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Uranium-Series Dating of Lacustrine Limestones from Pan Deposits with Final Acheulian Assemblage at Rooidam, Kimberley District, South Africa

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Lacustrine limestone samples from sedimentary pan deposits at Rooidam, near Kimberley, South Africa, that contain late Acheulian (Fauresmith) artifacts have been dated by ^{230}Th/^{234}U and ^{231}Pa/^{235}U methods. Results indicate a minimum age of about 200,000 yr B.P. for the terminal Acheulian in the interior of South Africa.

A complex of pan (playa) deposits at Rooidam, near Kimberley, South Africa contains late Acheulian (Fauresmith) artifacts, indicating major occupation along the margin of a seasonal lake. The sedimentary sequence, about 10 m in thickness, is shown in Fig. 1. A detailed stratigraphic description is given by Butzer (1974), and the artifacts are described and illustrated in preliminary form by Fock (1968) and Clark (1970, Fig. 22). Two limestone samples (sampled by Butzer) were dated by the uranium-series methods (analyzed by Szabo). They are from unit C (Bu-2, about 6.4 m from bottom of section) overlying unit B with abundant archaeological materials, and from unit G (Bu-1, about 8.2 m from bottom of section), that overlies units E and F, both of which contain some artifacts.

Inorganically precipitated carbonates may be dated by the uranium-series methods provided that the samples initially had uranium but no thorium and protactinium isotopes, and that the samples were free of postdepositional migration of uranium and its long-lived daughter elements, ^{230}Th and ^{231}Pa. The problem with dating limestones is that they usually contain large amounts of detrital materials that cannot be separated effectively from the carbonate fraction by physical means. Because of the difficulties involved there are few published data on dating inorganic carbonates. The most extensive study is reported by Kaufman (1971), who successfully dated inorganically precipitated marls. He analyzed a number of samples from each deposit that contained different amounts of detrital contaminants. Using an isochron plot of ^{230}Th/^{234}U versus ^{232}Th/^{234}U, he was able to ascertain the ^{230}Th/^{234}U activity ratios of the pure carbonate components from which the correct ^{230}Th ages of the deposits can be calculated. This approach is appropriate when a suite of samples are available from different localities of the same deposit; however, it is not suitable for dating samples from a single locality having approximately the same amounts of detrital contaminants. For this study, the isochron approach of Kaufman (1971) is modified for single sample dating using chemical means of separation of the carbonate and detrital fractions.

The limestone samples were crushed, ground to a fine powder, and then ashed for a period of about eight hr at 900°C. Each sample was divided to two aliquots. Aliquot

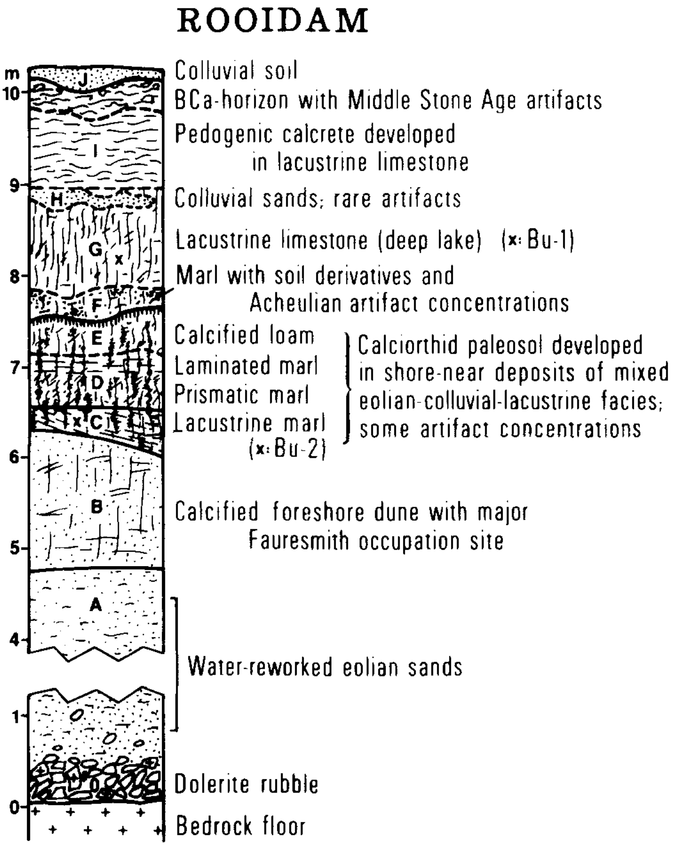

FIG. 1. Lithostratigraphy of Rooidam showing, locations of dated samples.

A was totally dissolved by concentrated HNO_3, $HClO_4$, and HF mixtures. Uranium and thorium concentrations were determined by mass-spectrometry using ^{230}Th and ^{235}U spikes; the $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ were determined by alpha-spectrometry using a combined ^{229}Th and ^{228}Th spike (Szabo and Rosholt, 1969). The $^{231}Pa/^{235}U$ was determined by activation analysis and alpha-spectrometry (Rosholt and Szabo, 1969). Aliquot B was treated with 0.1 *M* acetic acid to dissolve the carbonate fraction. The acid-insoluble residue was separated from the solution by centrifugation and was dried. The acid-insoluble residue was then totally dissolved by the addition of concentrated HNO_3, $HClO_4$, and HF mixtures. The uranium and thorium contents and $^{230}Th/^{234}U$ and were determined by alpha-spectrometry using ^{236}U and combined ^{228}Th and ^{229}Th spikes.

The thorium and uranium concentrations and isotopic activity ratios of total samples and acid insoluble residues are shown in Table 1. The $^{230}Th/^{234}U$ versus $^{232}Th/^{234}U$ plot of the respective total sample and insoluble residue pairs were shown in Fig. 2. Lines are extrapolated to $^{232}Th/^{234}U = 0$ where $^{232}Th = 0$ to obtain the $^{230}Th/^{234}U$ ratios of the pure carbonate components.

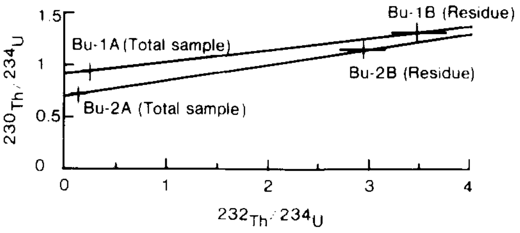

FIG. 2. $^{230}Th/^{234}U$ versus $^{232}Th/^{234}U$ plot of total samples and respective acid insoluble residues. Lines are extrapolated to $^{232}Th/^{234}U = 0$ where $^{232}Th = 0$ in order to obtain the $^{232}Th/^{234}U$ ratios of the pure carbonate components. The ratios that are obtained by this extrapolation are then used for calculating ages in Table 1.

TABLE 1

CHEMICAL DATA AND CALCULATED URANIUM-SERIES AGES OF LIMESTONE SAMPLES FROM CALCAREOUS PANS AT ROOIDAM, KIMBERLEY, SOUTH AFRICA

Sample	Uranium (ppm)	Thorium (ppm)	^{230}Th^{a}/^{232}Th	^{234}U^{a}/^{238}U	^{230}Th^{a}/^{234}U	^{231}Pa^{a}/^{235}U	^{230}Th^{b} age (× 10^3 yr)	^{231}Pa^{c} age (× 10^3 yr)
			Rooidam—Unit G					
Bu-1A[d]	0.67 ±0.01	1.5 ±0.1	3.76 ±0.11	2.96 ±0.05	0.94 ±0.06	0.97 ±0.06	174. ±20.	151. $^{+\infty}_{-35}$
Bu-1B[e]	0.87 ±0.02	3.2 ±0.1	0.379 ±0.011	1.08 ±0.02	1.32 ±0.08	n.d.[f]	n.a.[g]	n.a.
			Rooidam—Unit C					
Bu-2A[d]	0.32 ±0.01	0.69 ±0.02	5.00 ±0.15	4.01 ±0.06	0.72 ±0.04	0.93 ±0.06	108. ± 9.	108. +40. −20.
Bu-2B[e]	0.92 ±0.02	2.6 ±0.1	0.392 ±0.012	0.96 ±0.02	1.16 ±0.07	n.d	n.a.	n.a.

[a] Isotopic activity ratios.

[b] Corrected using isochron plots of Figs. 2 and 3, calculated using half-lives of ^{230}Th and ^{234}U of 75,200 and 244,000 yr, respectively.

[c] Corrected for unsupported ^{231}Pa: $(^{231}\mathrm{Pa})_{\mathrm{unsup.}} = 0.6\ ^{232}\mathrm{Th}\ \exp(-\lambda_{231}t)$; calculated using half-live of ^{231}Pa of 32,500 yr.

[d] Total sample.

[e] Acid insoluble residue.

[f] n.d. = not determined.

[g] n.a. = not applicable.

The ^{234}U/^{238}U versus ^{232}Th/^{238}U plot is shown in Fig. 3. Lines are extrapolated to ^{232}Th/^{238}U = 0 where ^{232}Th = 0 to obtain the ^{234}U/^{238}U of the pure carbonate components. From the corrected ^{230}Th/^{234}U and ^{234}U/^{238}U, the ^{230}Th ages of samples Bu-1 and Bu-2 are calculated to be 174,000 ± 20,000 and 108,000 ± 9,000 yr old, respectively (Table 1). The ^{231}Pa/^{235}U ratios of the total samples are corrected for the initial ^{231}Pa contamination due to the detrital components by assuming that the initial ^{231}Pa/^{232}Th = ^{230}Th/^{232}Th. The initial ^{230}Th/^{232}Th is calculated to be 0.6 from the slopes of the lines of Fig. 2, also taking into consideration the decay of the unsupported ^{230}Th since the time of deposition. The measured ^{231}Pa/^{235}U ratios are then corrected using the relationship that $(^{231}\mathrm{Pa}/^{235}\mathrm{U})_{\mathrm{initial}} = 0.6\ ^{232}\mathrm{Th}/^{235}\mathrm{U}e^{-\lambda 231t}$. The calculated ^{231}Pa ages of samples Bu-1 and Bu-2 are 151,000 + ∞/ − 35,000 and 108,000 + 40,000/ − 20,000 years old, respectively (Table 1).

Both limestone samples yield concordant

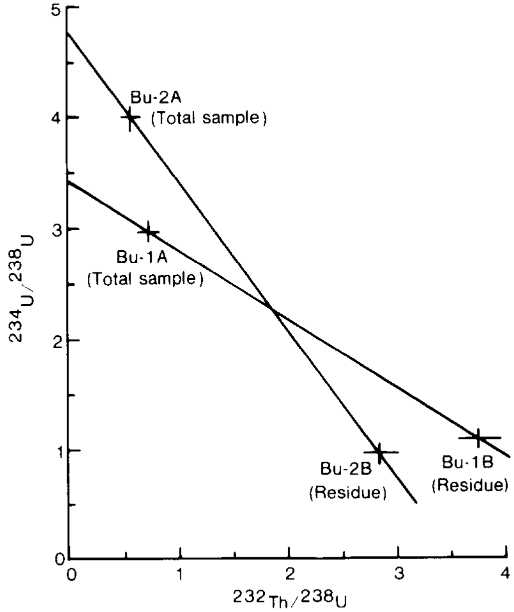

FIG. 3. ^{234}U/^{238}U versus ^{232}Th/^{238}U plot of total samples and respective acid insoluble residues. Lines are extrapolated to ^{232}Th/^{238}U = 0 where ^{232}Th = 0 in order to obtain the ^{234}U/^{238}U activity ratios of the pure carbonate components. These ratios are then used for calculating the ^{230}Th/^{234}U ages in Table 1.

^{230}Th and ^{231}Pa ages, within limits of experimental errors, indicating that the closed system assumption for these samples is valid. However, in spite of these consistent results the dilemma still remains that the stratigraphic position of unit C indicates that it is older than unit G, thus the radiometric age of sample Bu-2 should be older than that of Bu-1. To resolve this problem the crystallographic composition of these carbonates was determined by X-ray diffraction. Sample Bu-1 is over 60% aragonite, whereas sample Bu-2 is over 90% calcite in composition. The results suggest that sample Bu-2 has recrystallized from aragonite to calcite. Further evidence for recrystallization is that the ^{234}U/^{238}U ratio is considerably higher in sample Bu-2 (4.01) than in sample Bu-1 (2.96), suggesting that the uranium in the ground water, with its apparently high ^{234}U/^{238}U composition, exchanged freely with the uranium of the limestone in unit C during recrystallization. The concordant ^{230}Th and ^{231}Pa ages suggest that the radiometric clock was then reset at about 104,000 yr ago and this appears to be the age of recrystallization not of deposition. Sample Bu-1 did not appreciably recrystallize, thus the age of about 174,000 yr for the deposition of unit G appears reliable.

The chaotically bedded and probably reworked artifactual materials in unit F indicate sporadic local occupation by Acheulian people around the temporary lakes, represented by units D and E, at some time prior to about 174,000 yr ago. The major late Acheulian (Fauresmith) occupation contemporary with deposition of unit B cannot be dated because the overlying unit C, containing sample Bu-2, yielded a minimum age estimate only. Nonetheless, sample Bu-1 provides an important *terminus ante quem* for the terminal Acheulian in the interior of South Africa. The deep lake phase (unit G), dated at about 174,000 yr B.P., was preceded by a pedogenetic interval, prior to which Acheulian settlement focused on the fluctuating shore zone of shallow lakes. This suggests a minimum age of about 200,000 yr B.P. for the terminal Archeulian, an estimate compatible with recent evidence that the basal Middle Stone Age of Border Cave dates back to almost 200,000 yr B.P. (Butzer, *et al.*, 1978), or with the faunal dating of the Acheulian in the Vaal River gravels (Helgren, 1977).

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