10.1.8 Luminescence Results – Sediments for OSL Dating by Carl P. Lipo and Sachiko Sakai

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Re: Luminescence Results – Sediments for OSL dating

In 2011, nine soil samples were submitted for luminescence dating to the staff of the Institute for Integrated Research in Materials, Environments, and Society (IIRMES) Lab at California State University Long Beach. Using the lab's Risø TL/OSL Reader with blue-light (BOSL) and infrared (IROSL) stimulation and a procedure that consists of a coarse-grained, quartz single-aliquot regeneration sequence (SAR) protocol with an IR "wash" to eliminate luminescence signals from feldspar, we analyzed each sample and calculated ages for the event in which the materials were last exposed to light (i.e., bleached). Our methods and results for the analyses are described in this brief report.

BACKGROUND: LUMINESCENCE DATING

Luminescence dating is based on the premise that charged particles generated from environmental radiation (through radioactive decay and the release of alpha, beta and gamma particles) accumulate over time in flaws in the structure of crystalline materials. When sufficient energy is applied, these stored particles are released in the form of light (Feathers 2003: 1493). The amount of light released is a function of time and energy exposure. If the amount of light released is measured, the rate of luminescence accumulation is determined, and the amount of radiation present in the environment of deposition estimate, an age can be thus calculated that is the amount of time passed since the last point of heating or exposure to energy. Quartz and feldspar are common crystalline materials present in ceramics and sediments with properties that result in stable and well-known accumulation of luminescence over time. In this analysis, we chose to use coarse grained quartz, since there seems to be a

fairly large amount of quartz in these samples. Coarse grained quartz analysis has several benefits over the fine grained mix mineral analysis. Quartz has little internal sources of radiation, so the interiors of grains of this size will not be subject to alpha radiation which need not be considered in the calculations. The grains are small enough to limit beta attenuation. Most importantly, coarse grained quartz analysis can avoid potential fading associated to feldspar which could make dates younger. In this analysis, we chose to focus on 90-125 micron coarse grained quartz grains since we believed that this grain size would have the best chance of being bleached (exposed to light and "zeroed") during an event of interest. In the case of the sediment samples, we expect the grains to have been exposed to light during transport and before being covered by further deposits.

The soil samples were taken by pounding a 2 in x 8 in black PVC pipe. An end cap was taped in place the procedure took place under a light proof tart. The samples we analyzed for our analysis were extracted from the middle of the tube submitted. We then used a mortar and pestle to disaggregate the mineral grains.

All sample preparation was conducted in a dark room illuminated with minimal filtered light (Gel 106 Primary Red filter). A small portion of each sample was used for dosimetry analyses. All of the extracted material was treated with HCl to remove carbonates and H_2O_2 to remove organic material. After chemical treatment, we employed a sieve to extract grains that were 90 < 125 micron materials. After grain size separations, quartz particles are extracted using heavy liquid method. Quartz and feldspar are removed by floating the fraction in a dense liquid, sodium polytungstate with densities of 2.68 g/cm3. Quartz particles are extracted from this light fraction by using sodium polytungstate with densities of 2.58 g/cm3. In case of analyzing quartz, which is applied in this study, etching the surface of the quartz using hydrofluoric acid (HF) is necessary. This is done to eliminate the portion of the grain that has been given a signal due to alpha particles. Etching removes the surface of the grains (alpha particles only travel through 30-50 microns). Quartz grains are placed on several disks.

When measuring optically stimulated luminescence one stimulates samples with light, usually a particular wavelength that is known to release luminescence from the material. The amount of light released is then measured with a photomultiplier tube. The release of energy simulates a "zeroing" event that empties crystals of charged particles that accumulated since the paleo-"zeroing event" such as one that would occur during exposure of crystals to the sun. Once the accumulated paleo-signal is measured, subsequent measures are made by exposing the material to calibrated amounts of radiation to determine the rate at which luminescence signals are generated in the sample.

In addition to measurements of the paleodose and the rate at which luminescence accumulates in the sample, one must also have a good estimate of the amount of radiation that was in the environment that would have provided the particles (via alpha, beta and gamma radiation) that would be the source energy for the accumulated the luminescence signal. The annual dose rate of radiation is determined by measuring radioactivity (in uranium, thorium and potassium) in the sample and in the surrounding sediments. We also estimate the

contribution of gamma via cosmic rays based on an estimated the latitude and longitude of the sample for its deposition. Using this information – the amount of the archaeologically accumulated luminescence signal, the sensitivity of a sample to radiation, and the annual dose rate of radiation – a direct date (from the time of the previous zeroing event) can be calculated for the samples.

METHODS

Samples were prepared according to standard procedures modified from Aitken (1985) and Banerjee et al. (2001) and adopted from the University of Washington Luminescence Dating Laboratory under the direction of Dr. James Feathers. The submitted sample were processed and analyzed using a coarse grained quartz protocol utilizing grains at 90-125 µ in size (see Table 1).

Table 1: Coarse Grain Sample Preparation Protocol

Step	*Procedure*
1	Calculate percent water absorption
2	Crush sample and disaggregate sample in shaker mill/mortar and pestle.
3	Treat samples with HCL and H202 to remove carbonates and organics.
4	Grain size separation using sieve (90-125 µ).
5	Mineral separation using sodium polytungstate.
6	Etching quartz surface by HF.
7	Place quartz particle on the disks.

We made luminescence measurements using an automated Risø TL/OS 12B/C reader that incorporates calibrated beta (^{90}Sr) radioactive sources for evaluating the rate of luminescence signal accumulation. For the samples, we employed blue-light OSL (BOSL) stimulation with single aliquot regenerative dose (SAR) protocol outlined by Feathers (2003; Murray and Wintle 2000). Blue light LED on the Risø TL/OS 12B/C stimulates samples in the 400-550 nm range (centered at 470 ± 30 nm). A U-340 filter is used eliminate spillover from stimulation light. A double-IR wash was employed to help eliminate contribution by any feldspar contaminants (Banerjee et al. 2001), although we do not expected much of this due to extraction of quartz for the analysis. For this step, the samples were stimulated using infrared diodes in the 800-900 nm transmission range. Table 2 below outlines the BOSL protocol stimulation sequence used to measure the samples. Five to eight aliquots were measured on each sample generally.

We made measurements for accumulated (paleo) luminescence signal as part of the stimulation sequence. The rate at which radiation creates luminescence signals was measured through a series of incremental beta irradiations. The response curve based on these artificial doses is used to determine the amount of radiation that must have been present to generate the paleoluminescence signal.

Table 2: OSL/SAR Sequence (BOSL)	
Step	*Procedure*
1	Preheat sample to 240 C for 10 seconds
2	Give dose, D1, for 5 s
3	Preheat sample to 240 C for 10 s
4	Stimulation with infrared light at 125 C for 50 s
5	Stimulation with infrared light at 200 C for 50 s
6	Stimulation with blue light at 125 C for 100 s
7	Measure OSL (natural signal)
8	Give test dose, Dt, for 15 s
9	Heat reduced to 160 C for 5 s
10	Stimulation with infrared light at 125 C for 50 s
11	Stimulation with infrared light at 200 C for 50 s
12	Stimulation with blue light at 125 C for 100 s
13	Measure OSL (regenerated signal)
14	Repeat steps 2-13

Using the facilities at IIRMES, CSULB, dosimetric measurements were made to determine the amount of radioactivity that is present in the sample and in the local environment. Measurement of the annual radiation dose rate is calculated from the amount of these elements in surrounding sediments as well as estimates of cosmic rays at the location of the deposition. For analysis of Th and U, we utilized GBC OptiMass 8000 ICP Time of Flight Mass Spectrometer attached to a New Wave Research UP-213 Laser Ablation system (LA-TOF-ICP-MS). Samples from the sediment samples were ball-milled to ~5 µm and thoroughly mixed with 40 ppm indium internal standard and briquetting additive before being pressed into pellets using a 15-ton geological sample press. The resulting pellet was analyzed for more than 45 elements including U and Th concentrations using laser ablation ICP-MS. Replicates of 5-second acquisitions were averaged and the standard error of each analysis was reported with the sample averages. All intensity counts were normalized to the internal standard and calibration curves for each element were generated using external calibration standards (Table 3).

Table 3: Laser and sample gas settings, ICP-MS sampling parameters

Sample Pre-Ablation:
Single pass, 100 µm/second scan speed, 5 µm sampling depth, 60% laser power, 20 Hz laser repetition rate, 200 µm spot size

Sample Ablation:
Single pass, 30 µm/second scan speed, 5 µm sampling depth, 100% laser power, 20 Hz laser repetition rate, 100 µm spot size

Sample flow:
1.2 liters per minute Argon through sample chamber into ICP-MS

ICP-MS method properties:
5 second sample introduction delay, 5 second acquisition, 4 replicates

ICP-MS external calibration standards:
NIST SRM 612 and NIST SRM 612 glass reference materials, and NIST SRM 679 brick clay at 20% and 40% dilution in briquetting additive
the previously accumulated dose.

In order to obtain the concentration of K, the same pellets used in the ICP analyses were also measured using a Bruker portable X-Ray Fluorescence (XRF). The pellets were measured by XRF using Ti filter with current setting 25 micro amp and voltage 15 kV utilizing vacuum for 5 minutes to analyze low energy elements including K. All raw counts were calculated into the concentrations by the calibration curves based on eleven ceramic samples with known concentration by INAA and ICP-MS (Table 4 and Table 5). These data was used to calculate the years since the last zeroing event. Additionally, the elemental data from the dosimetry of the samples provides information useful for sourcing and compositional studies.

Table 4: XRF settings
For low energy elements (Mg, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe)
Voltage: 15 kV
Current: 26 micro amp
With vacuum
Time: 5 minutes

XRF calibration standards:
eleven ceramic samples with INAA and LA-ICP-MS known values.

Table 5. Dosimetry Results (all measures in ppm)

Sample ID	U-238 (ICP-MS)	Th-236(ICP-MS)	K-39 (XRF)
Sample 1 (LB901)	0.88	3.29	9091.44
Sample 1 (LB901) background sediment	0.79	6.12	8513.1
Sample 2 (LB902)	0.31	2.01	6812.98
Sample 2 (LB902) background sediment	0.35	2.31	8726.08
Sample 3 (LB903)	0.28	5.02	8084.67
Sample 3 (LB903) background sediment	0.24	3.18	9144.5

Sample 4 (LB904)	1.02	5.63	10249.33
Sample 4 (LB904) background sediment	0.59	5.71	8090.39
Sample 5 (LB905)	0.47	20.92	8037.28
Sample 5 (LB905) background sediment	0.28	4.35	7911.37
Sample 6 (LB906)	0.35	2.39	7797.76
Sample 6 (LB906) background sediment	0.60	2.72	8938.09
Sample 7 (LB907)	0.56	4.27	8266.48
Sample 7 (LB907) background sediment	0.99	7.43	9696.65
Sample 8 (LB908)	053	3.49	8436.31
Sample 8 (LB908) background sediment	0.69	3.16	8434.31
Sample 9 (LB909)	1.30	4.75	8618.97
Sample 9 (LB909) background sediment	1.27	6.47	10277.10

DISCUSSION OF RESULTS

All dates presented are based on the coarse grain quartz using Blue LED light source and Hoya U-340 filter. Overall, the luminescence signals stimulated by blue-light LED (BOSL) for the aliquots were very strong. Once the accumulated paleo-signal is measured, subsequent measures are made by exposing the material to calibrated amounts of radiation to determine the rate at which luminescence signals are generated in the sample. To obtain equivalent dose, several different curve fittings are examined. In some case, especially, for the relatively smaller dose, the equivalent dose will not change much based on the different curve fitting. However, in the case of this study, the different curve generate slightly different equivalent dose (Figure 1 and 2).

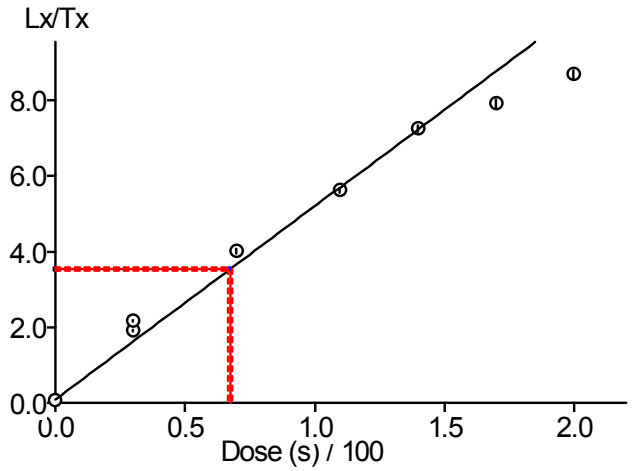


Figure 1. The *linear curve fitting* to generate equivalent dose of Sample 6 (LB0906) #5 aliquot
Y=a+bx, equivalent dose (s) 67.34 +/-0.85, average error in fit= 0.2466

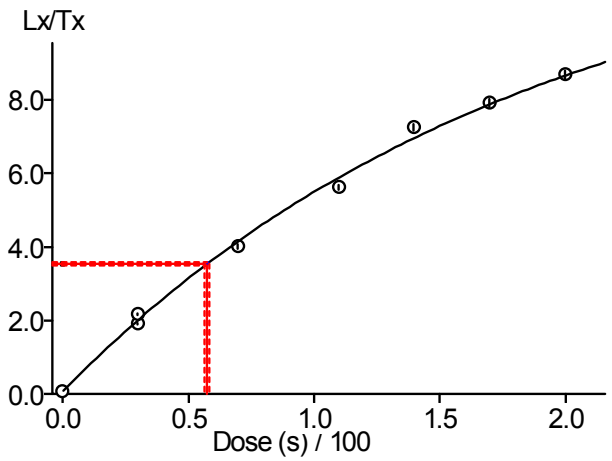


Figure 2. The *exponential curve fitting* to generate equivalent dose of Sample 6 (LB0906) #5 aliquot
Y=a [1-exp[-(x+c)/b, equivalent dose (s) 57.37 +/- 0.84, average error in fit= 0.057
This is the **best curve fitting**. This curve fitting generates the **latest dates** in this particular aliquot.

As seen above, the linear curve fitting generates equivalent dose (s) 67.34 +/- 0.85 in this particular aliquot, Sample 6 #5 (Figure 1). The different curve fitting such as the linear curve or cubic fitting generates equivalent dose on the same aliquot differently. The dating sediments represent the history of accumulation of sediment. Thus, the possible youngest date was also examined based on different curve fittings. In this particular case of Sample 6 #5

aliquot, the exponential fitting generate the smallest equivalent dose (s) 57.37 +/- 0.84 which make the youngest date (Figure 2). The average error in fit is 0.057, which is the smallest error in all curve fittings, thus, it is the best curve fitting. It is noted that in most aliquots in this study, the best fit curve generates the latest date. Therefore, the best fit curve fitting was applied in this study. Using the dosimetric information in Table 5 and the measured paleodose values (equivalent dose in Gy), we were able to calculate age values for each of the samples (Table 6).

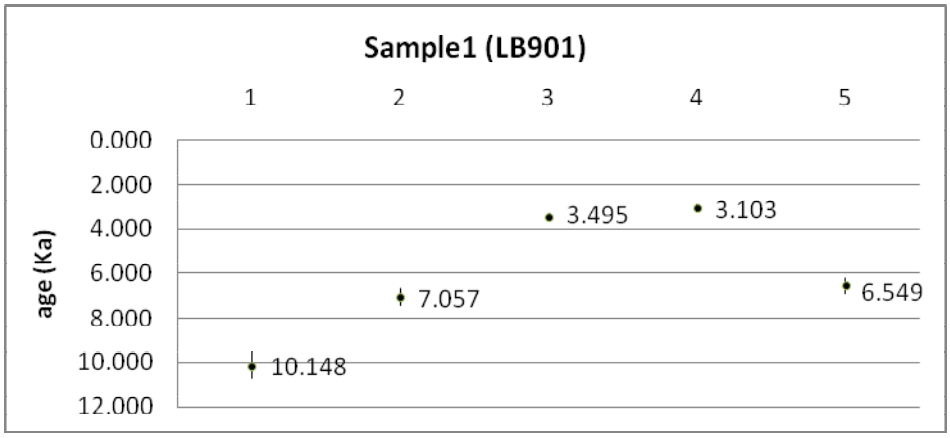
Table 6 . Luminescence measurements equivalent dose is based on best fitting curve which generates the youngest date.

Sample ID	lab ID	Mineral	Sample Prep	Equivalent Dose (Gy)	Error (+/-)	Age (Ka)	error (Ka)	BC/AD	Date	Error
sample 1	LB0901	quartz	Coarse grain	17.30	0.44	10.148	0.573	BC	8136	573
sample 1	LB0901	quartz	Coarse grain	12.03	0.25	7.057	0.386	BC	5045	386
sample 1	LB0901	quartz	Coarse grain	5.96	0.09	3.495	0.185	BC	1483	185
sample 1	LB0901	quartz	Coarse grain	5.29	0.07	3.103	0.162	BC	1091	162
sample 1	LB0901	quartz	Coarse grain	11.16	0.23	6.549	0.357	BC	4537	357
sample 2	LB0902	quartz	Coarse grain	11.31	0.39	9.828	0.612	BC	7816	612
sample 2	LB0902	quartz	Coarse grain	7.94	0.16	6.899	0.384	BC	4887	384
sample 2	LB0902	quartz	Coarse grain	12.64	0.21	10.988	0.600	BC	8976	600
sample 2	LB0902	quartz	Coarse grain	16.52	0.44	14.361	0.839	BC	12349	839
sample 2	LB0902	quartz	Coarse grain	11.29	0.41	9.809	0.621	BC	7797	621
sample 3	LB0903	quartz	Coarse grain	10.33	0.14	6.248	0.421	BC	4236	421
sample 3	LB0903	quartz	Coarse grain	6.95	0.08	4.203	0.282	BC	2191	282
sample 3	LB0903	quartz	Coarse grain	9.91	0.17	5.995	0.409	BC	3983	409
sample 3	LB0903	quartz	Coarse grain	8.68	0.16	5.250	0.359	BC	3238	359
sample 3	LB0903	quartz	Coarse grain	9.43	0.16	5.705	0.388	BC	3693	388
sample 4	LB0904	quartz	Coarse grain	6.41	0.07	2.692	0.181	BC	680	181
sample 4	LB0904	quartz	Coarse grain	7.53	0.11	3.166	0.215	BC	1154	215
sample 4	LB0904	quartz	Coarse grain	8.03	0.13	3.376	0.230	BC	1364	230
sample 4	LB0904	quartz	Coarse grain	11.06	0.23	4.648	0.323	BC	2636	323
sample 4	LB0904	quartz	Coarse grain	6.60	0.19	2.775	0.200	BC	763	200
sample 4	LB0904	quartz	Coarse grain	4.98	0.09	2.091	0.144	BC	79	144
sample 5	LB0905	quartz	Coarse grain	7.57	0.07	2.674	0.347	BC	662	347
sample 5	LB0905	quartz	Coarse grain	5.60	0.07	1.978	0.258	AD	34	258
sample 5	LB0905	quartz	Coarse grain	6.97	0.10	2.461	0.321	BC	449	321

sample 5	LB0905	quartz	Coarse grain	7.77	0.08	2.744	0.357	BC	732	357
sample 5	LB0905	quartz	Coarse grain	5.78	0.07	2.041	0.266	BC	29	266
sample 5	LB0905	quartz	Coarse grain	8.52	0.10	3.009	0.392	BC	997	392
sample 6	LB0906	quartz	Coarse grain	7.99	0.07	5.225	0.275	BC	3213	275
sample 6	LB0906	quartz	Coarse grain	7.67	0.09	5.013	0.267	BC	3001	267
sample 6	LB0906	quartz	Coarse grain	7.52	0.08	4.918	0.261	BC	2906	261
sample 6	LB0906	quartz	Coarse grain	7.06	0.13	4.618	0.253	BC	2606	253
sample 6	LB0906	quartz	Coarse grain	6.00	0.08	3.922	0.210	BC	1910	210
sample 6	LB0906	quartz	Coarse grain	7.17	0.09	4.686	0.250	BC	2674	250
sample 7	LB0907	quartz	Coarse grain	8.82	0.16	5.179	0.274	BC	3167	274
sample 7	LB0907	quartz	Coarse grain	9.58	0.11	5.627	0.288	BC	3615	288
sample 7	LB0907	quartz	Coarse grain	8.75	0.19	5.142	0.279	BC	3130	279
sample 7	LB0907	quartz	Coarse grain	7.97	0.14	4.683	0.246	BC	2671	246
sample 7	LB0907	quartz	Coarse grain	8.65	0.27	5.081	0.299	BC	3069	299
sample 8	LB0908	quartz	Coarse grain	7.16	0.14	4.946	0.279	BC	2934	279
sample 8	LB0908	quartz	Coarse grain	9.15	0.19	6.323	0.361	BC	4311	361
sample 8	LB0908	quartz	Coarse grain	7.89	0.10	5.451	0.299	BC	3439	299
sample 8	LB0908	quartz	Coarse grain	6.89	0.14	4.759	0.270	BC	2747	270
sample 8	LB0908	quartz	Coarse grain	6.73	0.10	4.651	0.258	BC	2639	258
sample 9	LB0909	quartz	Coarse grain	18.98	0.35	9.811	0.577	BC	7799	577
sample 9	LB0909	quartz	Coarse grain	16.62	0.37	8.592	0.515	BC	6580	515
sample 9	LB0909	quartz	Coarse grain	15.87	0.27	8.204	0.479	BC	6192	479
sample 9	LB0909	quartz	Coarse grain	10.53	0.22	5.442	0.324	BC	3430	324
sample 9	LB0909	quartz	Coarse grain	13.13	0.13	6.790	0.384	BC	4778	384
sample 9	LB0909	quartz	Coarse grain	14.73	0.25	7.616	0.444	BC	5604	444

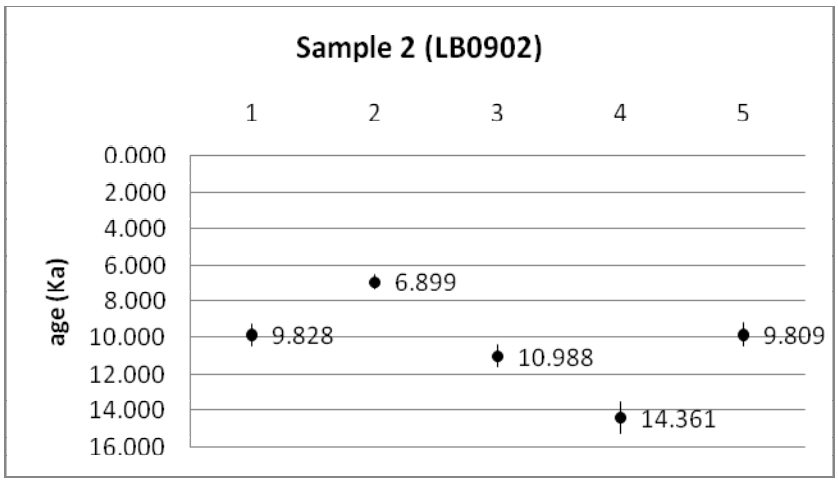
- Sample 1 (LB0901)
  Five coarse grain aliquots were analyzed. OSL signals are very strong. The latest date is 3103 +/- 162 years ago (1091 B.C. +/-162) and the earliest date is 10148 +/- 537 years ago (8136 B.C. +/-573).

Figure 3. Distribution of dates -- Sample 1: LB0901



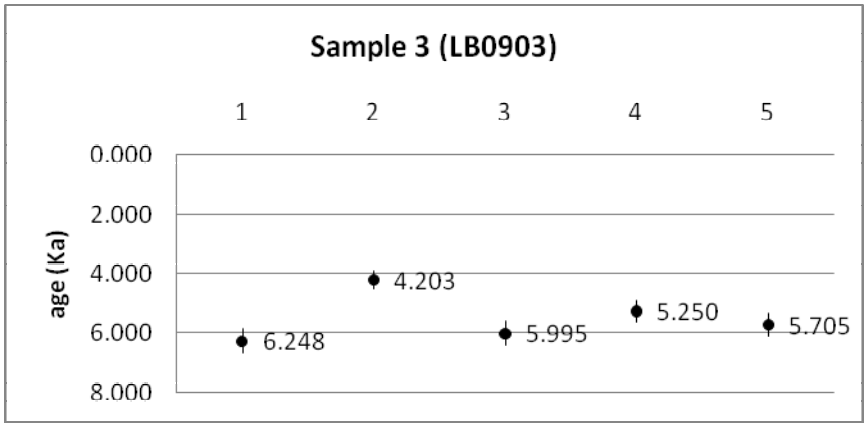
- Sample2 (LB0902)
  Five aliquots were analyzed. OSL signals are very strong. The earliest date is 14361 +/- 839 years ago (12349 B.C. +/- 839)and the latest data is 6899 +/- 384 years ago (4887 B.C.+/-384).

Figure 4. Distribution of dates -- Sample 2: LB0902



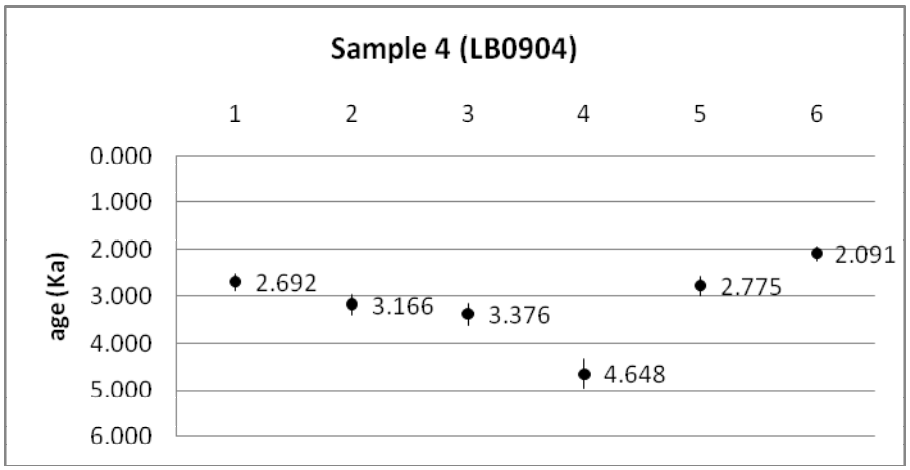
- Sample 3 (LB0903)
  Six aliquots were analyzed but one of them is outlier then excluded. OSL signals are very strong. The earliest date is 6242 +/- 421 years ago (4236 B.C. +/- 421) and the latest data is 4203 +/- 282 years ago (2191 B.C. +/- 282).

Figure 5. Distribution of dates -- Sample 3: LB0903



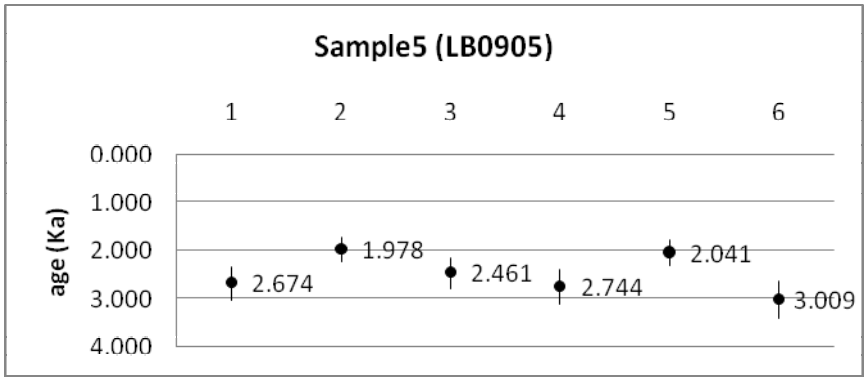
- Sample 4 (LB0904)
  Six aliquots were analyzed. OSL signals are very strong. The earliest date is 4648 +/- 323 years ago (2636 B.C. +/- 323) and the latest data is 2091 +/- 144 years ago (79 B.C. +/- 144).

Figure 6. Distribution of dates -- Sample 4: LB0904



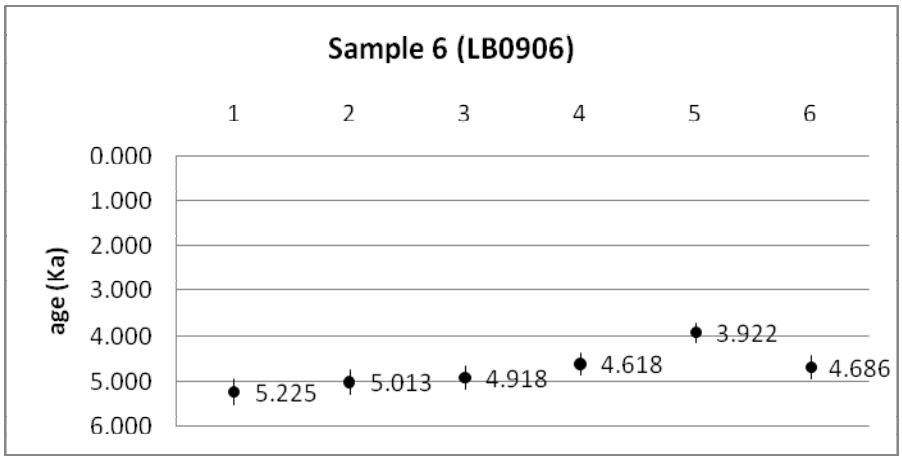
- Sample 5 (LB0905)
  Six aliquots were analyzed. OSL signals are very strong and the range of the dates is relatively small. The earliest date is 3009+/- 392 years ago (997 B.C. +/-392) and the latest data is 1978 +/- 258 years ago (A.D. 34 +/- 258).

Figure 7. Distribution of dates -- Sample 5: LB0905



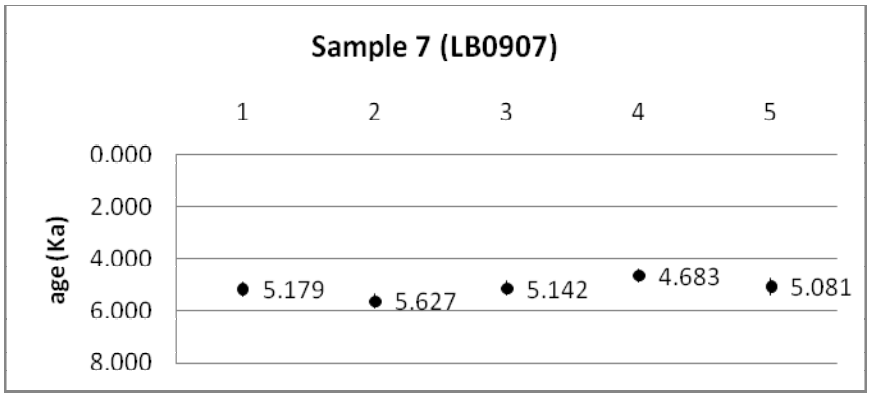
- Sample 6 (LB0906)
  Six aliquots were analyzed. OSL signals are very strong and the range of the dates is relatively small. The earliest date is 5225 +/- 275 years ago (3213 B.C. +/- 275) and the latest data is 3922 +/- 210 years ago (1910 B.C. +/- 210).

Figure 8. Distribution of dates -- Sample 6: LB0906



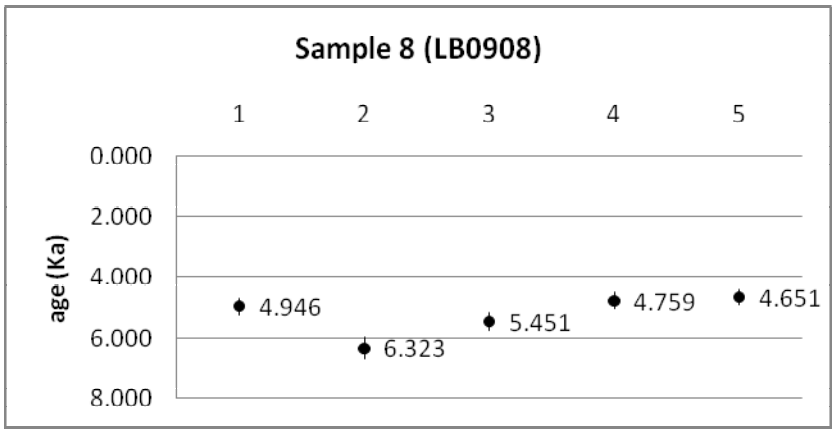
- Sample 7 (LB0907)
  Six aliquots were analyzed. OSL signals are very strong but one of them is outlier then excluded. The earliest date is 5627 +/- 288 years ago (3615 B.C. +/- 288) and the latest data is 4683 +/- 246 years ago (2671 B.C. +/- 246).

Figure 9. Distribution of dates -- Sample 7: LB0907



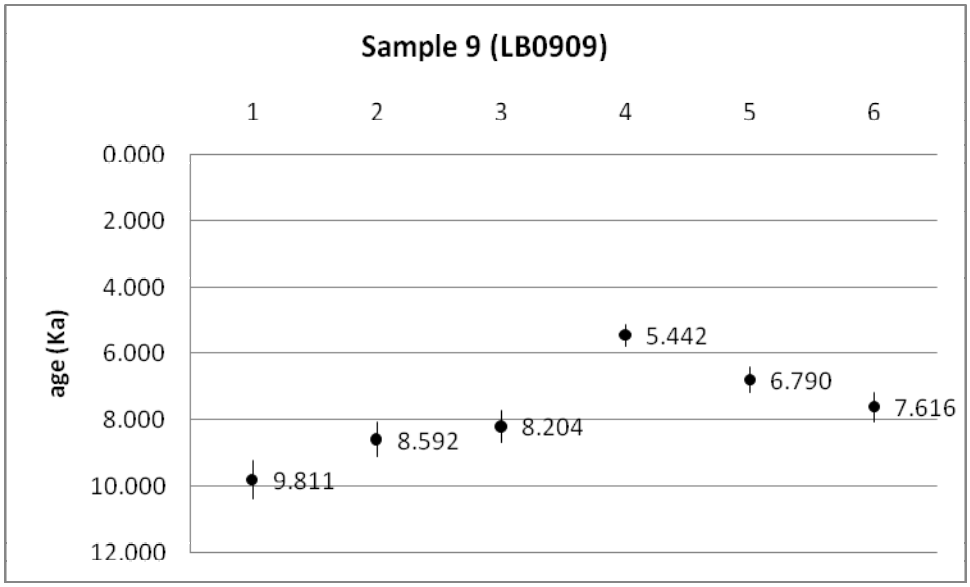
- Sample 8 (LB0908)
  Six aliquots were analyzed. OSL signals are very strong but one of them is outlier then excluded. The earliest date is 6323 +/- 361 years ago (4311 B.C. +/- 361) and the latest data is 4651 +/- 258 years ago (2639 B.C. +/- 258).

Figure 10. Distribution of dates -- Sample 8: LB0908



- Sample 9 (LB0909)
  Six aliquots were analyzed. OSL signals are very strong. The earliest date is 9811 +/- 577 years ago (7799 B.C. +/- 577) and the latest data is 5442 +/- 324 years ago (3430 B.C. +/- 324).

Figure 11. Distribution of dates -- Sample 9: LB0909



CONCLUSIONS

Overall, these results and interpretations provide our current best estimate of the age of the last zeroing events for the submitted samples. The results are based on the material we analyzed and the current laboratory procedures.

We hope these results are suitable for your study and are in alignment with your expectations. If you have any questions, need additional information or wish to discuss the results please feel free to contact us at (562) 985- 2393 or email us at clipo@csulb.edu (Carl Lipo) or sachikosak@gmail.com (Sachiko Sakai).

Sincerely,

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