Luminescence dating at Rose Cottage Cave: a progress report

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Infrared-stimulated luminescence and thermoluminescence dates from Rose Cottage Cave are consistent with one another and form an apparently coherent sequence with depth. That these criteria do not ensure the validity of the dates is shown by a comparison with associated radiocarbon dates. The discrepancy between the luminescence and radiocarbon dates is attributed to the migration of uranium and potassium salts causing an increased radiation dose rate in deeper strata. The limits of this effect are set by the amount of soluble uranium and potassium that contributes to the dose rate in any given layer. Recalculation of the luminescence dates using a model of dose rate build-up illustrates that the 'mobile' component is large enough to account for the discrepancy. Further variation in the dose rate may be attributed to the compaction of sediments through time. The results suggest that luminescence dating should be carried out on archaeological cave deposits with circumspection, particularly where independent dates cannot be used to test the accuracy of the dose rate analysis and where water flux through the deposit may have been high through time.

Luminescence dating has been found to provide reliable dates for Upper Pleistocene sediments that are more than 50 000 years old, and has also been shown to have the potential to date events that occurred as long ago as 800 000 years.[1] This makes it an eminently suitable method for establishing an absolute chronology for the Middle Stone Age (MSA) in southern Africa. There are, however, criteria that must be met for the successful application of luminescence dating. The most important of these is that the ambient radiation dose rate in the sediment remains constant through time. A common contravention of this prerequisite is brought about by uranium leaching, which can result in either a decrease or an increase of this element in the deposit. In the latter case the uranium is not in radioactive equilibrium with daughter products and this results in a continuous increase in the dose rate.

In dating the MSA, the present focus is on cave deposits. Here the assumption of radioactive dose rate stability that is intrinsic to luminescence dating needs closer scrutiny. The problem of disequilibrium is still relevant, but the biogenic contribution to the deposit introduces further problems that do not occur in other geological contexts where luminescence dating is usually applied. Cave sediments incorporate highly concentrated wood ash and other organic material that contain a significant amount of radioactive material. The most important of these is potassium, which is particularly concentrated in wood ash. When the biogenic component in the sediment decomposes, the radioactive elements may dissolve in water and migrate through the deposit. A further consequence of the decomposition of organic material is the associated compaction of the sediment. The progressive reduction in sediment volume through time will affect the density of the deposit and consequently the attenuation of the radiation dose.

If luminescence techniques are to be used to date the MSA, then it is important that the potential sources of error are assessed at each site and for each date from each site. The most efficient means to achieve this is to compare the dates that are obtained with those obtained by an independent dating method. Rose Cottage Cave near Ladybrand in the eastern Free State, South Africa, provides a unique opportunity for such an intercomparison. It contains a stratified sequence that spans the MSA and the Later Stone Age (LSA), which has been systematically excavated and dated. At least 22 finite radiocarbon dates have been obtained for the top sedimentary units of the sequence, the oldest of which is 31 300 ± 900 BP (Pta-5592),[2–4] and there are several infinite dates from lower in the MSA sequence. Comparing the luminescence dates with the radiocarbon dates for these levels will establish the veracity of the luminescence dates and determine the quality of further luminescence dating on the MSA strata at this site.

Method

Rose Cottage Cave is a large rock shelter that is eroded into Karoo sandstone. At some time in the past a large part of the roof collapsed across the front of the cave, conveniently allowing for sunlight zeroing of the sediments that accumulated within. The shelter is north facing and receives direct sunlight during winter and is shady during summer. The sediments are made up of roof debris eroded from the sandstone substrate as well as intrusive wash derived from a spring in the back of the cave.

Three sediment samples were collected from strata with associated radiocarbon dates. RCC4 was taken from square Mg, level Lb at 140-cm depth and is associated with a ^{14}C date on charcoal of 9 560 ± 70 BP (Pta-7275) obtained for this analysis. RCC10 was taken from square N5, level Db at *c*. 100-cm depth. Associated ^{14}C dates are 12 690 ± 120 BP (Pta-5593) from square L5, level Db and 13 360 ± 150 BP (Pta-5601) from square K3, level Db2.[3] These samples are associated with the Robberg stone tool industry. The third sample, RCC9, was taken from square N5, level Ru at *c*. 120-cm depth. This level contains the terminal MSA, and has associated ^{14}C dates of 27 800 ± 1 700 BP (Pta-6202) from square M5, level Ru, and 27 200 ± 350 BP (Pta-5596) from square L5, level Dc.[3] The samples were collected under a black tarpaulin and transported and stored in light-tight containers. Subsequent laboratory analysis was done under low red light conditions.

The samples were chemically pre-treated by boiling in excess concentrated HCl for 20 min, and then in excess 5% NaOH for 20 min. The sediments were sieved into 75–150 mm (100 mm) and 150–300 mm (200 mm) fractions. These were subjected to a magnetic separation to remove metallic and heavy mineral grains. Quartz and feldspar grains were separated on the basis of their density. Sodium polytungstate solution of SG 2.58 was used to float off the potassium-rich feldspar, and SG 2.62 was used to sink out the quartz. The feldspar grains were mounted on aluminium disks (approximately 7 mg per disk) using silicon oil for infrared stimulated luminescence (IRSL) analysis, and thermoluminescence (TL) measurements were made on approximately 10-mg aliquots of the quartz grains evenly spread in stainless steel planchettes. IRSL measurements were made on a Daybreak stand-alone system with BG39 and Corning 7-59 detection filters. TL measurements were made on an unfiltered Toledo 654

Table 1. Luminescence dates for Rose Cottage Cave based on an assumption of constant dose rate in the deposit through time (10% errors are associated with the luminescence dates).

Sample	Size (μm)	Technique	Mineral	Natural dose (Gy)	Dose rate (μGy/a)	Age	Calibrated ^{14}C age [6,7]
RCC4	100	IRSL	K-Feldspar	29.52	2491	11 900	10 500
	100	TL	Quartz	25.70	2140	12 000	
RCC10	100	IRSL	K-Feldspar	45.25	2826	16 000	14 900
	200	TL	Quartz	40.17	2294	17 500	
RCC9	100	IRSL	K-Feldspar	57.43	3080	18 600	*c.* 28 500
	200	TL	Quartz	47.59	2531	18 800	

reader. The accumulated dose was determined by the single aliquot regeneration technique for IRSL[5] and multiple aliquot regeneration technique for TL samples. Samples were bleached in bright sunlight for a minimum of 8 h in the case of IRSL analyses, and for 32 h for TL analyses. Laboratory irradiation was done with a calibrated $^{90}Sr/^{90}Y$ beta source with a dose rate of 1.46 Gy min^{-1}.

The *in situ* dose rate was calculated from the uranium, thorium and potassium concentration in subsamples of the bulk sediment prior to pre-treatment. The K was measured by X-ray fluorescence, and the U and Th concentrations were determined by thick source alpha counting. Cosmic radiation was estimated on the basis of the thickness of the sediment and the overhanging rock that forms the cave. Any error in this estimation is negligible in comparison with the dose contribution from the U, Th and K in the sediment. Periodic inundation of the sediment as a result of spring action during historic times suggests that any measurements of moisture content would be inappropriate and an estimated WF value (degree of water saturation = saturation water weight/dry weight) of 13.5 ± 5% was used in the calculation of the average dose rate.

Results

A summary of the initial set of dates that was obtained is presented in Table 1. For RCC4 and RCC9 the IRSL and TL dates agree very well for the100 μm and 200 μm feldspar and quartz grains. The RCC10 TL date is slightly older than the IRSL date. This discrepancy could be expected if there had been inadequate zeroing of the TL signal at the time of deposition due to its much slower bleaching rate. Using the same argument, the agreement in ages for samples RCC4 and RCC9 suggests that these sediments were adequately zeroed.

The luminescence dates do not agree very well, however, with the calibrated[6,7] radiocarbon dates. The RCC4 and RCC10 luminescence dates (both TL and IRSL) slightly overestimate the age, and the RCC9 dates are substantial underestimates. Insufficient zeroing may account for the overestimation of the RCC10 dates, and the RCC4 dates are statistically equivalent when both the 10% errors on the luminescence dates and the errors on the radiocarbon dates are considered. However, the RCC9 disparity is too big and needs to be explained. Anomalous fading or thermal fading of the luminescence signal may produce such an age underestimation. Since anomalous fading has not been reported in quartz,[8] the correspondence between TL and IRSL dates suggests that it has not occurred in the feldspars. Furthermore, the mineralogy is similar throughout the deposit and an age underestimation for RCC4 and RCC10 would also have been expected had anomalous fading occurred. It is also improbable that thermal fading has occurred, since it is highly unlikely that it would proceed at the same rate in both quartz and feldspar.

An alternative source of the error in the RCC9 dates could be found if there had been mobility of the radionuclides that provide the radiation. The ages given in Table 1 are based on the assumption that the measured amounts of K, U and Th have remained constant through time. Since the RCC9 luminescence date is an underestimation of the true age, it is possible that the measured modern dose rate is higher than the average dose rate through time and an increase in the dose rate must have occurred.

Since some of the strata at Rose Cottage Cave were introduced by spring action,[9] periodic fluctuations in the water content and perhaps the water table in the deposit will have occurred in the past. Besides attenuating the ambient radiation, the water could mobilise radioactive elements that are present in the form of soluble salts. Uranium is soluble and any movement of this element would lead to disequilibrium between it and its radioactive decay products. Potassium is also mobilised in water, and the portion that is not bound within the feldspar grains could also migrate.[10] To account for dose rate build-up in the sediment, a model of short-term leaching of radioactive elements from the surface layers balanced by accumulation in the lower levels over the long term is possible. In the case of both uranium and potassium, the contribution to the dose rate is thus made up of a component that is potentially mobile, and a component that is fixed within mineral grains. A change in the mobile component may account for the underestimation of the luminescence dates.

In order to determine whether there was a mobile component, sediment sub-samples were washed with water for 24 h and then with 1N HCl for 24 h, to provide an extreme simulation of the effect of water percolation in the deposit over time. The effect of the leaching process on the radioactive trace elements in the sediment is presented in Table 2. The U and K remaining in the leached sediment was assumed to be the 'fixed' fraction of these elements. The difference between the raw concentrations and the leached values was attributed to the 'mobile' uranium and potassium.

The dose rate for each sample was then recalculated using the leached values. This represents a scenario of 'late uptake' of U and K, and the corresponding date is the maximum possible date. The dose rate and age were also calculated for a third model, namely, for 'linear uptake' of the 'mobile' fraction. The results are presented in Table 3. Note that the linear model is not the average of the dose rates obtained for the early and late uptake models, but is more complex in that U mobility necessarily implies disequilibrium with the U daughter products. As a first order

Table 2. Concentration of radioactive elements in Rose Cottage Cave sediments before and after leaching with 1N HCl.

	Raw concentration			Leached concentration		
	U (ppm)	Th (ppm)	K (%)	U (ppm)	Th (ppm)	K (%)
RCC4	2.19	3.86	1.37	1.21	3.86	1.09
RCC10	3.77	2.72	1.38	0.85	2.72	1.12
RCC9	3.75	3.92	1.56	1.23	3.92	1.27

Table 3. Luminescence dates for Rose Cottage Cave modelled on early, linear and late uptake of the 'mobile fraction' of the dose rate through time.

		Model dose rate			Model date		
Sample	Technique	Early	Linear	Late	Early	Linear	Late
RCC4	IRSL	2491	2198	1991	11 900	13 400	14 800
	TL	2140	1489	1644	12 000	13 900	15 600
RCC10	IRSL	2826	2325	1841	16 000	19 500	24 600
	TL	2294	1694	1406	17 500	23 700	28 600
RCC9	IRSL	3080	2513	2170	18 600	22 900	26 500
	TL	2531	1988	1707	18 800	23 900	27 900

approximation the linear uptake dose rate was calculated assuming negligible growth of ^{230}Th and its daughter products since the mobilisation of the U. The dose rate is then made up of the fixed component and half the alpha and beta radiation contribution from ^{238}U and ^{234}U.

Because of the relatively high 'fixed' internal K component in the feldspar dose rate and the absence of internal K in the quartz dose rate, the leaching of the sediments had different effects on the TL and IRSL results. The linear uptake dates for each sample are still very similar. In the case of RCC4 and RCC10 the linear uptake model produces dates that are too old when compared with the calibrated ^{14}C ages in Table 1. This suggests that there has been little or no mobilisation of radionuclides in these levels. In the case of RCC9, a linear uptake model is insufficient to account for the disparity with the radiocarbon date. This may reflect differences between the laboratory conditions of leaching and those that may have occurred in the cave, and a model of late uptake appears to be more appropriate. An additional effect that may also contribute to the age error is sediment compaction, which would also contribute towards an increase in the dose rate through time. The possibility that this process has happened is partly supported by the dip of the levels away from the cave walls, particularly in the deeper strata in the cave. The extent to which this will have increased the dose rate is difficult to assess. Altogether the progressive processes of water percolation through the sediment in conjunction with profile compaction may have produced a dose rate build-up that is sufficient to account for the large offset in the initial luminescence dating analysis of RCC9.

Conclusion

In the application of luminescence, and other dating techniques that measure accumulated radiation dose, the prerequisite that the dose rate has remained constant through time is not necessarily met. At Rose Cottage Cave the apparent TL and IRSL dates disagree with the corresponding ^{14}C dates, with the deepest sample showing the largest discrepancy. This cannot be dismissed as thermal or anomalous fading, and it is concluded on the basis of leaching experiments that the assumption of invariable dose rate is likely to be invalid. A model for changing radiation flux as a result of water percolation through the deposit is proposed. Measurements of the effect of water on the U and K in the sediment indicate that this mechanism can produce sufficient change of the dose rate to account for the age discrepancy. The effects of sediment compaction may exacerbate these effects.

Luminescence dating has a vital role to play in establishing an absolute chronology for the MSA. However, application of the technique is subject to suitable circumstances at the site. At Rose Cottage Cave the dose rate appears to have fluctuated through time. Although this does not exclude the possibility of dating the site by this technique, it does mean that caution must be exercised in obtaining and evaluating the results. Current research is aimed at refining the model of dose rate build-up so that it can be used to date other samples from the MSA at Rose Cottage Cave, notably those from the Howiesons Poort layers. Unfortunately, the use of a dose rate model compromises the precision that can be obtained by luminescence dating. Nevertheless, the problems encountered in obtaining these results serve as a warning to users of dates based on radiation dose accumulation. The critical evaluation that has been made of the Rose Cottage Cave luminescence dates should extend to dates obtained at other sites at which it is not possible to check the results against an independent dating method, especially at sites where water flux through the deposit is high.

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