THERMOLUMINESCENT DATING OF PREHISTORIC POTTERY SHERDS FROM GOMOLAVA NEAR HRTKOVCI (YUGOSLAVIA)

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CONTENTS

INTRODUCTION

The thermoluminescent method of dating ancient ceramics and some other fired materials is a combined application of nuclear and solid state physics. This method is based on the phenomenon that mineral inclusions such as quartz, feldspars and calcite, which are embedded in the clay matrix, have a much higher thermoluminescent sensitivity than the matrix at the same amount of absorbed dosage. On the basis of the observations of Fremlin and Srirath (1964), as well as by applying the radiation dosimetry principles to the conditions that exist in the structure of pottery, Fleming (1966) proposed the method of absolute age determination entitled "inclusion technique". The thermoluminescence (TL) observed is a measure of the cumulative dose of radiation to which the inclusions have been exposed since the previous heating. In the case of pottery the event dated is the firing of the pot by ancient man.

The natural thermoluminescence induced in mineral inclusions originates from the ionization effects of alpha, beta and gamma radiation coming from uranium and thorium chains, and beta and gamma radiation from radiogenic potassium. Those radioactive impurities are present in the pottery material and in the surrounding soil in which the pottery is buried. A small contribution from cosmic rays must be taken in account, especially in the cases where the radiation doses from above-mentioned radioactive impurities are small. Figure 1 presents the basis of the TL age determination method.

In the applied inclusion technique, TL measurements are made on grains of about 100 μm for which the alpha particles contribution is negligible. Alpha particles originating from the inclusion/matrix interface have an average range about 25 μm, so that for inclusions of 100 μm diameter, the alpha radiation dose is diluted to a level of 21% for the uranium and 25% for the thorium series (Fleming 1970). On the other hand, the alpha particles are much less effective in inducing thermoluminescence than the same dose of beta or gamma radiation (Aitken *e.a.* 1967; Zimmerman 1971).

Hence, for the adopted grain size, the accumulated radiation dose and the appropriate annual dose originate only from beta particles from the radioelements in the pottery material itself (after removing the surface layer), the gamma-ray contribution from the surrounding soil and a small contribution from cosmic rays (Aitken 1969).

In principle, the absolute age is obtained by comparing the archaeological accumulated dosage with the appropriate annual dose-rate received by the sherd (Aitken *e.a.* 1968):

$$\text{Age} = \frac{\text{Accumulated radiation dose}}{\text{Dose per year}}$$

The thermoluminescent method for determining the age of pottery has been applied to the ceramic material of the prehistoric site "Gomolava", Hrtkovci, Yugoslavia. The archaeological ages of the pottery fragments range from about 100 to about 5000 years BC.

This work presents the first attempt in our country to date ancient pottery by TL dating technique.

Six groups of sherds with different ages were tested; from each group of pottery, the measurements were performed on three different pieces of various thickness and colour. All the sherds were found in a homogeneous type of soil, mainly clay, at the depth of about one to four meters, near a river.

ACCUMULATED ARCHAEOLOGICAL DOSAGE

The pottery was crushed in an agate mortar after removing the surface layer. The surface layer, between 1 and 2 mm of the pottery, has been partially irradiated with the beta particles from the surrounding soil and partially by that of the pottery. To avoid unreliability from the latter effect, the samples for TL measurements must be taken from the inner part of the fragment. The inclusion grains have been extracted from the pottery by the standard mineralogical (Ichikawa 1965) techniques of magnetic separation. The grains were washed with diluted acids (Fleming 1970) to remove the diffusion elements from the surface of crystalline grains. After sieving, we got the grains of about 100 μm grain diameter. Namely, the crystalline component with a grain diameter of about 100 μm, gives a greater TL

glow than the grains of a smaller or greater diameter (Fleming 1968).

The natural thermoluminescence has a glow curve usually composed of a number of overlapping peaks originating from the presence of different types of thermoluminescence centers in the measured sample.

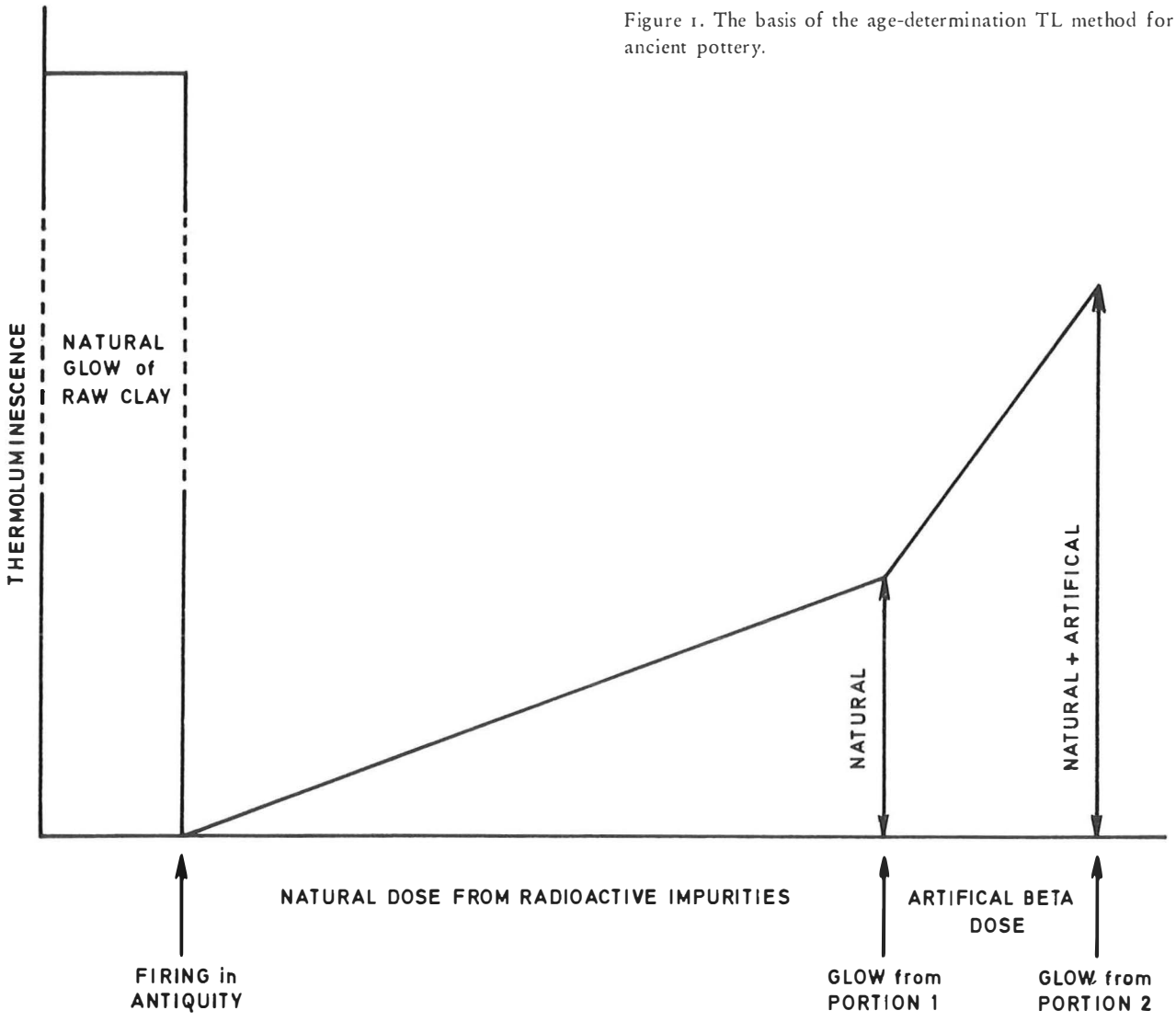
The age formula assumes that the accumulation of thermoluminescence by ancient ceramics is linear with the dose but this is not always true. In our age test only one of the examined samples was supralinear.

To determine the dose necessary to induce an amount of artifical TL equal to the natural TL is to plot the glow curve intensity as applied radiation dose. The unheated (Tite 1966; Aitken 1970; Zimmerman & Huxtable 1971) samples were irradiated with a known artifical dose; the natural TL was measured with one portion of the sample, and the natural plus artifical TL was measured with a second portion. Figure 2 shows the typical TL growth for fragment K2. The values of the accumulated archaeological dosage values for a series of examined sherds are shown in Table 1.

ANNUAL RADIATION DOSE

For the inclusion technique it is necessary to perform (1) an evaluation of beta radiation dose-rate of the pottery fragment, and (ii) a separate

Figure 1. The basis of the age-determination TL method for ancient pottery.



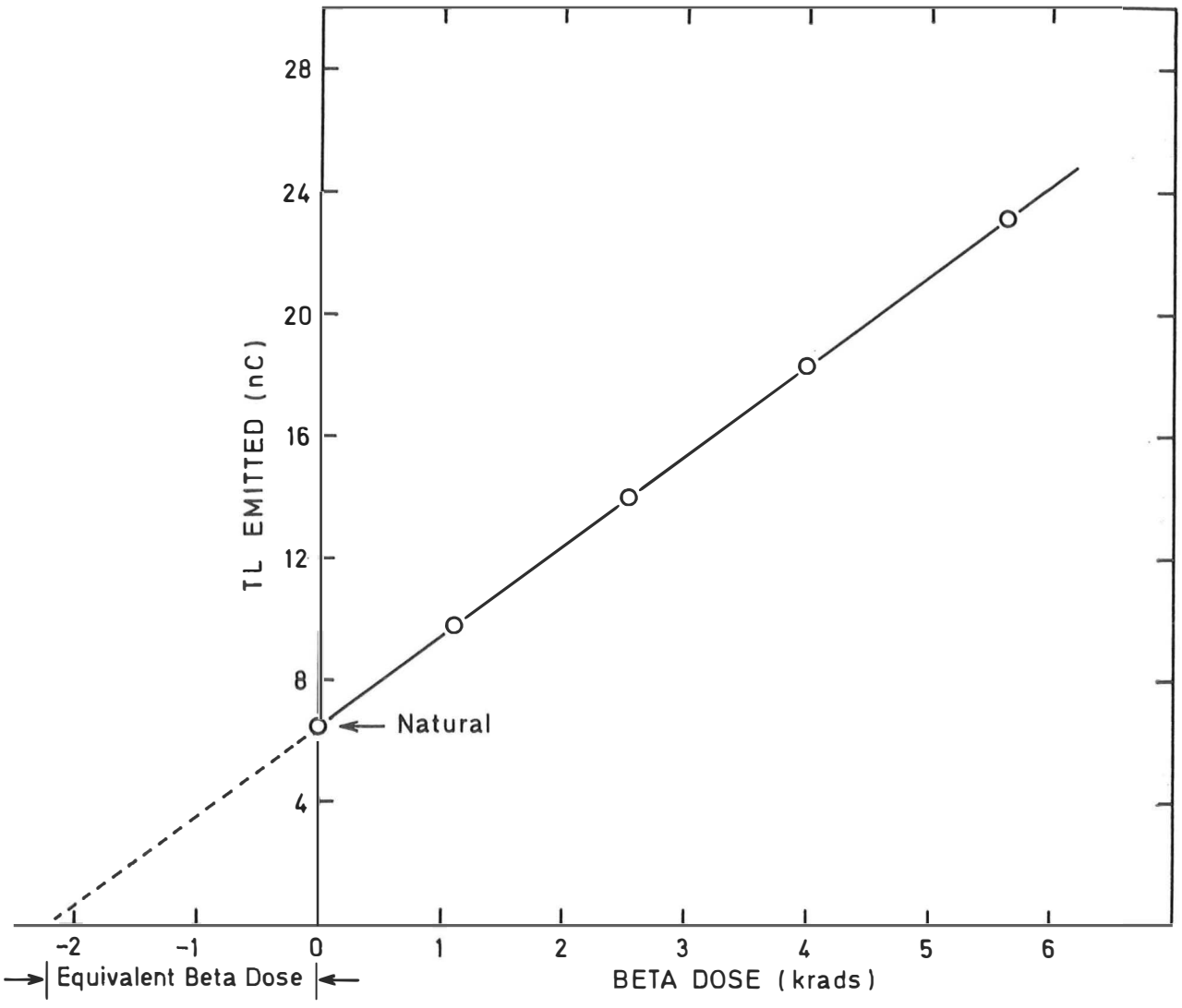
evaluation of environmental dose-rate, i.e. gamma radiation from the surrounding soil plus a cosmic ray dose component.

The beta radiation in the fragment itself originates from the radioactive decay of the uranium and thorium series and the radiogenic potassium. Gamma radiation of the relevant soil originates from the same type of radionuclides.

In this dating program we calculated the annual beta and gamma doses from alpha counting and potassium analysis of sherds, and relevant soil samples, respectively. The potassium content was determined by standard chemical analysis (flame photometry).

The uranium and thorium contents of pottery and soil are determined by thick-source alpha counting based on the Turner's method (Turner *e.a.* 1958) with some modifications (Prokić 1973), Knowing (i) the value of the thorium/uranium ratio obtained by the "pair" technique, and (ii) the specific alpha activity originating from eight alpha transformations of the uranium and from six alpha transformations of the thorium series, we get the value of U-238 and Th-232 contents per gram of sherd and soil samples. The contents of U-238 and Th-232 are obtained by estimating the $Z^{2/3}$ for the sherds and soil sample. The dose-rates received by a fragment of pottery buried in soil were calculated according to the Aitken's

Figure 2. The TL response as a function of beta dose for sample K 2.



conversion factor data (Aitken 1968).

At the excavation site, the soil was mainly homogeneous clay, without stones. This fact makes the estimation of the gamma dose which the pottery fragment has received more reliable (Prokić 1974). In this case, long-term *in situ* measurements were not necessary (Fleming 1970; Mejdahl 1970).

The presently employed technique has two sources of uncertainty. The presence of water in the sherds and soil will raise their average density and increase the absorbtion of radiation. This results in a decrease of radiation intensity.

The second effect occurs when the pores of the soil and sherd are filled with water, so that the emanation of radioactive gases – mainly Rn-222 is suppressed. This causes an increase of the radiation intensity. These two effects are dependent, but operate in opposite direction. The amount of reduction of dose-rate is nearly proportional to the percentage weight change due to water content in sherd and soil respectively.

The estimated errors from water content and from the radon escaping should not be added because the two effects are not independent.

The assumed water uptake *in situ* of sherds and soil during the archaeological time amounted to 95% of the saturation level with a ± 5% uncertainty. This is acceptable, as the excavation site is placed near the river bank.

The percentage of radon escaping from dried samples lies usually between 10% and 30%, but in soaking wet conditions *in situ*, the gas diffusion is reduced. According to the latest studies and conclusions of Desai and Aitken (1974), wet conditions do not drastically inhibit the escape of radon. Ideally the dry and wet escape-rates should be measured for each fragment before it is crushed in preparation for TL measurements, but this is only important for pottery types for which the percentage of escape is high. For pottery and soil

TABLE 1. TL AGES FOR A SERIES OF SHERDS FROM GOMOLAVA NEAR HRTKOVCI

Pottery fragment	Archaeological nomenclature	Annual dose-rate (rads/year)		Archaeological dosage (rads)	Ages (years B.P.)			
		Beta	Environmental		TL	TL	Conventional C-14 dates (T½ 5570)	Globally corrected C-14 dates
K 1	Vinča	0.185	0.097	1909	6770	6959	6000-5500	6900-6300
K 2		0.210	0.097	2204	7180			
K 3		0.213	0.097	2140	6929			
03-309 1	Vinča	0.211	0.105	2193	6939	6684	6000-5500	6900-6300
03-309 2		0.203	0.105	1987	6451			
03-309 3		0.170	0.105	1832	6662			
02-179 1	Kostolac	0.175	0.117	1353	4634	4684	4400-4200	5100-4800
02-179 2		0.193	0.117	1505	4855			
02-179 3		0.199	0.117	1442	4563			
02-225 1	Vučedol	0.233	0.117	1420	4057	4058	4200-4000	4800-4500
02-225 2		0.219	0.117	1405	4182			
02-225 3		0.229	0.117	1362	3936			
02-213 1	Late Bronze Age	0.204	0.097	857	2847	2994	about 2900	about 3150
02-213 2		0.231	0.097	1022	3116			
02-213 3		0.209	0.097	924	3020			
1-69 1	Iron Age	0.195	0.117	619	1984	2079	2300-2100	2400-2150
1-69 2		0.203	0.117	667	2084			
1-69 3		0.139	0.117	555	2168			

containing 3 ppm uranium, 12 ppm of thorium and 1% potassium, from which 40% of the radon escapes, the erroneous assumption that there is no escape in wet conditions, leads to a date that may be too recent by about 10%.

The annual dose-rate values for the measured samples are given in Table 1.

DATING RESULTS

The instrumentation used for thermoluminescent analysis was a commercial Harshaw's Model 2000 TL Analyzer. All readings were made in nitrogen atmosphere to reduce the "spurious" TL that is induced by some means other than ionizing radiation. The significant amount of thermal radiation for temperatures higher than 300°C was suppressed with an additional filter (DG-23, Spezial Glas G.m.b.H., Mainz).

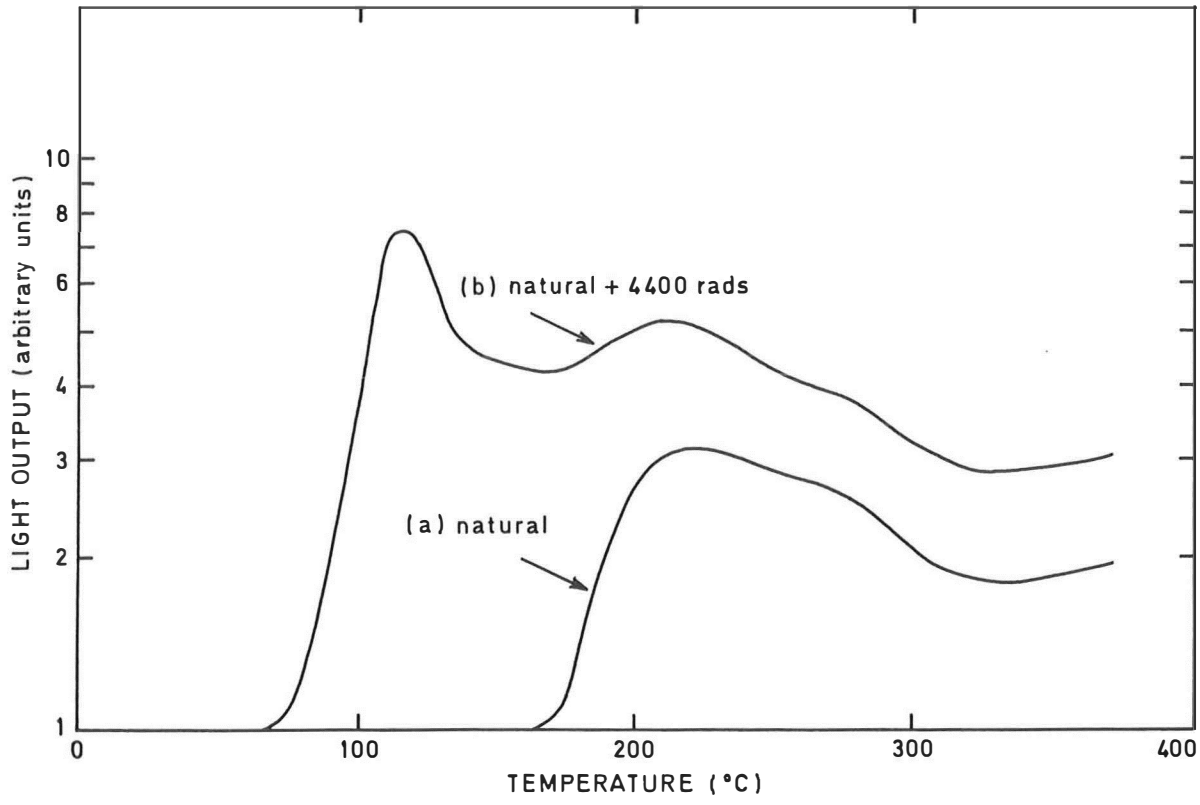
Powdered samples were exposed to beta particles from Sr-90 + Y-90 calibrated plaque source (RCC Amersham). Calculation of the absorbed beta doses were carried out on basis of the equation (Anlincev 1957) which gives the dose-rate at the different distances from the finite circular-plane-disk-source. Our calibration of the dose-rates is considered to be correct to within ± 5 per cent.

General discussion

The main glow-peak for natural TL occured for all the samples at about 220-240°C and the second peak occured at about 280-300°C. The irradiated samples showed an added intensive peak at about 110°C (Figure 3).

We have obtained the similar shape of glow curves for pottery samples as Mejdahl (1972) and Ichikawa (1965). The principal glow peaks of examined material were at relatively low temperatures, thus the effect of fading during the burial period may be considered. However, a comparison of the presented TL ages with the archaeological ages, as well as the comprehensive

Figure 3. The typical shape of the glow curves for (a) natural TL, (b) TL of natural +4400 rads of laboratory applied beta radiation of mineral inclusions for sample 02-225 b.



results obtained by Mejdahl, indicates that fading, cannot be a serious factor.

Large variations in sensitivity were exhibited by samples from different sherds. These may be related to the different impurities in the mineral grains which function as activators. In connection with this problem, Inagaki (1972; 1973) studied the TL of nonirradiated natural quartz, the TL of artifically irradiated natural quartz from various geological origins, and the differences in concentration of crystal imperfections. He concluded that natural TL as well as artifical induced TL are closely related to the origin of the quartz. Especially, the difference in glow curves of quartz samples from three examined types seems to be associated with the content and the position of lithium and sodium ions which compensate the large defects resulting from the replacement of Si^{4+} by Al^{3+}. It is known that quartz containing Li^{+} has a glow peak at 170-180°C, whereas quartz containing Na^{+} has a glow peak in the vicinity of 300°C. Ichikawa (1968) added various impurities (Li^{+}, Na^{+} and Al^{3+}) by diffusion to quartz samples and observed TL after irradiation with gamma rays. When Li was diffused into quartz, glow peaks appeared at 185°C and 245°C. Quartz treated with Na showed a broad peak at 280°C and quartz into which Al and Li were diffused showed a large peak at 185°C. In the case of quartz with Al, Li and Na, glow peaks appeared at 185°C and between 245 and 280°C. Gamma irradiated quartz samples from various geological origins showed three glow peaks at 100-120°C, 185°C and 230-290°C.

In samples containing a mixture of quartz and feldspars, the high internal radiation in the potassium feldspar allows the equilibrium between traping and release of electrons to be extended to shallower traps.

According to the Mejdahl (1969) considerations the absence of fading in this temperature region (220-300°C) might be a consequence of the broad distribution of traps in the material; an extension of the fading period would not only result in the establishment of equilibrium between traping and escape of electrons (or holes) at a lower level, but also in a displacement of the glow peak to a higher temperature.

CONCLUSION

The results of this test program are regarded as encouraging and indicate that a number of possible interfering effects are not of serious importance. The accuracy of results presented were estimated to be about at the 10% level. At the present level of accuracy, the method is of considerable importance in prehistoric archaeology.

In further work the measurement of accumulated dosage and annual dose-rate will be refined along with the other TL techniques.

The nature and the kinetics of the intermediate temperature peaks of the ancient ceramics glow-curve need further investigation.

Acknowledgements

I am indebted especially to Prof. Dr. B. Brukner and the archaeologists from the Museum of Vojvodina for the support and providing the pottery for analysis performed.

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