Thermoluminescent dating of burned flint tools

Yeter Göksu

Introduction

Dating of burned flint like dating bones or teeth has the advantages of dealing directly with archaeological material. But unlike organic materials, the flints additionaly have the advantage of being imperishable. Age determination of burned flints by thermoluminescence (TL) provides a feasible and potentially inexpensive means to date archaeological materials older than the limits of radiocarbon and younger than the mininum range of Potasium-Argon methods.

Age determination of pottery which has been used with succes for a long time AITKEN et. al (1967), MEJDAHL (1968) measures the date of fiering of the pottery. Similarly, dating of burned flints by TL gives the date of last pyrolization. But unlike pottery it was found that to date powdered samples were impossible to date for two main reasons. One, thermoluminescence produced due to the grinding of samples, which is known as tribo-thermoluminescence; and two, regeneration thermoluminescence produced in the absence of radioactivity even in the dark which seems to be accelated by the presance of moisture, GÖKSU, FREMLIN (1972).

It was found that is was not possible to reduce tribo-TL regeneration TL by simple methods. Etching the outher surface of the grains with HF, or chrushing them under liquid nitrogen introduced undesirable TL such as chemi-TL and regeneration TL. It was found that the most convennient way of reducing tribo-TL and eliminating the regenerating-TL was to use thin slices of flint which were cut with diamond wheel. These were then ground to 350 micron thickness and polished.

Measurement of the internal radioactive content of the flint and measurement of enviromental activity makes possible the absolute determination of the date of pyrolization of the flint tools with an accuracy of 15%.

Principle of the method

To understand the thermoluminescence dating of flintstone, the composition of materials in the flint must be considered. Flint is a sedimentary rock and consists of mainly cryptocrystalline silica. Like all the other rocks flint also cantains minute amouts of radioactivity. Typically 0.1 ppm U, 0.3 ppm Th, and 0.7% K. Burial soil also contains these radioactive elements. Each of these radioactive elements releases minute amount of nuclear energy and some of this energy is stored by the crystals inside the flint. The defects inside the crystal are responsible for storing this energy. These defects, although present in only small numbers, have a

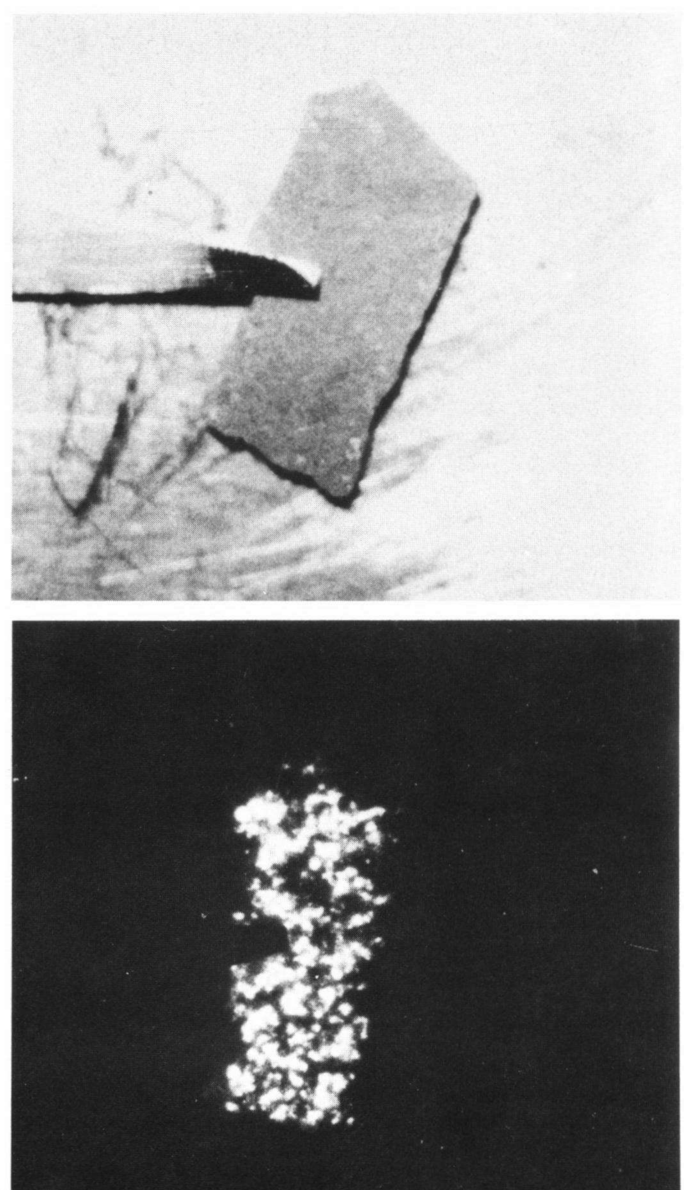


Photo 1. Thin section of flint and the Termoluminescence glow seen in the dark

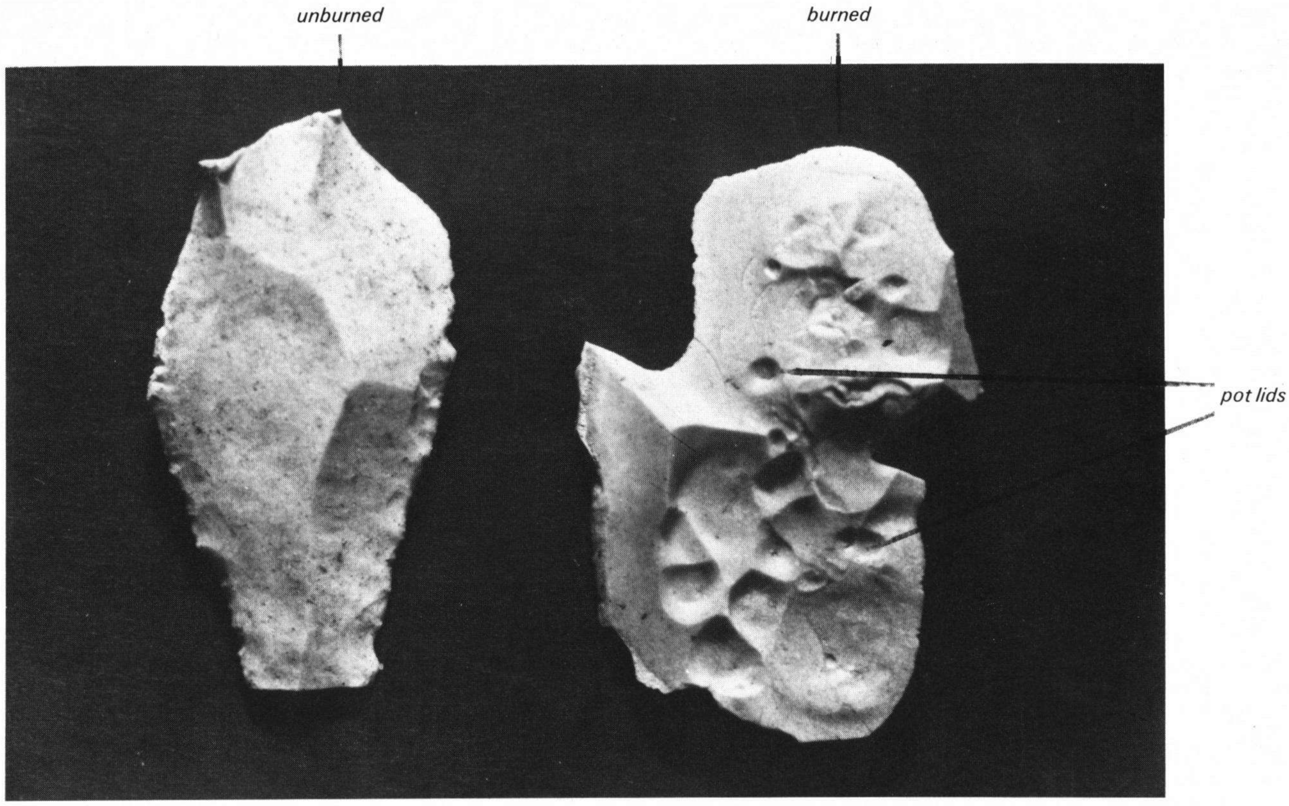


Photo 2. Pot lids on burned flints.

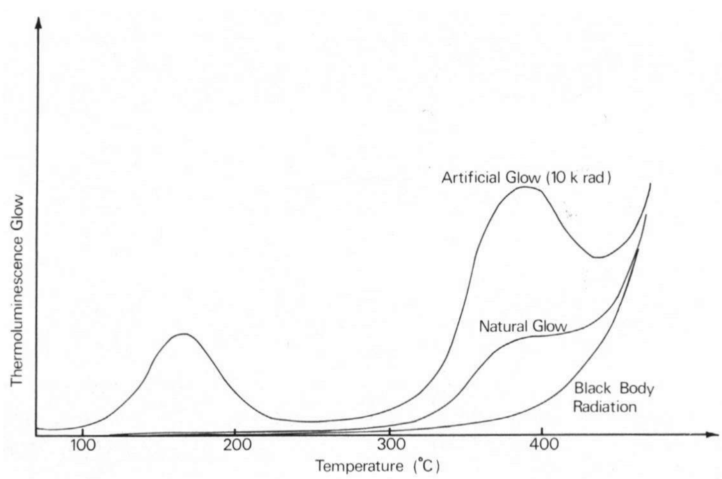
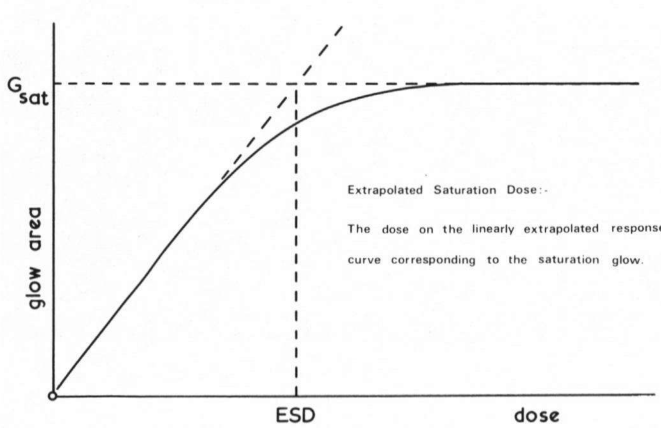


Fig. 1 Thermoluminescence glow for Natural and artificially irradiated flint sections.
Fig. 2 Schematic explanation of saturation dose.



significant effect on the storage mechanism of this energy. Since the type of defect varies numerously, the way each crystal stores energy is different from each other. When flint is heated below its incandescence temperature the energy stored in each crystal will be released by means of light. Fig. 1 shows the TL glow for natural and artificailly irradiated flint sections and Photo 1 shows thin section of flint and thermoluminescence glow photograph taken in the dark.

The requirements for age determination of burned flint by TL

The basic assumptions in the application of TL to archaeological age determination of flint is that they have been heated earlier in their history so that any TL acquired during previous geological times had been drained. For this reason various examinations of these stones have to be performed in the laboratory in order to verify the burning. The simplest test is to look for potlids. Potlids are very regular shaped cavities which are created by the build up of pressure during the heating, the potlids are one of the strongest evidence that the flints were burned. Photo 2 shows the difference between the burned and unburned samples in which the burned one contains potlids. When the potlids were not visible, the stones were studied under a microscope to see the crazes due to the pyrolization. But crazes observed can not always be the best evidence that the stones are burned. They could also be created by frost. It has been reported recently that prior heat treatment can be observed by electron spin resonans technique, ROBINS et all (1978). Most reliable test for burning is found to be the saturation level test. For this reason a small chip is broken into two parts and one of them is exposed to a test dose of a few hundred rads. The both parts are heated and TL glow is recorded. If the samples were saturated ie. unheated no difference is observed between the TL glow curves of this two parts. Fig. 2 shows the schematic explanation of saturation dose.

After the identification of the samples for pyrolization the following measurements shown schematicaly in Fig. 3. are necessary.

1. The natural accumulated TL must be measured in temperature range typically around 350-450°. This range of temperature can be determined by ordinate ratio test AITKEN (1968). The temperature range determined in ordinate-ratio test is large enough for drainage by ambient temperatures to be negligible.

TABLE I

Listing of Samples from Cariguele Cave

Sample	R_n (krad)	E (mrad/y)	U (ppm)	Th (ppm)	K (%)	k	I (mrad/y)	Age (years)
B1	21.5	380	0.30	0.90	0.10	0.80	146	39,400
B2	18.5	-	0.60	1.80	0.10	0.85	284	28,000
B3	28.0	-	0.30	0.90	0.10	0.47	485	57.700
B4	2.8	370	0.80	0.40	0.10	0.80	240	4.500
B5	17.0	415	1.20	0.10	0.10	0.16	76	33,000
B6	10.0	330	0.50	1.70	0.10	0.78	146	20,000
B7a	7.0	-	0.60	1.80	0.04	0.47	155	13,600
B7b	13.5	-	1.24	3.72	0.10	0.49	328	18,500
B8a	58.0	-	-	-	-	-	-	Unburned
B8b	14.5	-	0.66	1.89	0.10	0.32	123	27,700
B9a	30.0	-	0.38	1.14	0.10	0.51	110	58,800
B9b	175.0	-	-	-	-	-	-	Unburned
B10	40.0	-	-	-	-	-	-	Unburned
B11	27.0	-	-	-	-	-	-	Unburned
B12	17.0	-	0.53	1.50	0.10	0.80	220	27,400
B13a	16.0	-	0.30	0.90	0.10	0.40	80	33,300
B13b	90.0	-	-	-	-	-	-	Unburned
B14	153.0	-	-	-	-	-	-	Unburned
B15	33.0	-	-	-	-	-	-	Unburned
B16	8.5	-	0.44	1.32	0.10	0.38	104	17,000
B17	9.0	-	0.30	0.90	0.03	0.15	20	21,000
B18	Not suitable for testing							
B19	14.5	-	0.60	1.80	0.10	0.33	118	28,000
B20	23.5	-	0.80	2.40	0.05	0.68	290	34,000
B21a	24.0	-	1.10	0.20	0.10	0.40	148	43,000
B22	15.0	-	0.40	1.20	0.08	0.90	192	25,300
B23	2.0	-	0.30	1.10	0.10	0.70	129	3,800
B24	21.0	-	0.50	1.50	0.17	0.15	57	45,900
B25	42.0	-	-	-	-	-	-	Unburned
B26	45.0	-	-	-	-	-	-	Unburned
B27	225.0	-	-	-	-	-	-	Unburned
B28	8.0	-	0.45	1.50	0.05	0.28	78	16,700
B29	25.0	-	0.65	2.00	0.07	0.40	145	45,800
B30	6.0	-	0.64	2.00	0.05	0.35	128	11,400
B31	1.75	-	0.40	1.20	0.09	0.51	115	3,400
B32	37.0	-	1.50	4.50	0.05	0.63	526	40,000
B33	31.0	-	0.40	1.20	-	0.38	91	63,300
B34	20.0	-	0.15	0.45	-	0.43	44	45,000
B35	Not suitable for testing							
B36	10.0	-	0.90	0.90	-	0.80	273	15,000
B37	180.0	-	-	-	-	-	-	Unburned
B38	16.5	-	0.35	1.05	0.13	0.59	118	31,400
B39	110.0	-	-	-	-	-	-	Unburned
B40	110.0	-	-	-	-	-	-	Unburned
B41	43.0	-	-	-	-	-	-	Unburned
B42	30.0	-	0.30	0.90	0.05	0.90	136	56,000
B43	10.8	380	0.30	1.20	0.05	0.56	106	20,100
B44	24.2	320	0.60	1.80	0.07	0.98	308	37,350
B45	17.9	340	0.60	1.80	0.06	0.60	192	32,400
B46	41.1	400	0.51	1.53	0.05	0.25	78	82,500
B47	12.2	420	0.70	2.10	0.06	0.34	141	20.950
B48	7.3	460	0.50	1.50	0.08	0.17	53	13,400
B49	21.8	330	0.47	Ux3	0.08	0.33	95	49,200
B50	17.0	460	0.45	Ux3	0.07	0.55	138	27,500
B51	20.0	357	0.70	Ux3	0.09	0.43	180	35,900
B52	9.9	300	0.80	1.80	0.09	0.45	199	19,300
B53	31.3	320	0.80	1.10	0.10	0.33	120	68,000
B54	24.0	410	1.80	0.90	0.07	0.22	155	42,500
B55	60.0	-	-	-	-	-	-	Unburned
B56	37.0	-	0.41	1.23	0.06	0.40	93	75,000
B57	19.0	-	0.55	1.65	0.03	0.28	87	39,000
B58	27.0	-	0.32	0.96	0.10	0.56	103	53,600
B59	20.0	-	1.70	5.10	0.06	0.28	254	30,600
B60	14.5	-	0.70	2.10	0.08	0.38	150	26,400
B61	25.0	-	0.37	1.10	-	0.60	126	47.500
B62	22.0	-	0.23	0.69	0.03	0.41	52	48,500
B63	10.0	-	0.26	0.80	0.10	0.40	65	21,500
B64	12.5	-	0.36	1.08	-	0.10	33	28,800
B65	26.0	-	0.22	0.66	0.08	0.60	76	54,300
B66	18.0	-	0.13	0.40	-	0.25	27	42,000
B67	120.0	-	-	-	-	-	-	Unburned
B68	9.2	-	0.30	0.90	-	0.40	73	19,300
B69	9.0	-	0.35	1.05	-	0.40	84	18,600
B70	11.5	-	0.30	0.90	-	0.40	73	24,300
B71	15.0	-	0.26	0.78	-	0.63	94	30,400
B72	Not suitable for grinding							
B73	Not suitable for testing							
B74	11.0	-	0.17	0.51	-	0.73	72	23,300
B75	2.3	-	0.26	0.78	-	0.40	94	4,650
B76	1.8	-	0.28	0.84	-	0.58	93	3,650
B77	3.5	-	0.58	1.74	0.04	0.50	157	6,300
B78	6.0	-	0.45	1.35	-	0.24	71	12,700
B79	-	-	-	-	-	-	-	Unburned
B80	27.0	-	-	-	-	-	-	Unburned
B81	140.0	-	-	-	-	-	-	Unburned
B82	49.0	-	0.53	1.59	-	0.53	156	87.000
B83	16.0	-	0.40	1.20	0.10	0.45	106	31,700
B84	16.0	-	0.30	0.90	0.40	0.21	41	36,300
B85	Not suitable for testing							
B86	11.8	-	0.40	1.20	0.10	0.17	49	26,200
B87	170.0	-	-	-	-	-	-	Unburned

* *When soil was not available, 380 mrad/year was assumed as an average.*
** *The average of 0.1% of K was assumed when no measurement was available.*

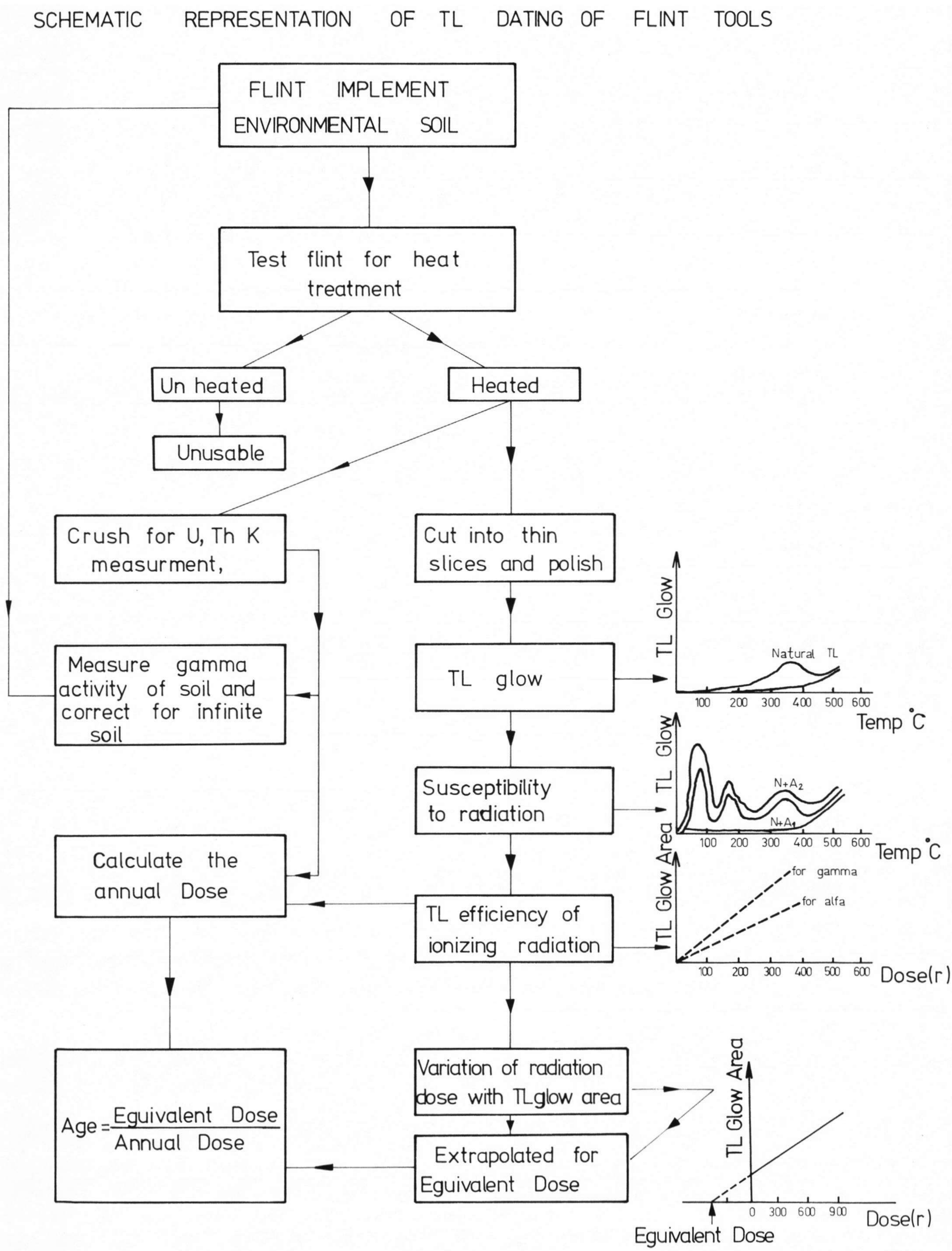


Fig. 3 Schematic explanation of dating of flints by Thermoluminescence.

2. Equivalent radiation dose has to be determined. For this artifical TL glow is observed from the substance after it has been exposed to a known dose of radiation. It is convenient to measure this glow in terms of radiation dose which induces TL of the same order of magnitude as the natural TL.
3. The combined effect of the radioactive content of the flint and the dose received from its environment has to be measured. This is called the natural dose rate. Environmental activity measured by $CaSO_4$: Dy dosimeters from 1 kg of soil then the correction for infinite has to be calculated.
4. The efficiency of different types of ionizing radiations for producing TL must be measured. ZIMMERMAN (1972). This has to be measured because not only the efficiency of radiation was different but also efficiency varies with the type of flint involved.

   Form the first two measurements one can determine the total equivalent dose in rads (Rn) received by the sample since it was last heated. From the last two measurements, one can determine the annual dose rate in rads/year (r) received by the substance. This has to be corrected for the different efficiencies of different radiations in producing TL as compared to the kind of radiation used for artificial irradiations. Then the age is simpley determined by

$$\text{Age} = \frac{\text{Rn}}{\text{r}} = \frac{\text{Total Equivalent Dose (rads)}}{\text{Annual dose (rads/year)}}$$

Conclusion

Age determination with TL method being an absolute one, gives ages that are independent of any other chronology. Therefore the gap between 50-100,000 years might possibly be bridged by TL dating, which has proven difficult by other methods. Hence TL can be developed as an absolute method of checking the result of either of the other widely used methods (C14, K/A).

The experimental results showed that the archaeological age determination of flint stones by using the TL method with powder samples was not possible due to Tribo TL and the phenomenon described as regeneration TL. The method could be used in for geological age determination in the range of 300,000-3,000,000 years, provided that the samples do not reach saturation very early, and the storage conditions are controlled in the laboratory after the preparation. But the archaeological dating of flint stones is limited by the use of fire by man.

The selection of the samples for age determination was found to be very important because some of the flints reach saturation at very low doses. Before using each flint, the saturation level of samples must be studied.

For flints, no attempt was made to correct for Radon escape, first, because flint is very compact compared to other materials and, second, because the limiting factors from other sources are still high compared to the errors introduced by Radon escape. For the same reasons, flint were very resistant materials to leaching by ground water. Thus, the possible effect of Uranium accumulation due to ground water is not important. However, this could be studied by possible leaching various materials with artificially Uranium-enriched water. The analysis could perhaps, be more useful if various types of materials under the same artificial conditions were studied.

The following conclusions can be made concerning the reduction of dose rate by ground water. As was mentioned earlier, the most accurate results were obtained form flints where 1-2 kgm of soil from the site was provided. In this study samples were found under rather fortunate conditions in which the cave where they were found was thought to be sheltered from seasonal variations in rainfall. When the dose rate from the soil was measured by using $CaSO_4$: Dy dosimeters, the soil was carefully sealed to prevent water evaporation during the storage for six months. The sealing of the bottles probably reduced the escape of Radon to some extent. In this study, no sensitization nor supralinearity was observed in flint. But taking into consideration the variety of the sources and the types of flint, this has to be checked for each sample.

But as a summary, if the samples have been carefuly selected, if the environmental conditions have been closely studied, and if a few kgm of soil are available from the site TL dating of flint can be done with less than 15% error. Table I gives the age determination of burned flints from Cariguele Cave frrm Southern Spain. GÖKSU et all (1974).

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Doç. Dr. Yeter Göksu

Çukurova University, Department of Physics and Space Sciences, Adana, Turkey.