaneously picked with the bones from screens on which this collection was washed. The open system date for M-B-4 is about the same as the closed system date for M-B-3 at Hueyatlaco.

Samples L-B-1 and C-B-9 are from two different sedimentary environments in Colorado. By detailed study of Roberts' field notes for the Lindenmeier site, Wilmsen refers sample L-B-1 to the "Folsom horizon", which is dated by ¹⁴C at 10780 ± 375 years [10]. Although we do not yet understand why the radiocarbon and uranium-series dates differ by more than 5000 years, such a discrepancy is perhaps a measure

Table 2
Isotopic activity ratios and radiometric ages of fossil bones.

Sample No.	234U/238U	Sample 234U/238U 230Th/234U No.	230Th/232Th 231Pa/235U	231Pa/235U	²³⁰ Th date (years)		231Pa date (years)	Open system date (years)	14C date (years)
M-B-6	1.30 ± 0.02	M-B-6 1.30 ± 0.02 0.172 ± 0.008	610	0.38 ± 0.02	20000 ± 1500	1500	22000 ± 2000		21850 ± 850 (a)
M-B-5	1.30 ± 0.02	0.161 ± 0.006	870	0.31 ± 0.02	$19000 \pm$	1500	18000 ± 1500		$30600 \pm 1000 (a, b)$
M-B-3		0.939 ± 0.038	4990	1.03 ± 0.05	$245000 \pm$	40000	>180000	245000 ± 40000	
M-B-8	1.26 ± 0.02	1.03 ± 0.05	24 500	1.02 ± 0.05	> 280000		>165000	> 280 000	
M-B-4	1.40 ± 0.02	1.04 ± 0.04	1120	1.11 ± 0.06	340000 ± 100000	00000	>180000	260000 ± 60000	>35 000 (a)
L-B-1	1.18 ± 0.02	0.040 ± 0.002	33	0.076 ± 0.008	4500 ± 500	200	4000 ± 500		10780 ± 375 (c)
C-B-9	1.95 ± 0.03	0.92 ± 0.09	8 0 7 0	1.09 ± 0.06	190000 ± 50000	50000	>180000	160000 ± 60000	

Radiocarbon dates on molluscan fossils associated with vertebrates from Valsequillo determined by M.Rubin, U.S. Geological Survey (a)

(b) Association of shell and bone is not clear.(c) Date of "Folsom horizon" at Lindenmeier site, Colorado.

of the error to be expected near the limit of resolution of the uranium method. Sample C-B-9 was found near the base of Slocum Alluvium, considered to be of Illinoian or Sangamon age [G.R.Scott, U.S. Geological Survey, oral communication]. The calculated open system date is consistent with the geologic age.

Geologically, according to Malde, the uranium-series dates for the Valsequillo samples are difficult to evaluate from field relations because not enough stratigraphic markers have yet been identified to correlate the various sample localities. Work in progress by Virginia Steen-McIntyre on volcanic ash chronology and by Clayton E.Ray on vertebrate fossils in the Valsequillo deposits is expected to provide useful clues for a geological appraisal of these dates.

Archaeologically, according to Irwin-Williams, at least two of the uranium-series dates (M-B-3 at Hueyatlaco and M-B-8 at El Horno) cannot be correct. The sample from Hueyatlaco was from the same layer that vielded sophisticated stone tools such as bifaciallyworked knives, scrapers, burins, and tanged projectile points (unit C in fig. 3). These tools surely were not in use at Valsequillo more than 200000 years before the date generally accepted for development of analogous tools in the Old World, nor indeed more than 150000 years before the appearance of *Homo Sapiens*. The same argument applies to artifacts around the butchered mastodon at El Horno; though somewhat less sophisticated than artifacts in the upper part of Hueyatlaco, these are nonetheless technologically excellent. To accept dates for these tools in excess of 200 000 years would require some sign of early hominoid development in the New World, but evidence for such beings here is entirely lacking in the record of fossil primates. In the light of present knowledge, therefore, a sudden New World development of sophisticated stone tools by biologically primitive beings, completely without parallel in the Old World, can only be regarded as highly improbable.

We realize that uranium-series dating of terrestrial samples, especially bone, is still experimental. We have not yet established firmly the time required to incorporate uranium in bones after an animal dies. If the uranium is assimilated slowly, then the dates determined by uranium decay are too young, even though requirements of the closed system are satisfied. For molluscan shells, it has been shown that the uranium is assimilated shortly after death [11].

	, knives;		CAULAPAN Single edge- retouched scraper on	flake.	S,
TECHNOLOGY	Well-made bifacially worked artifacts: projectile points, knives; percussion and pressure flaking; burins, scrapers, wedges, knives on flakes and blades; prepared striking platform.	Edge-retouched artifacts: projectile points, scrapers made on blades and flakes with prepared striking platform.	Edge-retouched artifacts: scrapers, knives; blades and flakes with prepared striking platform.	Single edge-retouched projectile point on blade with prepared striking platform.	Edge-retouched flake tools: projectile points(?), scrapers, burins; prepared striking platform; no blades.
TYPOLOGY					
STRATIGRAPHIC SEQUENCE	PPER HUEYATLACO	LOWER HUEYATLACO Unit I	TECACAXCO	EL MIRADOR	EL HORNO

Fig. 3. Technology and typology of artifacts from five Early Man sites in the Valsequillo Region. An unconformity at Hueyatlaco between Units I and E coincides with a change in the artifacts: from simple edge-retouched tools below, which were made on blades and flakes, to sophisticated bifacially worked tools above, which were made in a greater variety of forms. The artifacts are drawn at one-third natural size.

Recent work using the fission-track technique indicates that uranium is dispersed throughout both fossil shells and bones (the bone samples of this paper) in similar ways and that the distribution of uranium is unrelated to the measured date of the sample [12]. This suggests that the uranium assimilation is analogous in bones and shells or that uranium-series dates on bones are not misleadingly too young. However, the dilemma posed by the dates given here is not that they may be too young; rather, that some of them may be too old, according to archaeological arguments. Two processes could cause a sample to yield an incorrectly old date. First, unsupported ²³⁰Th and ²³¹Pa might be assimilated by the sample from the environment. This process is unlikely because both thorium and protactinium are virtually insoluble. Furthermore, it is unreasonable that ²³⁰Th could be added to bone without also the common thorium isotope (232Th) and, in fact, the 230Th/232Th ratio is unusually high in these samples. Second, crystallographic alteration might remove most of the uranium but leave all the long-lived decay products - the ²³⁰Th and ²³¹Pa isotopes. The X-ray analysis, however, gives no evidence of recognizable crystallographic change. In short, we cannot explain why some of these dates are much older than expected from archaeological evidence. Perplexed by this conflict, we present the dates in the belief that the results of one day will advance our understanding in the next, if only by provoking fruitful effort.

The field work at Valsequillo was supported by the National Science Foundation and the American Philosophical Society.

REFERENCES

- [1] H.F.Osborn, Recent vertebrate paleontology; fossil mammals of Mexico, Science new ser. 21 (1905) 931.
- [2] L.Aveleyra Arroyo de Anda, Antigüedad del hombre en Mexico y Centroamérica – Catálogo raronado de localidades y bibliografía selecta (1867-1961), Mexico Univ. Nac. Autónoma Inst. Historia Cuadernos, Ser. Antropol. 14 (1962) 72 pp.
- [3] C.Irwin-Williams, Association of early man with horse, camel, and mastodon at Hueyatlaco, Valsequillo (Puebla, Mexico), in: Pleistocene extinctions the search for a cause, eds. P.S.Martin and H.E.Wright, Jr., Internat. Assoc. Quaternary Research, 7th Cong., 1965, Proc. 6 (Yale University Press, New Haven and London, 1967) p. 337.

- [4] J.W.Barnes, E.J.Lang and H.A.Potratz, Ratio of ionium to uranium in coral limestone, Science 124 (1956) 175; W.S.Broecker and D.L.Thurber, Uranium-series dating of corals and oolites from Bahaman and Florida Key limestones, Science 149 (1965) 58; W.S.Broecker, D.L.Thurber, J.Goddard, T.-L.Ku, R.K. Matthews and K.J.Mesolella, Milankovitch hypothesis supported by precise dating of coral reefs and deep-sea sediments, Science 159 (1968) 297; C.E.Stearn and D.L.Thurber, Th²³⁰-U²³⁴ dates of late Pleistocene marine fossils from the Mediterranean and Moroccan littorals, Quaternaria 7 (1965) 29; D.L.Thurber, W.S.Broecker, R.L.Blanchard and H.A. Potratz, Uranium-series ages of Pacific atoll coral, Science 149 (1965) 55; H.H.Veeh, Th²³⁰/U²³⁸ and U²³⁴/U²³⁸ ages of Pleistocene high sea level stand, J. Geophys. Res. 71 (1966)
- [5] T.L.Ku, Protactinium 231 method of dating coral from Barbados Island, J. Geophys. Res. 73 (1968) 2271; J.N.Rosholt, Open system model for uranium-series dating of Pleistocene samples, in: Radioactive Dating and Methods of Low-Level Counting, Proceedings Series (International Atomic Energy Agency, Vienna, 1967), SM-87/50, p. 299; M.Sakanoue, K.Konishi and K.Komura, Stepwise determinations of thorium, protactinium and uranium isotopes and their application in geochronological studies, in: Radioactive Dating and Methods of Low-Level Counting, Proceedings Series (International Atomic Energy Agency, Vienna, 1967) p. 313.
- [6] B.J.Szabo and J.N.Rosholt, Uranium-series dating of Pleistocene molluscan shells from southern California. An open system model, J. Geophys. Res., in press.
- [7] V.V.Cherdyntsev, Determination of the absolute age of the Paleolithic, Sovet. Arkheol. 25 (1956) 64 (in Russian);
 - V.V.Cherdyntsev, I.V.Kazachevskii and E.A.Kuz'mina, Isotopic composition of uranium and thorium in the supergene zone, Geokhimiya 3 (1963) 254 (English translation, Geochemistry 3 (1963) 271); V.V.Cherdyntsev, I.V.Kazachevskii and E.A.Kuz'mina, Dating of Pleistocene carbonate formations by the thorium and uranium isotopes, Geochem. Internat. (English translation) 2 (1965) 794; J.N.Rosholt, Jr., Radioactive disequilibrium studies as an aid in understanding the natural migration of uranium and its decay products, in: United Nations Survey of raw material resources, Internat. Conf. Peaceful Uses Atomic Energy, 2d, Geneva, Sept. 1958, Proc. 2 (1958)
- [8] J.N.Rosholt, B.R.Doe and M.Tatsumoto, Evolution of the isotopic composition of uranium and thorium in soil profiles, Bull. Geol. Soc. Amer. 77 (1966) 987.
- [9] J.N.Rosholt and B.J.Szabo, Determination of protactinium by neutron activation and alpha spectrometry, Proc. 1968 Internat. Conf. on Modern Trends in Activation Analysis, Gaithersburg, Maryland (1968) 368.

- [10] C.V.Haynes, Jr. and G.A.Agogino. Geological significance of a new radiocarbon date from the Lindenmeier site, Denver Mus. Nat. Hist. Proc. 9 (1960) 23.
- [11] W.S.Broecker, A preliminary evaluation of uranium series inequilibrium as a tool for absolute age measurement on marine carbonates, J. Geophys. Res. 68 (1963) 2817:
 - A.Kaufman and W.S.Broecker, Comparison of Th²³⁰ and C¹⁴ ages for carbonate materials from Lakes Lahontan and Bonneville, J. Geophys. Res. 70 (1965) 4039.
- D.L.Thurber, W.S.Broecker and A.Kaufman, The comparison of radiocarbon ages of carbonates with uranium series ages, in: Internat. Conf. Radiocarbon Tritium Dating, 6th, Proc., no. 650652, Washington State Univ. (1965) 367.
- [12] B.J.Szabo, J.R.Dooley, Jr., R.B.Taylor and J.N.Rosholt, Distribution of uranium in uranium-series dated fossil shells and bones shown by fission tracks, submitted to Science.