Reports

Uranium Series Dating of Human Skeletal Remains from the Del Mar and Sunnyvale Sites, California

Abstract. *Uranium series analyses of human bone samples from the Del Mar and Sunnyvale sites indicate ages of 11,000 and 8,300 years, respectively. The dates are supported by internal concordancy between thorium-230 and protactinium-231 decay systems. These ages are significantly younger than the estimates of 48,000 and 70,000 years based on amino acid racemization, and indicate that the individuals could derive from the population waves that came across the Bering Strait during the last sea-level low.*

Increasingly since 1971 dates have been obtained for human skeletal material from California which suggest that anatomically modern man (*Homo sapiens sapiens*) was in the New World before 12,000 and perhaps as much as 70,000 years ago. The individuals representing the lower end of this range include the Laguna and Los Angeles skeletons dated by ^{14}C analyses of bone collagen at 17,150 years and > 23,600 years (*1*) and the Yuha skeleton dated at about 20,000 years on the basis of indirect ^{14}C and ^{230}Th analyses (*2*) and uncalibrated amino acid analysis (*3*). The upper end of the range is represented by Del Mar (*4*) and Sunnyvale skeletons (*5*) dated at 48,000 years and 70,000 years by amino acid racemization, using the ^{14}C date of the Laguna individual for calibration. The inferred ages for the Sunnyvale and Del Mar individuals in particular have created controversy because they imply that anatomically modern man appeared in North America significantly earlier than in Europe and the Near East (*6*).

This report presents the results of direct uranium series dating of the Del Mar and Sunnyvale individuals along with results for mammal bones from the Rancho La Brea tar pits and the Mountain View dump site, both of which are well dated by ^{14}C. Only diagnostic cranial material of the Laguna and Los Angeles individuals still exists, the postcranial materials having been consumed for ^{14}C analyses, and the Yuha skeleton has been reported missing and presumed stolen as of this writing (*7*).

Uranium series dating has been applied primarily to carbonate materials rather than bones. The method was first applied to fossil bones by Cherdyntsev (*8*) in 1956 and has been advanced considerably by Szabo and co-workers since the late 1960's (*9*). The technique has given reliable dates in many cases, but in others contamination has been a serious problem.

For samples with ages up to about 120,000 years, it is possible to judge the validity of a uranium series date on a single sample by testing for internal concordancy between two independent decay schemes: $^{238}U \rightarrow {}^{230}Th$ and $^{235}U \rightarrow {}^{231}Pa$. Because ^{230}Th and ^{231}Pa have different decay rates and different chemical properties, any perturbation of the system will give discordant ages. Although ^{230}Th can yield ages back to about 350,000 years, the concordancy test is limited to about 120,000 years by the shorter half-life of ^{231}Pa.

Besides the internal test for concordancy, other advantages of the technique are long range (about 5,000 to 350,000 years) and small sample size, usually less than 20 g of bone, if well preserved. Successful application of the technique requires that the bone initially take up uranium but no thorium or protactinium and then become closed within a relatively short time. The many concordant dates obtained (*9*) attest that these requirements are often met. The technique works because uranium is relatively mobile in ground waters compared to thorium and protactinium. The limited time that the bone is open to uranium is believed to result from the relatively rapid breakdown of active (or labile) organic matter in the bone apatite, which serves to reduce and fix uranium. A $^{234}U/^{238}U$ ratio close to unity and absence of, or low activity of, ^{232}Th (common thorium) relative to ^{230}Th are additional criteria for a closed system and lack of contamination.

In the present study dense cortex (compacta) of long-bone fragments was selected and prepared according to procedures in (*9*). After acid dissolution, uranium and thorium isotopes were isolated by ion exchange and solvent extraction, and activities of isotopes were determined by alpha spectrometry, generally following the methods of Ku (*10*). Interferences caused by the phosphatic matrix were eliminated by fractional precipitations (*11*). Protactinium-231 was determined on a separate portion by analysis for the short-lived daughter ^{227}Th (*12*). Generally, 3 to 5 g of samples sufficed for the ^{230}Th analysis, and an additional 10 to 15 g was required for the ^{231}Pa analysis. Dates for each sample were calculated with equations given in (*10*) and decay constants given in (*9*). Results are given in Table 1.

Fossil mammal bones from the Rancho La Brea tar pits constitute the type locality for the Rancho La Brea fauna (*13*). Although the uranium content of the *Smilodon* femur we analyzed was very low (0.11 ppm), as expected in such a reducing environment, sufficient ^{230}Th was present to allow calculation of a date; ^{231}Pa was undetectable. The calculated age of 37,200 years agrees with ^{14}C ages of 35,500 and 36,000 years for collagen extracted from two other *Smilodon* femurs from the same level in the same pit (Table 1).

Excavation of a 10-m-deep refuse pit in the city of Mountain View, on the edge of San Francisco Bay, exposed well-stratified deposits containing Pleistocene mammal fossils (*14*). Our dates on a *Camelops* bone from this deposit, 19,900 ± 500 years for ^{230}Th and 20,800 ± 1,000 years for ^{231}Pa, are internally concordant and are in excellent agreement with seven ^{14}C dates of 20,800 to 23,600 years obtained for wood from the same deposit (Table 1).

The burial site of the Sunnyvale skeleton was about 9 km from the Mountain View dump site (*15*). Excavated in 1972, the skeleton occupied a well-defined pit which extended downward about 1.5 m from a buried soil horizon (and 2.5 m below the present land surface) and intruded into pond deposits containing shells of freshwater snails, *Limnea* and *Physa*. Two of the shells at the burial site yielded ^{14}C dates of 10,110 and 10,430 years, respectively (*15*). In essentially the same exposures, but at points farther downstream from the burial, the pond deposits overlie a unit containing a late

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Pleistocene mammal fauna, including *Camelops*, believed equivalent to the deposits in the Mountain View dump site. Our ^{230}Th and ^{231}Pa dates for the human skeletal material are 8,300 and 9,000 years, respectively (Table 1). We consider these two independent dates to be internally concordant and to be consistent with the ^{14}C results for the shells, which should be somewhat older than the skeleton.

The Del Mar skull and associated tibia fragment were found in 1929, eroded out of a midden-capped sea cliff at Del Mar, near San Diego (*16*). The 24-m section of sea cliff consists of a 10-m basal unit of indurated Tertiary marine sediment unconformably overlain by 13 m of poorly consolidated unfossiliferous marine sands, which in turn are truncated and capped by about 1 m of shell-bearing midden (*17*). Careful examination of exposures of the midden revealed only incipient pedogenesis and, on the basis of criteria presented in (*18*), suggested that the midden does not predate the Holocene. Fragments of mollusk shell were found within the sinus cavities of the skull and adhering to the bones, suggesting that the remains had been a burial within the midden (*16*). The fact that the jaw was intact supports this conclusion and argues against the possibility that the remains could have come from the underlying marine sands. Carbon-14 dates for mollusk shells from the midden range from 4,590 to 12,000 years (*19*).

In the present study, uranium series analyses of a tibia fragment of the Del Mar skeleton indicate an age of 11,000 years (Table 1). All of our criteria for accepting a date as reasonable were met in this sample. The ^{230}Th and ^{231}Pa results demonstrate excellent concordancy. The $^{234}U/^{238}U$ ratio of 1.05, absence of detectable ^{232}Th, and good detectability and good counting statistics of all the pertinent isotopes attest that the system has been closed and also support the validity of the date. These results are consistent with the ^{14}C dates and the general soil-geomorphic relations in the midden.

Amino acid analysis of fragments of the same Del Mar tibia suggested an age of 48,000 years (*4*). Amino acid dates for both the Del Mar and the Sunnyvale individuals were calibrated to the Laguna individual. In such a calibration it is assumed that the ^{14}C date is correct and that the samples to be dated have a thermal history in common with the calibration sample.

The rate of amino acid racemization is strongly dependent on temperature.

Table 1. Uranium series analytical data and calculated dates for bones from California sites.

Laboratory number	Material	U (ppm)	Activity (dpm/g)					Age (× 10^3 years)		
			^{238}U	^{234}U	^{232}Th	^{230}Th	^{231}Pa	^{230}Th date	^{231}Pa date	Other dates
80-46	*Camelops* long bone (M-1227), Mountain View dump	44.0	32.8 ± 0.6	43.8 ± 0.8	0.07 ± 0.01	7.4 ± 0.08	0.54 ± 0.02	$19.9^{+0.5}_{-0.2}$	20.8 ± 1.0	20.8 to 23.6 (^{14}C)*
80-44	*Smilodon* femur (K-3282), Rancho La Brea, pit 4 (depth, 5.48 m)	0.11	0.085 ± 0.005	0.118 ± 0.006	< 0.005	0.035 ± 0.005	< 0.005	$37.2^{+6.6}_{-6.0}$		35.5 (^{14}C)† 36.0
80-37	Sunnyvale skeleton, composite of postcranial fragments	55.0	41.0 ± 0.9	62.5 ± 1.3	< 0.005	4.67 ± 0.07	0.33 ± 0.02	$8.3^{+0.23}_{-0.10}$	9.0 ± 0.6	70.0 (Asp)‡ 10.1 to 10.4 (^{14}C)§
80-60	Del Mar skeleton (16704), tibia fragment	8.1	6.07 ± 0.07	6.40 ± 0.07	< 0.005	0.63 ± 0.02	0.06 ± 0.01	$11.0^{+0.5}_{-0.1}$	$11.3^{+1.3}_{-1.2}$	48.0 (Asp)‖

*Radiocarbon dates on associated wood samples (*15*). †Radiocarbon dates on bone collagen of two *Smilodon* femurs at 5.48 and 6.0 m from same pit (UCLA 1292N and 1292M). ‡Based on measured D/L ratio of 0.522 (*5*); Asp, aspartic acid. §Two ^{14}C dates on mollusk shells taken from layer believed to have been intruded by burial (*15*). ‖Based on measured D/L ratio of 0.53 on specimen 16704 (*4*).

Wehmiller (*20*) showed that the temperature extremes to which a sample is subjected are more important than the average temperature in controlling rates of racemization and developed the concept of effective diagenetic temperature. The effective diagenetic temperature is strongly affected by a slight variation in burial depth, if within the top 160 cm. Below this depth the thermal environment is more constant and the effective diagenetic temperature is close to the mean annual air temperature. We consider the possibility that burial depth is the cause of the apparent discrepancies in age. The relationship of the rate constant of aspartic acid racemization (log k_{asp}) to diagenetic temperature, based on well-dated Holocene bones from Olduvai and Muleta Cave, was approximated in (*3*). Applying this calibration to the Laguna individual, for which the average log k_{asp} is −4.96 (*4*), indicates that the average effective diagenetic temperature for the past 17,000 years has been 15.5°C. This temperature is consistent with the present mean annual air temperature of 16.1°C at Laguna (*4*). These results suggest that the ^{14}C date and degree of amino acid racemization for the Laguna individual are consistent. Confirmation of the single ^{14}C date for this individual by uranium series dating would be desirable.

Using the same approach to the Del Mar and Sunnyvale individuals, with the uranium series dates reported here and published aspartic acid analyses (*4, 5*), we calculate log k_{asp} as −4.36 and −4.24, respectively. The corresponding effective diagenetic temperatures are 22.5° and 23.9°C. Applying the results to Wehmiller's (*20*) model of effective rate constant versus depth for the Del Mar site gives an effective temperature of 22.5°C at an estimated depth of 30 cm (*21*). Thus the amino acid results can be related to the uranium series dates if the skeleton has been buried with less than about 30 cm of overburden for most of its history. Because the bones were not found in situ, this possibility cannot be further assessed.

Burial depth cannot, however, explain the amino acid results for the Sunnyvale skeleton. The skeleton was recovered from below a paleosol and clearly had been buried by at least 160 cm of overburden for all its history. We agree with Lajoie *et al.* (*15*) that factors other than thermal history must affect rates of amino acid racemization in bone in some environments.

In summary, the general reliability of the uranium series dates for bones presented in this report is indicated by the good internal agreement between the ^{230}Th and ^{231}Pa decay systems and by the good agreement with radiocarbon results for the mammal sites. These results indicate that the Del Mar and Sunnyvale skeletons are much younger than was previously estimated and could be derived from the population waves that came across the Bering Strait during the last lowering of sea level about 13,000 years ago (*22*).

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Trace Water Content of Salt in Louisiana Salt Domes

Abstract. *The trace water content of salt in six Louisiana salt domes has been determined and has been found to be the lowest of any terrestrial rock type. The average water content of normal domal salt is on the order of 0.003 percent by weight, but anomalous zones within salt stocks can have more than ten times this amount. From the average value, the minimum amount of water in liters,* W, *available to collect around a radioactive waste repository is given as* $W = 0.28\ r^3$, *where* r *is the radius in meters of the sphere in which water may be thermally activated to migrate completely to the repository.*

In considering salt domes as repository sites for nuclear wastes, a major question is the significance of brine inclusions, which have been observed to migrate through salt in response to a thermal gradient (*1*). Salt dissolves from the warmer side of the inclusion and precipitates on the cooler side, and thus the brine inclusion moves toward the heat source. Microscopic brine inclusions are observed in natural salt samples, and it is possible that this brine will migrate to a nuclear waste repository. It is therefore important to assess the total reservoir of trace water within salt domes that might be affected by this process.

In the work reported here, salt samples (3 to 56 g) from six Louisiana salt domes were heated under high vacuum to volatilization. Water released on heating was reduced quantitatively over uranium metal at 700°C to produce hydrogen gas. The hydrogen was collected by a Toepler pump and its volume was measured manometrically (*2*). Less than 10^{-6} mole of water can be measured with this procedure. For an 18-g sample, the water content of salt can therefore be determined to ±1 ppm.

Figure 1 illustrates the water release with temperature for salt sample VK-3-49 when it was heated from 23° to 1000°C at an average rate of 1° to 2°C per minute. A relatively large water component is released at 23°C and appears to outgas until 218°C. Another water component outgasses from 280° to 800°C. Other salt samples of various sizes and water contents display similar water evolution patterns, although changes in the rate of heating can affect the pattern somewhat. In particular, exposure of the samples to high vacuum at 23°C for 30 minutes or longer removes the low-temperature water component entirely. This low-temperature component is interpreted as water adsorbed or condensed on the salt surface and along fractures (*3*).

To test the interpretation that adsorbed water can be pumped away at room temperature, a 2-g sample of salt from Weeks Island, sample F-2-34, was soaked in an NaCl-saturated aqueous solution for 23 hours to introduce as much adsorbed water as possible. This sample was air-dried in a desiccator and analyzed routinely (*2*). As shown in Table 1, the amount of water released over the range 23° to 1000°C was not significantly greater than that from the other Weeks Island samples. In addition, single crystals of halite, samples RK-5, RK-7, and RK-10, were cut dry, in water, and in oil (*4*), respectively. As shown in Table 2, there was no significant variation in the amounts of trace water measured for these samples. It is concluded that adsorbed water can be removed from domal salt by exposing the samples to high vacuum for at least 30 minutes. Nevertheless, all samples analyzed were taken from freshly broken hand samples or cores and were exposed to air for as short a time as possible. Water evolved from the salt above 23°C and under high vacuum is trace water within the salt and is considered to have geological significance.

In all salt samples analyzed, gas other than water is evolved during heating. In the case of sample VK-3 (Fig. 1) this gas contains a major CO_2 component, as determined by mass spectrometer. The pattern of evolution of H_2O is not parallel to that of the CO_2-rich gas, suggesting that the water is not derived by pyrolysis of trace amounts of organic matter. The high temperature of the gas release suggests decomposition of trace amounts of solid phases, including carbonate. In any case, the water evolves separately, giving further evidence that it represents an actual water component in the salt.

Table 1 gives the results of the trace water measurements on salt samples from six Louisiana salt domes. The values range from less than 0.001 percent by weight for single crystals to 0.034 percent by weight for certain samples in the Weeks Island dome. The highest water contents are for the salt stalagmites, which formed recently around water seeps or condensation zones in mine

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