

Geologic Map of the Masters 7.5' Quadrangle, Weld and Morgan Counties, Colorado

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Appendix 1

$^{230}\text{Th}/\text{U}$ ages Supporting Geologic Map of the Masters 7.5' Quadrangle, Weld and Morgan Counties, Colorado

By James B. Paces

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U.S. Geological Survey**

Appendix 1. ²³⁰Th/U ages Supporting Geologic Map of the Masters 7.5' Quadrangle, Weld and Morgan Counties, Colorado

By James B. Paces

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Conversion Factors

International System of Units

Multiply	By	To obtain
	Length	
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
mile (mi)	0.6214	mile (mi)

Appendix 1. $^{230}\text{Th}/\text{U}$ ages Supporting Geologic Map of the Masters 7.5' Quadrangle, Weld and Morgan Counties, Colorado

By James B. Paces

Introduction

Geologic mapping of surficial units in the Masters 7.5' Quadrangle (<http://dx.doi.org/10.3133/sim3344>) includes an evaluation of the history of sediment transport and deposition in relation to regional climate, hydrologic, and soil-forming events in the high plains of northeastern Colorado. Numerical age estimates of depositional events were made on different materials using several methods, including optically stimulated luminescence, radiocarbon, and uranium-series disequilibrium.

This report describes efforts made to date two samples collected from man-made excavations using uranium-series methods (specifically $^{230}\text{Th}/\text{U}$ dating). One of the samples consists of a fossilized fragment of horn-core bone (presumed to be bison) and the other consists of thin rinds of secondary carbonate coating the alluvial clasts. Although both of these materials are amenable to uranium-series dating, neither directly dates the age of deposition due to the nature of post-depositional uranium accumulation. Nevertheless, $^{230}\text{Th}/\text{U}$ ages described here provide useful constraints on minimum ages for the deposits in which these materials occur.

Samples

Sample Wp67 consists of a 4×8-cm fragment of bone collected from a deposit of fine-grained sediment associated with mainstream deposits of Broadway Alluvium (map unit Qba) from site EF (see map for sample location and stratigraphic context <http://dx.doi.org/10.3133/sim3344>). A section of compact bone 6–7 mm thick was cut and polished revealing a dense, cream-colored, ivory-like interior with sub-millimeter growth layering (figure 1–1). The outer surface is coated with a thin veneer of darker, harder calcite cement up to about 0.5 mm thick. Although the compact bone contains internal laminations, tubular osteons characteristic of cortical bone are absent. To compare results using independent dating methods, a piece of the same bone sample was submitted to Aeon Laboratories for radiocarbon dating of the collagen residues. However, the sample was rejected by the laboratory because it had a low nitrogen content and a high carbon-nitrogen ratio. The low nitrogen concentration and associated high C:N ratio



Figure 1–1. Polished cross section of fossil bone sample Wp67 showing thin calcite-rich rind coating outer surface and dense, ivory-like interior. Numbered polygons show the distribution of sub-millimeter-thick subsamples obtained by sequential microdrilling.

indicate that the sample lacked sufficient amounts of residual collagen proteins, which are required for routine radiocarbon dating of the organic constituents of bone.

Sample Wp95 consists of several well-rounded clasts associated with intermediate alluvium (map unit Qai) from site EIC (see map for sample location and stratigraphic context <http://dx.doi.org/10.3133/sim3344>). Clasts range from 20 to 60 mm across and have thin (1–3 mm) calcite-rich rinds (figure 1–2). In some cases, rinds had become separated from their associated clasts; however, rind morphology clearly preserves inner and outer surfaces. Multiple clasts from the same soil horizon were collected in order to evaluate the consistency of their isotopic compositions and calculated ages.

Dated rinds consist predominantly of secondary calcite cement formed on the undersides (presumably) of gravel clasts. Textures are relatively simple consisting of lenses of dense, dark-tan to brown calcite with only minor amounts

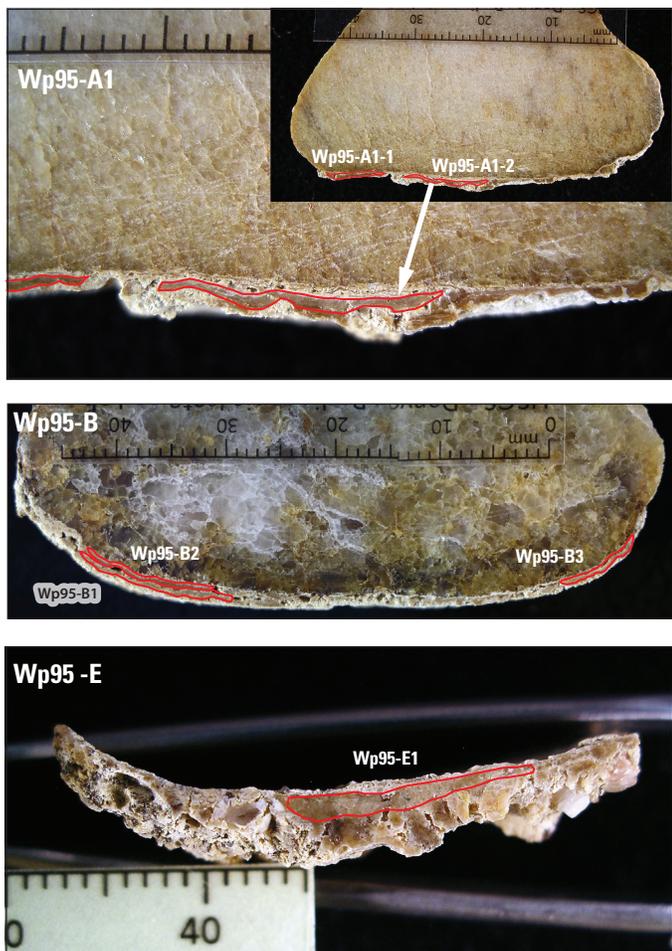


Figure 1-2. Examples of polished slabs of alluvial clasts from sample Wp95 showing thin calcite-rich rinds coating outer surfaces (Wp95-A1 and Wp95-B), or rinds separated from their associated clasts (Wp95-E). Sub-millimeter thick layers of calcite-rich material sampled for uranium-series analyses are shown in red-outlined areas.

of detrital matrix included. Rind growth generally occurs by progressive accumulation of secondary cements that precipitate from water films present in soils (Sharp and others, 2003). Therefore, layers adjacent to the clast/rind interface are likely to yield the oldest dates of pedogenic cements that in turn provide minimum age constraints for deposition of the sediment. These inner-rind layers were targeted for dating in this study.

Aliquots Prepared for U-Series Dating

Bone.—Subsamples of bone were obtained by mounting the polished slab in a manually operated horizontal milling stage and using a 1-mm-diameter carbide dental bur to excavate successive approximately 0.5-mm-thick layers starting from the outermost surface (figure 1-1). Powders were collected and the sample was cleaned between each depth interval using compressed air. Prior to subsampling bone, the thin (approximately

0.5 mm) calcite-rich crust coating the outer surface was sampled (Wp67-1) by milling the surface until the underlying contact was reached.

Clast rinds.—Thin layers (typically about 1-mm or less) of calcite cement adjacent to the clast/rind interface were sampled by prying off fragments or milling material and collecting the resulting powder. Layers that were relatively free of obvious detrital material (sand and silt) were targeted to minimize contributions from detrital components that contain rock-derived ^{230}Th not related to ^{230}Th formed within authigenic cements (that is, to minimize the need to correct for initial ^{230}Th not derived from in situ ^{234}U decay). Layers with higher degrees of cementation typically have the greatest hardness and density, and they tend to be darker in color than less-well-cemented layers. Prior to collecting calcite subsamples, surfaces were cleaned by removing softer or dirtier material using a carbide dental bur. To gain confidence that ages derived from these materials have geological significance, samples of rinds from multiple clasts within the same soil horizon were obtained. Ideally, dates for inner clast rinds from the same horizon should be concordant if they formed during the same pedogenic episode.

Chemical Processing and Mass Spectrometry

Dating activities followed standard operating procedure USGS-DRIL-01, R0 Uranium-Thorium Disequilibrium Studies for chemical preparation and isotope analysis (http://esp.cr.usgs.gov/projects/uth/USGS_DRIL_01cR0_U_series.pdf). This procedure addresses sample labeling and control, analysis of samples, maintenance of records, and reporting of results. These procedures are summarized below.

Aliquots of bone or clast rinds were weighed and spiked with known amounts of a high purity mixed-isotope tracer containing man-made spike isotopes (^{236}U - ^{233}U - ^{229}Th). Samples were digested using nitric and hydrochloric acid in Teflon™ PFA (perfluoroalkoxy copolymer resin) vials at atmospheric pressures and temperatures of 105° to 125 °C. The phosphatic and carbonate components were completely dissolved in this step; however, residue was common in rind samples and represents authigenic opal or detrital silicates including silt and clay. In order to avoid laboratory fractionation of U and Th and produce $^{230}\text{Th}/^{238}\text{U}$ measurements that accurately reflect values inherent in the subsamples, residue was separated from the supernatant, digested using hydrofluoric acid, and recombined with the original solute resulting in analyses that represent total digestions. U and Th were separated from the acid digestates and purified by ion chromatography using Biorad™ AG1×8 (200–400 mesh) resin. Resulting U salts were loaded on the evaporation side of rhenium double-filament assemblies. Th salts were loaded onto single rhenium filament assemblies as a sandwich between layers of graphite suspension. Isotope ratios were obtained on a Thermo Finnigan Triton™ thermal ionization mass spectrometer equipped with

a retarding potential quadrupole (RPQ) electrostatic filter. Ratios were determined using a single ETP™ discrete-dynode electron multiplier operating in peak-jumping mode.

Quality control was monitored by analyzing standards processed and run along with unknown samples. A NIST uranium-isotope solution was used as the primary standard, and several in-house materials of known age and isotopic composition were used as secondary checks. U isotopic compositions of NIST SRM 4321B U-isotope standard determined over the same time period yielded an average $^{234}\text{U}/^{235}\text{U}$ value of $0.0072862 \pm 0.25\%$ ($2 \times$ standard deviation for 122 analyses conducted between 2/11/2013 and 1/5/2015) which is within analytical uncertainty of the certified value of 0.0072939. Results for solutions of uranium ore from the Schwartzwalder mine yielded an average $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) of 1.0003 ± 0.0040 and an average $^{230}\text{Th}/^{238}\text{U}$ AR of 0.998 ± 0.011 ($\pm 2 \times$ standard deviation for 19 analyses conducted between 6/26/2013 and 1/5/2015), both of which are within analytical uncertainty of the secular equilibrium values of 1.000 expected for the 69.3-Ma ore (Ludwig and others, 1985). Results for an in-house late Pleistocene *Acropora* coral dating standard (age of 119.6 ± 1.9 ka; Watanabe and Nakai, 2006) yielded an average age of 119.0 ± 3.5 ka ($\pm 2 \times \text{SD}$, $N=11$) and an average initial $^{234}\text{U}/^{238}\text{U}$ AR value of 1.152 ± 0.006 ($\pm 2 \times \text{SD}$, $N=11$), which is within uncertainty of accepted values for seawater (1.150 ± 0.006 ; Delanghe and others, 2002).

All uncertainties presented in this report are given at the 95% confidence level (2-sigma, 2σ) and include errors arising from within-run analytical errors based on counting statistics, external errors based on reproducibility of standards, and errors propagated from uncertainties assigned to the assumed detrital component and the amount of detrital material present in a given sample (see section on Calculation of $^{230}\text{Th}/\text{U}$ Ages).

Analytical Results

Seven analyses of bone from sample Wp67 and eight analyses of carbonate rinds on three separate clasts from sample Wp95 were analyzed for U and Th isotopes (table 1–1). All samples had U and Th concentrations that were amenable to U-series dating with elevated U concentrations (83 to 116 $\mu\text{g/g}$ for bone and 5.9 to 10.2 $\mu\text{g/g}$ for carbonate rinds) and low Th concentrations (0.03 to 0.33 $\mu\text{g/g}$ for bone and 0.28 to 0.90 $\mu\text{g/g}$ for rinds). Low $^{232}\text{Th}/^{238}\text{U}$ AR (0.00007 to 0.00129 for bone and 0.0088 to 0.038 for clast rinds) and high $^{230}\text{Th}/^{232}\text{Th}$ AR (> 100 for bone and > 28 for clast rinds) reflect the elevated U/Th concentration ratios. For comparison, silicate rocks from which detrital components were derived commonly have Th/U concentration ratios of 3 to 6, which result in $^{232}\text{Th}/^{238}\text{U}$ AR values between about 1 and 2 with $^{230}\text{Th}/^{232}\text{Th}$ AR values of about 0.5 to 1.5. Because of their low ^{232}Th concentrations, corrections for non-authigenic ^{230}Th present at the time the U was incorporated in bone or rind-cements are negligible for most samples.

Calculation of $^{230}\text{Th}/\text{U}$ Ages

Dating by the $^{230}\text{Th}/\text{U}$ method is based on the in-growth of ^{230}Th derived from in situ decay of ^{234}U present in the sample since the time of its formation. Any ^{230}Th that was present initially must be identified and excluded to avoid calculating erroneously old ages. Because of the very low solubility of Th in most near-surface water, purely authigenic cements commonly form with no initial ^{230}Th , and measured $^{230}\text{Th}/^{238}\text{U}$ AR can be used to calculate ages. However, any silicate detritus present in the samples, including fine clay particles, will contain common Th (^{232}Th) as well as small amounts of ^{230}Th that must be mathematically subtracted from the measured ^{230}Th in order to obtain only the ^{230}Th that was contributed from in situ decay of U. Fortunately, measured $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ AR values can be corrected for the presence of a non-authigenic component (that is, silicate sediment) using measured $^{232}\text{Th}/^{238}\text{U}$ AR values and the assumptions that this material is uniform and has a known composition (Ludwig and Titterton, 1994; Ludwig and Paces, 2002).

The isotope composition of detrital material was not measured directly from subsamples, which would require physical separation of clays, silt, or sand from the small bulk subsamples, or chemical separation through partial leaching to remove authigenic cements. Instead, detritus was assumed to have a Th/U concentration ratio similar to values estimated for average continental crust (Th/U = 4; Shaw and others, 1976; Taylor and McLennan, 1985; Rudnick and Gao, 2003) and U-series isotopes in secular equilibrium (that is, $^{234}\text{U}/^{238}\text{U}$ AR = $^{230}\text{Th}/^{238}\text{U}$ AR = 1.0). Because there is a greater likelihood that the true composition of the detritus deviates from a value of 4 (equivalent to $^{232}\text{Th}/^{238}\text{U}$ AR = 1.276), a larger uncertainty was arbitrarily assigned to the $^{232}\text{Th}/^{238}\text{U}$ AR value ($\pm 50\%$). The assumption that the U isotopes are in secular equilibrium is reasonable given the likelihood that parental rock is older than a million years. Therefore, uncertainties assigned to $^{230}\text{Th}/^{238}\text{U}$ AR and $^{234}\text{U}/^{238}\text{U}$ AR, were smaller ($\pm 25\%$ and 10% , respectively). Uncertainties are propagated through the age calculation in such a way that errors for the corrected ratios are only slightly larger than analytical uncertainties if the measured $^{232}\text{Th}/^{238}\text{U}$ AR is negligible (say < 0.1), but may be very large if substantial amounts of ^{232}Th are present (that is, $^{232}\text{Th}/^{238}\text{U}$ AR > 0.2). Ages and initial ratios were calculated using routines in the program Isoplot/Ex (Ludwig, 2012) and decay constants for ^{234}U and ^{230}Th from Cheng and others (2013). Because of the small amounts of ^{232}Th present in bone and clast-rind subsamples, differences between uncorrected and detritus-corrected ages are small, ranging from 0.01 to 3.51% for all analyses except for the “dirtier” Wp67-1 bone-rind (uncorrected age of 12.9 ka versus detritus-corrected age of 11.0 ka = 16.9%).

Values for detritus-corrected $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ AR in the analyzed samples are given in table 1–1 and shown graphically on U-series isotope evolution plots (figure 1–3). Finite ages can be calculated using the first-derivative solution to the $^{230}\text{Th}/\text{U}$ age equation for all analyses. This calculation

Table 1–1. U-Th concentrations, U-series isotopic compositions, and calculated ²³⁰Th/U ages and initial ²³⁴U/²³⁸U activity ratios for subsamples of Wp67 and Wp95 from sites EF and EIC, respectively, on the Masters 7.5' Quadrangle, Weld and Morgan Counties, Colorado.

[Note that ±2σ represents estimates of uncertainty given at the 95% confidence level; µg/g, micrograms per gram; σ, sigma.]

Sample name	Sample weight, g	U concentration, in µg/g	Th concentration, in µg/g	Measured activity ratios ¹			²³⁰ Th/ ²³² Th AR	Detritus-corrected activity ratios ²			²³⁰ Th/U age ±2σ (ka) ³	Initial ²³⁴ U/ ²³⁸ U AR ±2σ ³	r _{age-go} ⁴
				²³² Th/ ²³⁸ U AR ±2σ	²³⁰ Th/ ²³⁸ U AR ±2σ	²³⁴ U/ ²³⁸ U AR ±2σ		²³⁰ Th/ ²³⁸ U AR ±2σ	²³⁴ U/ ²³⁸ U AR ±2σ	r ₄₈₋₀₈ ⁴			
EF-Wp67: Carbonate rind (subsample Wp67-1) and layers of bone (subsamples Wp67-2 through Wp67-11) across a section of horn-core (presumably bison): Location: UTM 564654mE, 4462502mN, zone 13, NAD 27 ⁵													
Wp67-1	0.039	22.5	1.64	0.02397±0.00007	0.1357±0.0008	1.216±0.003	5.7	0.117±0.011	1.221±0.004	-0.55	11±1.1	1.228±0.004	-0.46
Wp67-2	0.039	83.0	0.325	0.00129±0.00001	0.1348±0.0011	1.213±0.003	104	0.1338±0.0012	1.214±0.003	-0.02	12.70±0.13	1.221±0.003	-0.22
Wp67-3	0.041	107	0.044	0.00013±0.00000	0.1521±0.0006	1.210±0.003	1150	0.1520±0.0006	1.210±0.003	0.00	14.58±0.07	1.219±0.003	-0.46
Wp67-5	0.016	116	0.025	0.00007±0.00001	0.1588±0.0007	1.215±0.003	2300	0.1588±0.0007	1.215±0.003	0.00	15.21±0.08	1.224±0.003	-0.42
Wp67-7	0.019	115	0.028	0.00008±0.00001	0.1601±0.0007	1.221±0.002	2020	0.1600±0.0007	1.221±0.002	0.00	15.26±0.08	1.231±0.003	-0.39
Wp67-9	0.020	116	0.032	0.00009±0.00001	0.1459±0.0006	1.217±0.003	1600	0.1458±0.0006	1.217±0.003	0.00	13.87±0.07	1.226±0.003	-0.44
Wp67-11	0.016	104	0.124	0.00039±0.00001	0.1258±0.0005	1.217±0.003	322	0.1255±0.0006	1.217±0.003	0.00	11.82±0.06	1.225±0.003	-0.43
EIC-Wp95: Innermost carbonate rinds on alluvial clasts: Location: UTM 567342mE, 4458109mN, zone 13, NAD 27 ⁵													
Wp95-A1-1	0.041	5.92	0.280	0.01557±0.00009	1.041±0.007	1.123±0.007	66.9	1.040±0.008	1.125±0.007	-0.01	248±9	1.252±0.010	-0.30
Wp95-A1-2	0.047	7.36	0.309	0.01384±0.00006	1.062±0.006	1.083±0.003	76.7	1.061±0.007	1.084±0.003	-0.01	337±15	1.217±0.009	0.68
Wp95-A2-1	0.048	10.2	0.274	0.00881±0.00005	1.065±0.009	1.084±0.002	121	1.065±0.009	1.085±0.003	0.00	341±20	1.222±0.012	0.85
Wp95-A3-1	0.049	7.12	0.549	0.02539±0.00010	1.049 ±0.007	1.091±0.003	41.3	1.048±0.009	1.094±0.004	-0.02	294±13	1.216±0.008	0.47
Wp95-B1	0.043	7.9	0.901	0.03758±0.00011	1.058±0.006	1.074±0.002	28.2	1.057±0.01	1.077±0.004	-0.03	345±24	1.205±0.012	0.64
Wp95-B2	0.041	7.6	0.509	0.02204±0.00008	1.049±0.006	1.077±0.002	47.6	1.048±0.007	1.079±0.003	-0.02	324±15	1.197±0.008	0.54
Wp95-B3	0.046	9.58	0.672	0.02309±0.00007	1.070±0.005	1.070±0.002	46.3	1.069±0.007	1.072±0.003	-0.02	397±27	1.221±0.014	0.81
Wp95-E1	0.059	9.91	0.461	0.01534±0.00005	1.038±0.005	1.052±0.002	67.7	1.037±0.006	1.054±0.003	-0.01	372±21	1.153±0.008	0.60

¹ Measured activity ratios (AR) corrected for mass fractionation, spike contributions, procedural blank and normalized relative to an atomic ratio value for NIST SRM 4321B U-isotope standard of ²³⁴U/²³⁸U=0.0000529.

² Ratios corrected for an assumed Th-bearing detrital component having an atomic Th/U of 4 with the following activity ratios and 2σ errors: ²³²Th/²³⁸U=1.276±0.64; ²³⁴U/²³⁸U=1.0±0.1; and ²³⁰Th/²³⁸U=1.0±0.25.

³ ²³⁰Th/U ages, initial ²³⁴U/²³⁸U ARs, and associated errors calculated using detritus-corrected activity ratios.

⁴ r₄₈₋₀₈ = error correlation between ²³⁴U/²³⁸U AR and ²³⁰Th/²³⁸U AR. r_{age-go} = error correlation between ²³⁰Th/U age and initial ²³⁴U/²³⁸U AR.

⁵ 1927 North American Datum.

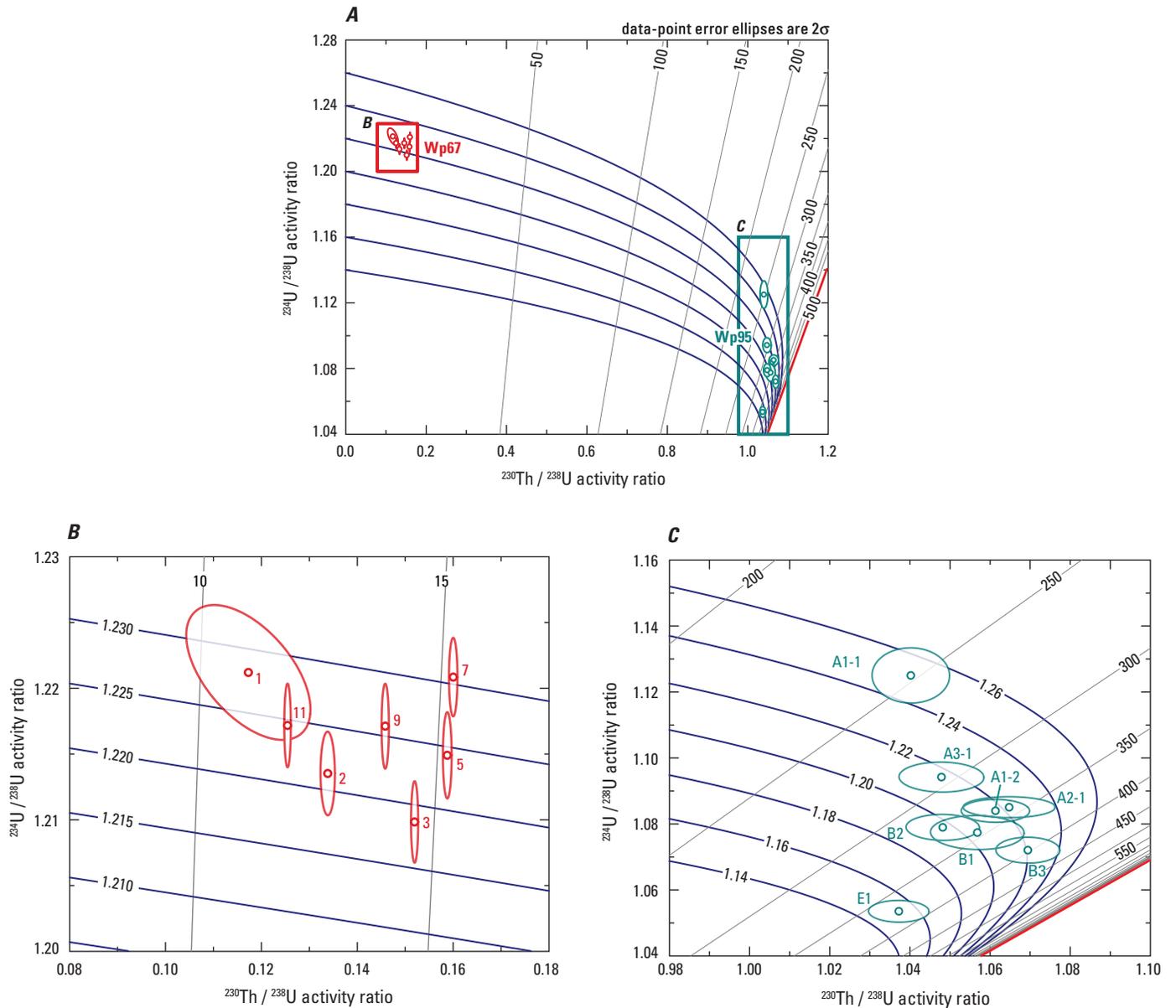


Figure 1–3. U-series isotope evolution plots showing U-Th isotopic compositions (circles) and 2-sigma (2σ) uncertainties (error ellipses) for analyses of bone (Wp67; red-colored points) and calcite rinds (Wp95; teal-colored points) listed in table 1–1. All data are shown in (A) and at expanded scales for analyses of Wp67 in (B) and Wp95 in (C). In all plots, the thick curves represent $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ compositional paths that evolve under closed conditions (no loss or gain of mass since the time of formation) for material with initial $^{234}\text{U}/^{238}\text{U}$ activity ratios ranging from 1.14 to 1.26. Straight sloping lines are isochrons given at intervals labeled on plots (in thousands of years). Isochrons older than about 500 ka become highly condensed, and define an infinite age line (red lines in A and C) representing the upper dating limit based on ^{230}Th decay.

uses the values for the detritus-corrected activity ratios, and yields valid solutions as long as the isotopic compositions fall to the left of the infinite-age line shown on isotope evolution plots (red lines on figures 1–3A and 1–3C). In those cases, analytical errors are used to directly estimate uncertainties for ²³⁰Th/U ages and initial ²³⁴U/²³⁸U AR. No points plot to the right of the infinite-age line, which indicates that obvious secondary U mobility has not occurred.

Initial ²³⁴U/²³⁸U Activity Ratios

Once a ²³⁰Th/U age (t) is determined for a given sample, it can be used to calculate the initial ²³⁴U/²³⁸U composition of the water from which the cement was precipitated knowing the present-day ²³⁴U/²³⁸U AR and the decay constant for ²³⁴U ($\lambda_{234} = 2.82203 \times 10^{-6}$ yr⁻¹):

$$\frac{{}^{234}\text{U}}{{}^{238}\text{U}} AR_{\text{initial}} = \frac{\left(\frac{{}^{234}\text{U}}{{}^{238}\text{U}} AR_{\text{present}} - 1 \right)}{e^{-\lambda_{234}t}} + 1$$

In hydrogenic deposits formed from water having ²³⁴U/²³⁸U AR values greater than unity (that is, >1.0), initial ratios will be equal to or larger than the measured ratio, following the curved isotope-evolution paths in figure 1–3 to the point where they reach the Y-axis (dark curves). This is a very valuable check on ages because all samples precipitated from a single water source should have the same initial ²³⁴U/²³⁸U AR values regardless of their ²³⁰Th/U age. Samples that are affected by post-depositional removal of U will have anomalously large ²³⁰Th/²³⁸U AR values, which results in erroneously old ages and anomalously large initial ²³⁴U/²³⁸U AR values.

Samples of bone and clast rinds analyzed in this study have a limited range of initial ²³⁴U/²³⁸U AR values (figure 1–4). Samples from sample Wp67 with latest Pleistocene ²³⁰Th/U ages have initial ²³⁴U/²³⁸U AR values of 1.225 ± 0.008 ($\pm 2 \times$ standard deviation) that overlap values of 1.219 ± 0.034 for the middle Pleistocene clast rinds from sample Wp95. The consistency of initial ²³⁴U/²³⁸U AR values is interpreted as evidence that both samples acquired their U from similar soil-water sources, and that despite their antiquity, pedogenic rinds from Wp95 retained their isotopic integrity and preserve reliable age information.

Ages for Individual Samples

Wp67 bone.—Subsamples of Wp67 bone (Wp67–2 through Wp67–11) have elevated U concentrations (83 to 116 µg/g) and very low Th concentrations (0.025 to 0.033 µg/g) resulting in U-series analyses that require very little or no corrections for initial ²³⁰Th. Subsamples of bone have apparent ²³⁰Th/U ages calculated from U-series isotope data that range from 11.82 ± 0.06 ka to 15.26 ± 0.08 ka (table 1–1). The calcite-rich crust coating the outer surface of the bone (Wp67–1) has a lower U concentration

(22.5 µg/g) and higher Th concentration (1.64 µg/g) relative to bone samples and yields a slightly younger ²³⁰Th/U age with greater uncertainty (11.0 ± 1.1 ka).

The date for the calcite crust represents a minimum depositional age for the bone as it was formed as part of the pedogenic process. U-series ages of bone also represent minimum ages as they reflect U that has been absorbed from infiltrating soil water after burial. Most vertebrates incorporate only small amounts of U in living bone tissue (typically <0.05 µg/g; Larivière and others, 2013). Therefore, the large amounts present in Wp67 were incorporated in the bone only after death and burial. The main challenge when dating bone by U-series methods is understanding when the U was added.

U is readily soluble in oxidizing near-surface water and interactions between those waters and the buried bone results in loss of much of the organic matter (collagen) and incorporation of U within the carbonated hydroxyapatite. Patterns of U uptake can take numerous forms depending on the degree of hydrologic saturation and water-migration history of the site, the diffusive characteristics of the bone, and the uranium concentrations in the diagenetic environment. Two simple conceptualizations of U behavior include early uptake where all U is acquired over a short time span (relative to the time of burial) and then held tightly in place, and linear uptake, where U uptake occurs slowly and continuously between burial and the present. True uptake histories can be more complex. Examination of profiles of U concentration and U-series ages across sections of compact (cortical) bone can offer insights into U uptake processes.

The diffusion-adsorption model (D–A model) was developed to explain profiles of U concentrations and U-series ages observed in bone samples (Millard and Hedges, 1996; Pike and others, 2002; Pike and Pettit, 2003). The model assumes that uranyl complexes (UO₂⁺²) in aqueous solutions are able to diffuse into porous compact bone and adsorb into the mineral fraction of bone, facilitated by its large internal surface areas. Oxidation of bone collagen may also contribute to this process by providing a mechanism for reduction of soluble hexavalent U(VI) to non-soluble tetravalent U(IV) within the bone structure.

The distribution of U (and resulting U-series ages) is dependent on a number of parameters inherent to a given bone including its diffusion coefficient, porosity, and the mineral/water partition coefficient, as well as chemical and physical factors present in the burial environment (Pike and others, 2002; Pike and Pettit, 2003). With time, U from migrating water is introduced into the bone starting from the outer and inner surfaces and progressing toward its center (figure 1–5). U uptake is non-linear and proceeds more rapidly during earlier stages and less rapidly during later stages. The U concentration profiles gradually flatten with time until the bone reaches a composition in equilibrium with U in the source water. The distribution of apparent U-series ages will result in similar U-shaped patterns, with apparent ages decreasing towards the center of the bone (Pike and others, 2002; Sambridge and others, 2012).

Profiles of U concentration measured for subsamples of Wp67 show a \cap -shaped pattern (figure 1–6A) rather than that expected for gradual, continuous uptake modeled in figure 1–5. This response implies that the bone has experienced a relatively recent loss of U after the initial uptake that lead to high concentrations in interior subsamples. Because U is mobile but Th is not, loss of U will eventually result in increased values of $^{230}\text{Th}/^{238}\text{U}$ AR that are not related to in situ ingrowth of ^{230}Th . As values of $^{230}\text{Th}/^{238}\text{U}$ AR increase, points on U-series isotope evolution plots (figure 1–3) will move towards the right without substantially altering the $^{234}\text{U}/^{238}\text{U}$ AR. This behavior results in

erroneously old ages and high apparent initial $^{234}\text{U}/^{238}\text{U}$ AR values. Therefore, U loss will result in M- or \cap -shaped concentration profiles and strongly U-shaped profiles of apparent closed-system $^{230}\text{Th}/\text{U}$ ages (see figure 3F and section 3.4 of Pike and others, 2002). Pike and others (2002) showed that U loss can dramatically affect ages calculated for outer subsamples and eventually cause erroneously old ages for interior subsamples as well.

In contrast, measured $^{230}\text{Th}/\text{U}$ ages for Wp67 subsamples also define a \cap -shaped profile (figure 1–6B). Furthermore, initial $^{234}\text{U}/^{238}\text{U}$ AR values are more-or-less uniform across the section and do not show systematic increases in samples with

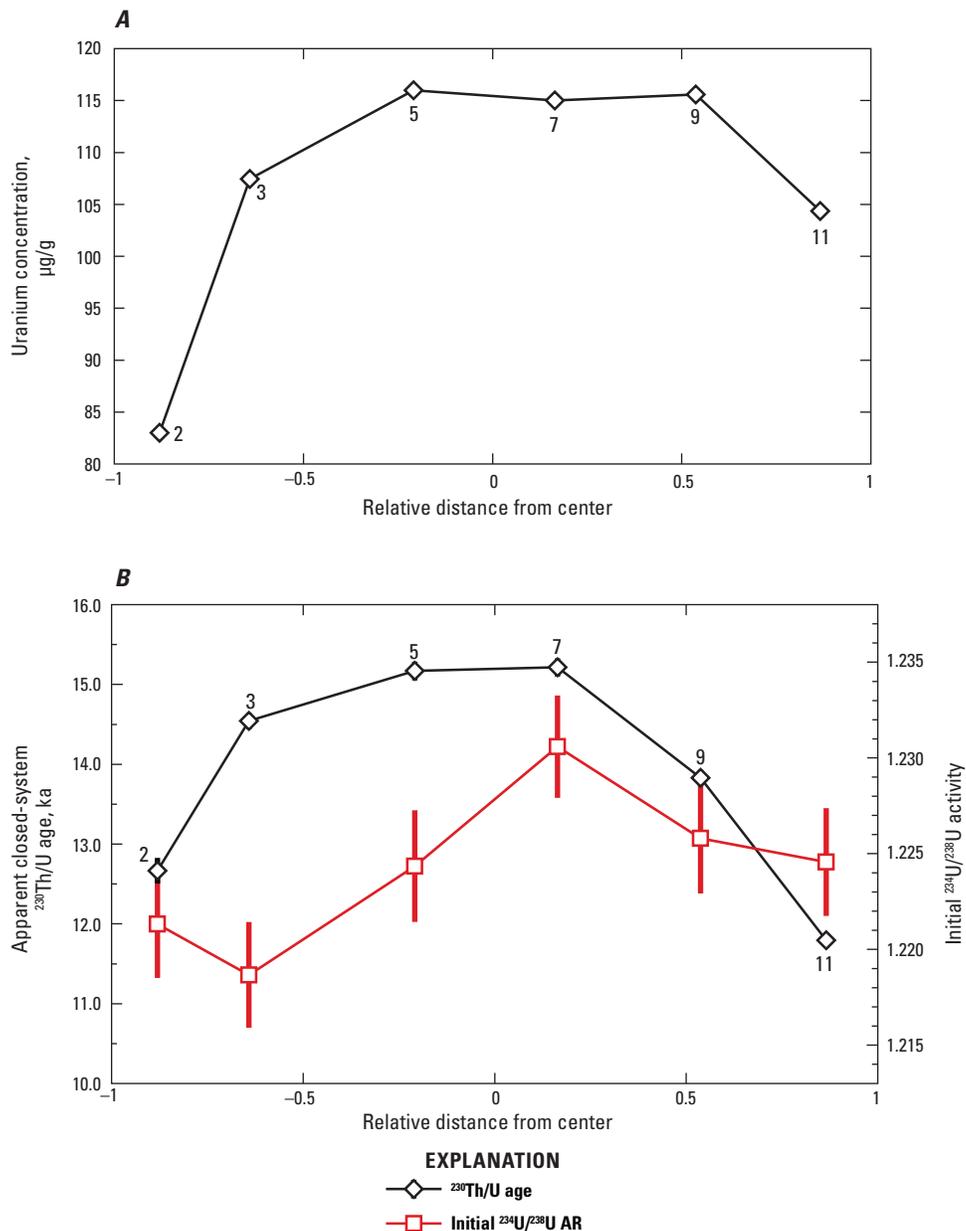


Figure 1–6. Profiles of uranium concentration (A) and $^{230}\text{Th}/\text{U}$ age and initial $^{234}\text{U}/^{238}\text{U}$ activity ratios (B) for subsamples of bone from sample Wp67. Data are from table 1–1. Two-sigma (2σ) analytical uncertainties are shown as error bars, which are mostly smaller than the symbols used for U concentrations and $^{230}\text{Th}/\text{U}$ ages. Points are labeled with the subsample numbers shown in figure 1–1. Data for Wp67–1 representing the carbonate rind coating the bone are not included.

the lowest U concentrations (figure 1–6B). Initial $^{234}\text{U}/^{238}\text{U}$ values for all but one bone sample are within analytical error of the value obtained for the calcite crust on the exterior of the bone. Therefore, data for Wp67 do not follow patterns expected for normal processes of U loss.

The available U-series isotope results for the single bone specimen analyzed from site EF do not allow a definitive age estimate. The date of 11.0 ± 1.1 ka for the calcite crust (Wp67–1) represents a minimum age that is less subject to processes of secondary U mobility than the bone matrix itself. Two subsamples from the fragment interior (Wp67–5 and Wp67–7) have apparent closed-system $^{230}\text{Th}/\text{U}$ ages that are within analytical uncertainty and yield an error-weighted average value of 15.24 ± 0.06 ka. The remaining subsamples of bone have ages between these two limits. Therefore, the best estimate for the minimum age of burial for sample Wp67 is between 11 and 15 ka. Data for additional specimens are required to better define this estimate.

Wp95 clast rinds.—Subsamples of innermost rinds on clasts from Wp95 have U concentrations ranging from 5.9 to 10.2 $\mu\text{g}/\text{g}$ and uniformly low Th concentrations ranging from 0.27 to 0.90 $\mu\text{g}/\text{g}$ (table 1–1). Consequently, measured $^{230}\text{Th}/^{232}\text{Th}$ AR values are high (28 to 121) and require only minor corrections for the presence of initial ^{230}Th . Resulting $^{230}\text{Th}/\text{U}$ ages range from 248 ± 9 ka to 397 ± 27 ka. Most clast-rind

analyses (6 of 8) yield initial $^{234}\text{U}/^{238}\text{U}$ AR values that span a narrow range and define a mean value of 1.212 ± 0.011 . Furthermore, ages and initial $^{234}\text{U}/^{238}\text{U}$ AR values of Wp95 clast rinds are poorly correlated (R^2 value of 0.33). The fact that initial $^{234}\text{U}/^{238}\text{U}$ AR values consistently cluster around a narrow range that is analytically indistinguishable from values determined for late Pleistocene material from the same area (figure 1–4) is a strong indication that clast rinds were not subject to secondary U mobility, and that resulting data yield reliable $^{230}\text{Th}/\text{U}$ ages.

Because pedogenesis is a dynamic process where new cement can be added at any time after alluvium was deposited, the oldest U-series dates observed for a given soil horizon are expected to better represent minimum ages for the depositional event. Ages for two of the rind subsamples are substantially younger than the rest (248 and 294 ka) and likely include soil components added well after the gravels were deposited. The remaining six subsamples have older ages that cluster in two groups (figure 1–7). Four subsamples from two separate clasts define an error-weighted-mean age of 334 ± 9 ka whereas two subsamples from separate clasts define a somewhat older error-weighted-mean age of 382 ± 16 ka. Therefore, available U-series data indicate with a high degree of confidence that alluvial clasts at site EIC were deposited prior to 334 ka. A depositional age somewhat older than 382 ka is considered likely based on the two oldest rind dates.

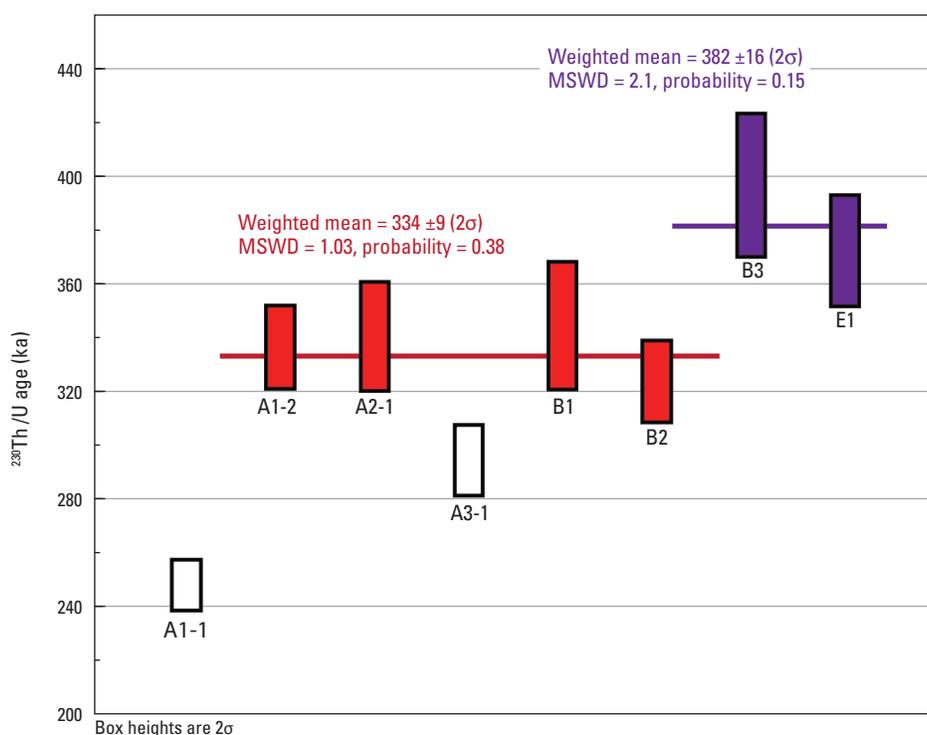


Figure 1–7. Plot of $^{230}\text{Th}/\text{U}$ ages for subsamples of clast rinds from Wp95. Data are from table 1–1. Boxes represent the 2-sigma (2σ) age range based on closed-system evolution of U-series isotopes that are grouped by color to show two different mean values. Mean values are weighted by the analytical errors assigned in table 1–1. The value for MSWD (mean square of weighted deviates) represents a measure of how well the assigned analytical errors explain the observed scatter of values—if the MSWD is close to unity (1.0), the assigned analytical errors are considered the main cause for scatter. Additional sources of non-analytical error are likely if the MSWD value is much greater than unity (Ludwig, 2012).

Conclusions

U-series ages determined on materials from two sites in the Masters 7.5' Quadrangle are consistent with Quaternary geologic relations. Multiple subsamples of a single bone fragment and its associated calcite rind from mainstream deposits of Broadway Alluvium (map unit Qba) at site EF indicate that burial of the specimen occurred between 11 and 15 ka. Although data for this specimen indicate a complex history of U uptake and subsequent leaching, the weighted average value of 15.24±0.06 ka is interpreted to more closely represent the minimum age. Multiple subsamples of innermost calcite rinds coating several clasts from a deposit of intermediate alluvium (map unit Qai) from site EIC indicate that the alluvium was deposited prior to 334±9 ka. Two of the oldest rind subsamples suggest the minimum age is likely closer to 382±16 ka.

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