LUNAR REGOLITH THERMOLUMINESCENCE GLOW CURVE FITTING TO EXTRACT ITS MOST IMPORTANT KINETIC PARAMETERS.

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Introduction: Durrani and his colleagues pointed out that, by making reasonable assumptions about environmental conditions and laboratory determination of the relative kinetics, the natural thermoluminescence (TL) of the lunar regolith can provide the storage temperature and duration of a sample on the lunar surface. Knowledge of parameters *E* and *s* are critical in this process. *E* (in eV) is the activation energy required for electrons to escape a trap in the crystal lattice, and *s* (s^{-1}) is an Arrhenius factor describing the probability of an electron escaping the trap. TL is emitted in the form of a glow peak that can be described via the relationship:

$$I(T) = n_0 s \exp(-E/kT)\exp\{-\int[s \exp(-E/kT)/\beta]\, dT\}, \quad (1)$$

where n_0 is the number of electron traps filled, k is Boltzman's constant, T is the absolute temperature, and β is the heating rate employed during sample heating. The *s* term is adjusted for second order kinetics [2].

Traditionally, parameters *E* and *s* in lunar samples were determined experimentally through a series of heating experiments (e.g., the "initial rise method") [1,3]. However, with the advance in computational power, algorithms can now be utilized to fit multiple glow peaks to measured glow curves using Eq. 1.

As part of our ANGSA (Apollo Next Generation Sample Analysis) studies, we began exploring the possibility to extract TL kinetic parameters through theoretical curve fitting.

We focus on Apollo 17 sample 76240,48 in our analysis, which was collected from the coldest area (in permanent boulder shadow) and was also stored in a freezer at -20 ºC shortly after it was returned to Earth. Therefore, this sample is expected to contain the most TL peaks in our sample suite, making it suitable to test the feasibility of curve fitting.

Motivation for Curve Fitting: While the experimental approach has proven to be useful in extracting *E* and *s* from glow curves, one major disadvantage is that samples, such as lunar regolith, are composed of complex mineralogy, meaning that glow curve shape may be complex: The presence of multiple, overlapping TL peaks in one glow curve is commonplace (Figure 1).

Previous work by Durrani [1] on sample 76240 collected in the shade of boulder 4 at station 6 suggests at least three peaks and three pairs of *E* and *s* values. The stepwise heating and draining of TL peaks to obtain *E* and *s* values therefore may drain two peaks at the same time, introducing uncertainty of the kinetic parameters.

Several authors in the literature advocate for curve fitting as a superior method to obtain TL kinetics parameters [4-6].

Considering the results by [3], who demonstrated the presence of TL in Apollo 15 samples down to -196 ºC, more overlapping peaks should be expected, presumably making experimental determination even more complex for samples in such environments (e.g., permanently, temporarily, and seasonal shadowed regions on the Moon).

Moreover, operating a TL instrument on the surface of the Moon would greatly benefit from curve fitting, as the interpretation of the data can be done on Earth. This would allow the instrument to make further measurements, rather than performing interpretative experiments on the same spot.

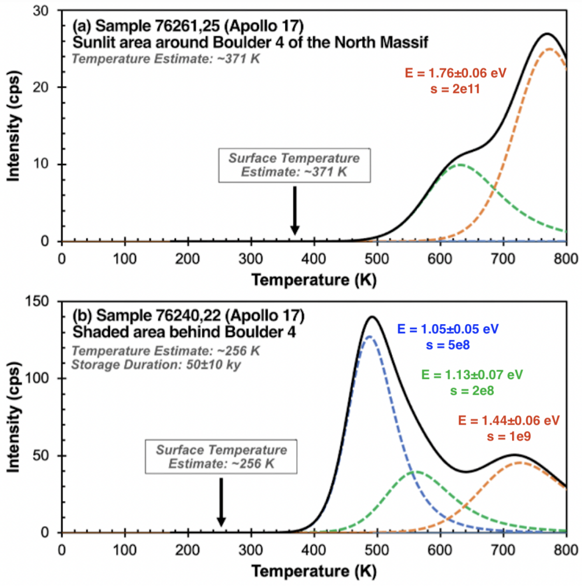

Fig. 1. Natural TL glow curves, storage temperature, and durations estimates for (a) sunlit and (b) permanently shaded lunar regolith [1]. E and s values shown in color were experimentally determined by Durrani [1].

Details of Curving Fitting Method: We explored curve fitting in Microsoft Excel by adapting the procedure described in [6]. Eq. 1 was programmed into Microsoft Excel to fit individual peaks to the observed glow curve. The curve fitting procedure involves multiple steps to obtain feasible *E* and *s* parameters. As the first step, we performed manual curve matching by

(a) Deciding how many peaks may be present and assigning an arbitrary intensity (e.g., 100 000) to each peak.

(b) Assigning reasonable *E* values. Based on the literature, this should be in the range of 0.9 to 1.7 eV from room temperature to 500 ºC. Assigned *E* values were consistent with TL theory, meaning higher temperature peaks have higher *E* values.

(c) Assigning reasonable *s* values between 1×10^8 1×10^{12}. After this step, we adjusted the intensity of individual peals to better match the theoretical to the measured glow curve as best as possible. We repeated steps a-c to refine *E*, *s*, and peak intensity for further improvement.

Once we were satisfied manipulating the parameters manually, we utilized the Microsoft Excel Solver routine:

(d) At first, we only optimize the peak height with the objective to match the height of the theoretical curve more precisely with the measured glow curve.

(e) We then only optimized the *s* values, which resulted in better theoretical glow curve overlap with the measured glow curve.

(f) We then only optimized *E* values, which further improved the peak overlap.

(g) We then repeat steps d-f to improve the offsets between the theoretical and measured glow curves. Particular attention was given to avoiding unreasonable or extreme *E* and *s* values (e.g., very low or high values). A log of all intermediate *E* and *s* values was useful to track changes and allowed us to revert back to previous values in case parameters became unreasonable.

(f) As one of the last steps for refinement, we found it useful to only adjust some peaks of the glow curve. For example, we manipulated *E*, *s*, and peak intensity only for the first two peaks to avoid unnecessarily altering other well-matched peaks at the higher temperature side of the glow curve.

(h) The final step involved optimizing all parameters (*E*, *s*, intensity) at once using the Solver routine, which further improved the fit.

Results: Applying the initial rise method, we obtained mean values for E = 1.15±0.06 eV, and s $=1.8\times10^{11}$ s^{-1} for a peak with its maximum at 498 K. The initial rise method only gives us *E* and *s* values only for the very first peak in the glow curve.

Considering a glow curve composed of three individual peaks as shown in Figure 1b, curve fitting gives us the first peak maximum E = 0.87±0.05 eV, and s = 1.9×10^7 s^{-1}, a second peak at 569 K with E = 0.71±0.05 eV, and s = 8.6×10^4 s^{-1}, and a third peak at 695 K with E = 1.14±0.05 eV, and s = 5.2×10^6 s^{-1} However, these values appear unreasonably low and do not follow the conventional expectations, such as that the *E* value for peak 2 is lower than the *E* value for peak 1. Four-peak fitting was no more successful.

Therefore, we also considered a total of five peaks in the glow curve. We obtained a first peak at 489 K with mean values for E = 0.95±0.05 eV, and s = 3.8×10^8 s^{-1}, which is widely overlapped by a second peak at 540 K with a mean E = 0.94±0.06 eV and s = 1.9×10^7 s^{-1}. A third peak is located 617 K with E = 1.13±0.05 eV, and s = 7.9×10^7 s^{-1}, a fourth peak at 691 K with E = 1.26±0.05 eV, and s = 5.4×10^7 s^{-1}, and a fifth peak at 765 K with E = 1.39±0.05 eV, and s = 3.2×10^7 s^{-1}.

Discussion: Our results show poor agreement with those of [1]. To check the viability of our fitting results, we calculated the mean lives of these peaks via the relationship

$$t = s^{-1} \exp(E/kT). \qquad (2)$$

While peak 3 is stable for millions of years, peaks 1 and 2 would decay away within years after storage in the freezer. This is clearly not the case, since we can measure their TL 50 years after they were collected on the Moon [7]. Hence, the fitting attempt using only three peaks returns false results.

The 5-peak curve fitting attempt results in half-lives ($\tau_{½}= \tau \times \ln2$) of 20 and 261 years for peaks 1 and 2, respectively. This decay is consistent with our recent results [7], especially considering experimentally uncertainties not discussed here. Peak 3 and 4 have half-lives of 200,000 years and 74 million years, respectively. Peak 5 is stable for tens of billions of years. The 5-peak fitting solution provides feasible *E* and *s* values.

Conclusion: Curve fitting can provide feasible results. However, glow curve fitting does not provide unique solutions and requires a thorough understanding of TL in samples with complex mineral mixtures such as lunar regolith. Manual and incremental refinement of TL parameters appear to be critical.

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References: [1] Durrani et al. (1976) *LPSC VII Proc.* 1157. [2] Garlick, Gibson, *Proc. Phys. Soc.* (London) 62, 574 (1948). [3] Durrani et al. (1972) *The Apollo 15 Lunar Samples.* The Lunar Science Institute. [4] Afouxenidis et al. (2012) *Radiat. Prot. Dosimetry* Vol. 149, No. 4, pp. 363–370. [5] Mandowski, Swiątek (1999) *Radiat. Prot. Dosimetry* Vol. 84, Nos. 1–4, pp. 123–126. [6] Kazakis (2019) *Radiat. Prot. Dosimetry* Vol. 187, No. 2, pp. 154–163. [7] Sehlke, Sears (2022) *Apollo 17 ANGSA Workshop Abstract #2030* Lunar and Planetary Institute.