THERMAL HISTORIES OF LUNAR COLD TRAPS: PROSPECTING FOR VOLATILES BY THERMOLUMINESCENCE. A. Sehlke[1], D.W.G. Sears[1], and the ANGSA Science Team, [1]NASA Ames Research Center, Bay Area Environmental Research Institute, Moffett Field, California 94035, USA. (alexander.sehlke@nasa.gov).

Introduction: Durrani and his colleagues pointed out that, making reasonable assumptions about environmental conditions and laboratory determination of the relative kinetics, the natural thermoluminescence (TL) of the lunar regolith could be used to determine its mean effective temperature [1].

The relationship between natural TL and temperature became particularly interesting with the discovery of water and its build-up in cold traps on the Moon [2]. Given enough knowledge of the natural TL properties of lunar materials, TL measurements could identify locations on the Moon with an extended history of low temperatures. Such measurements could be performed via cryogenic sample return, remotely by robotic assets, or crew-operated equipment on the surface [3].

Through NASA's ANGSA (Apollo Next Generation Sample Analysis) initiative, we are refining our understanding of the natural TL properties of lunar materials and their kinetics by taking advantage of what is effectively a fifty-year kinetics experiment in which NASA placed Apollo 17 regolith samples in a freezer at 253 K and also stored them at room temperature. We have measured the natural TL properties of eighteen Apollo 17 regolith samples from sunlit, partially and permanently shaded areas, as well as down to a depth of ~3 meters from the deep drill core.

Principle of Thermoluminescence: The amount of natural TL observed in a sample result from two competing processes: (1) the radiative filling of electron traps and (2) the thermal drainage of these traps in the natural environment of the sample. TL data are obtained as plots of light intensity against heating temperature. A single "glow curve" typically consists of several overlapping peaks (Figure 1), each of which can be described by activation energy, *E*, and Arrhenius (frequency) factor, *s*.

The mean life (τ) of electrons in a material held at a temperature is given by

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

where *k* is Boltzmann's constant and *T* is the environmental temperature. The frequency factor (*s*) can be obtained from *E* and peak temperature (T_P) using:

$$s = (\beta E / kT_p^2) \exp(E/kT_p) \qquad (2)$$

where β is the heating rate (7.5 ºC/s) employed during the measurement.

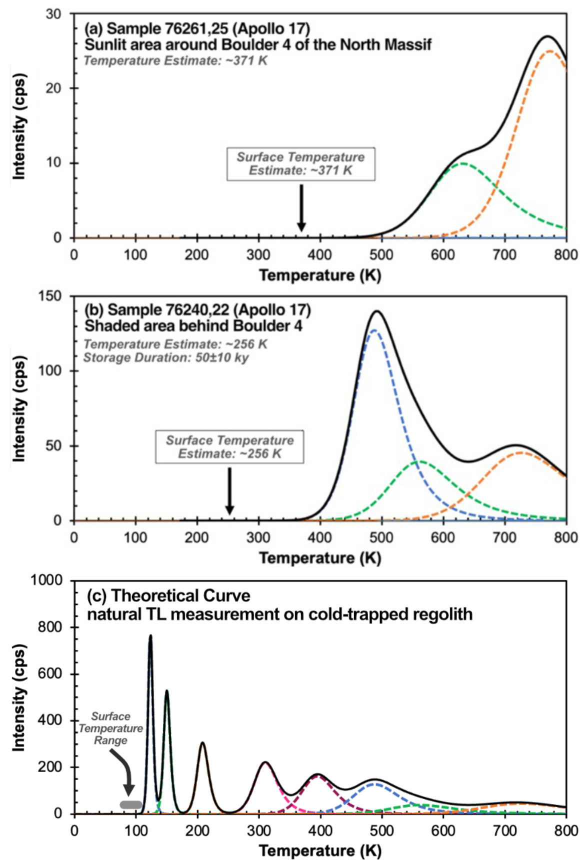

Fig. 1. Natural TL glow curves and equilibration temperature (T_{eq}) estimates for (a) sunlit and (b) permanently shaded lunar regolith [1]. (c) Theoretical glow curve for regolith in cold traps.

Applying the initial rise method [5] (i.e., the onset of the glow curve), our laboratory measurement of *E* on Apollo 17 regolith samples provided through the ANGSA program is 1.04±0.14 eV in the 475 K region, identical for room temperature and freezer samples. This result underscores that no anomalous fading processes occur in these types of samples. The TL kinetics experimentally determined within the first years after sample return hold true compared to our 50-year kinetics experiment [6]. Therefore, we argue that natural TL can yield reliable and robust estimates about the thermal environment of these samples.

Equilibration Temperatures for TL Peaks in Apollo 17 Regolith: The equilibrium temperature for a natural TL peak (T_{eq}, which Durrani et al. referred to as the "storage temperature") is determined by equating build-up in TL due to exposure to ionizing radiations and thermal decay. The resulting equation is:

$$T_{eq} = (E/k) / \ln\{ sR_{1/2} / 0.693\, r\, [(N/n_{eq}) - 1]\} \quad (3)$$

where r is radiation dose rate, $R_{1/2}$ is dose to half saturation, N/n_{eq} is the ratio of saturation dose to equilibrium dose. $R_{1/2}$ and N/n_{eq} are determined by laboratory experiments, r is known to be about 10 rad/y [7]. As pointed out by Durrani, E and s determine most of the characteristics of the TL peak, its T_{eq}, and stability (and glow curve temperature). Dose rate, $R_{1/2}$ and n/N determine the intensity of the peak. Peaks in samples held above their T_{eq} will have the TL drain faster than it builds up, while peaks in samples below their T_{eq} will build up TL levels. If a peak is present, it will not have been heated to its T_{eq} in the time taken to acquire the TL signal. Fig. 2 is a graphical presentation of Eq. 3. Figures 1a and 1b show storage temperatures for sunlit and permanently shadowed regions within the Taurus-Littrow Valley using natural TL [1].

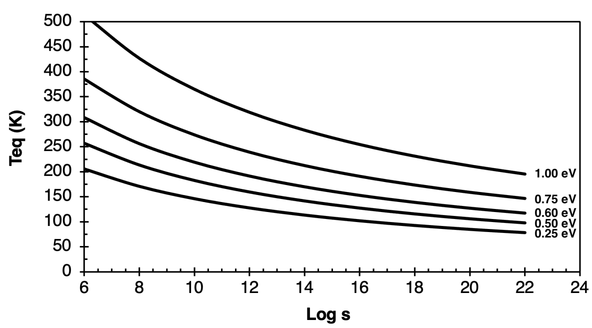

Fig. 2. Equilibrium temperatures (probably ±10 K) for various values of E and s as calculated from equation 3 using data suggested by ref [1].

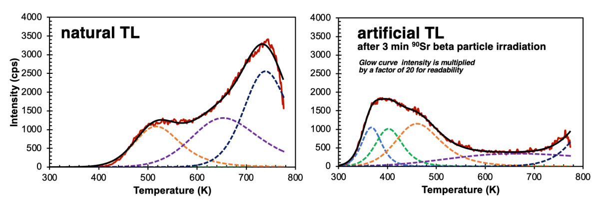

Fig. 3. Glow curves for Apollo 17 regolith sample 70004 in the natural state (left) and after draining the TL and irradiating with ^{90}Sr beta radiation (right).

TL Peaks Unstable at Room Temperature: Upon irradiation peaks appear at low glow curve temperatures that are unstable at room temperature (Fig. 3). The initial rise method gives a value for E of 0.79±0.02 eV for the lowest of these peaks at ~375 K for which we calculate a value for s of 6×10^{10} s^{-1}. This peak has a mean life of 16 min at room temperature, and one year in a freezer at 253 K. These E and s values correspond to an equilibration temperature of about 303 K. Note that T_{eq} is well below the TL peak temperature of 373 K.

Storage Temperatures for Artemis Samples: Lunar surface temperatures range from ~102 K to 387 K and can drop to 138 K within the first 30 cm [8]. In the polar cold traps surface temperatures are 20-40 K [9,10]. Theoretical work suggests that, subject to many environmental factors, in the lunar regolith water condensation occurs at ~100 K [11].

Prospecting for Water and other Volatiles: There are peaks in the TL glow curve that are stable only at these low temperatures that could be used for prospecting volatile-harboring cold traps.

Sun and Gonzales [12] reported glow curves for meteorite samples covering a temperature range spanning from liquid nitrogen (77K) to 525 K, showing a strong peak at 173 K. Such a peak is probably present in most silicates, such as lunar regolith; a theoretical glow curve is shown in Figure 1c.

Assuming an activation energy of 0.5 eV for a TL peak observable at 125 K, we calculate an s value of 4×10^{20} s^{-1}. Referring to Fig. 2, this suggests an equilibration temperature around 103 K. In other words, the presence of a 125 K peak in a TL glow curve indicates that the sample was stored at $\leq$100 K for a considerable time, in essence the time it takes for the TL to reach equilibrium, which is on the order of 2.5×10^6 years. It could be a location for the storage of water and other volatiles.

This kinetic corresponds to a mean life of 0.1×10^{-7} s (i.e., instantaneous decay) in the best scientific freezer (183 K), but the TL would be stable for millions of years at liquid nitrogen temperature (77 K). Thus, Durrani's arguments for low-temperature storage of lunar samples [13] are even stronger if samples are returned from the permanently shadowed regions of the Moon [14].

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References: [1] Durrani et al. (1976) *LPSC VII Proc.* 1157. [2] Hayne et al. (2021). *Nature Astronomy 5*, 169. [3] Sehlke and Sears (2021). *SSERVI ESF*. [4] Sehlke and Sears (2022) 53rd LPSC Abs #1257 [5] Garlick (1949) *Luminescent Materials*. [6] Sehlke and Sears (2022) ANGSA Workshop. [7] Zhang et al. (2020). *Science Advances 6* (39), p.eaaz1334. [8] Malla and Brown (2015). *Acta Astronautica 107*, 196. [9] Paige et al. (2010). *Science 330,* 479. [10] Paige et al. (2010). *AGU Fall Meeting Abstracts* (P31E-04). [12] Schorghofer. and Taylor (2007). *JGR-Planets 112* (E2). [12] Sun and Gonzales (1966) *Nature 212*, 23. [13] Durrani, S.A. (1972). *Nature 240* 96-97. [14] Mitchell et al. (2021). *52nd LPSC* (abs #1214).