A FIFTY-YEAR EXPERIMENT, THE NATURAL TL KINETICS OF APOLLO 17 REGOLITH, AND PROSPECTING FOR WATER AND OTHER VOLATILES ON THE MOON. 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]. They also pointed out that particularly unstable TL peaks would fade in days-to-months unless the samples were kept in a freezer. At -20ºC mean-lives for peaks unstable at room temperature would increase to hundreds of years or so [2].

The relationship between natural TL and temperature became particularly interesting with the discovery of water in cold traps on the Moon [3]. 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, or remotely by robotic or crew-operated equipment on the surface [4].

In order to further our understanding of the natural TL properties of lunar materials and their kinetics, and take advantage of what is effectively a fifty-year experiment in which NASA stored Apollo 17 regolith samples in a freezer, we have measured the natural TL properties of eighteen Apollo 17 regolith samples. We received samples stored at room temperature in November 2021 and equivalent samples stored in a freezer at -20ºC in March 2022. To date, we have obtained natural TL data for all of the samples and completed about 50% of the required data reduction.

The fifty-year experiment: TL data are obtained as plots of light intensity against heating temperature. A single "glow curve" typically consists of several overlapping peaks each of which can be described by an activation energy, E, and Arrhenius factor, s.

Fig. 1 compares the glow curves for samples collected in the permanent shadow of station 6 boulder 4 and in direct sunlight obtained by ref. [1] in 1976 and our present results collected in 2022. Because Durrani used arbitrary units we cannot compare our curves directly but can compare the shapes by lining up the high temperature region where little change is expected. The natural TL in the 200ºC region of the glow curve has faded about 40% for the shaded sample but not for the sample in direct sunlight. This is as expected since TL in the 200ºC region is unstable on the decade timescale but TL in the 400ºC region is stable for billions of years.

Secondly, the ratio of the natural TL at 200ºC for the room temperature permanently shadowed regolith samples to that of the freezer samples is 0.60±0.14, i.e. similar to decay observed in Fig. 1. TL in this region of the glow curve is stable at -20ºC but not room temperature.
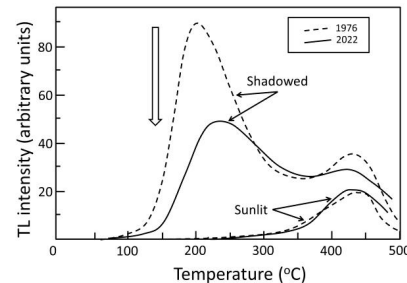

Fig. 1. The glow curves for Apollo 17 regolith samples collected in a boulder shadow and in direct sunlight as measured in 1976 and 2022. From ref [1,5].

The mean life, τ, of a TL peak is given by

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

where k is Boltzmann's constant and T is the environmental temperature. Laboratory measurement of E using the initial rise method [6] is, as expected, identical for room temperature samples (1.03±0.13 eV) and the freezer samples (1.06±0.14 eV). Calculating s from E and peak temperature using:

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

where β is the heating rate (7.5 ºC/s) and T_p is peak temperature, gives a value of 5.68 x 10^9 s^{-1}. This yields a mean life of 99 years so that decay after 50 years should be 50%, again consistent with Fig. 1. and the ratio of room temperature to freezer values.

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:

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

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 experiment, 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 their TL drain faster than it builds-up, while peaks in samples below their T_{eq} will build-up TL levels. This means that 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.
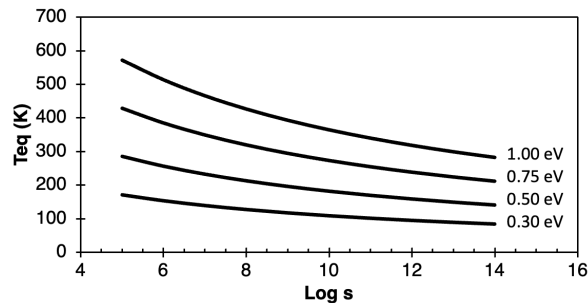

Fig. 2. Equilibrium temperatures (probably ±20ºC) for various values of E and s as calculated from equation 3 using data suggested by ref [1].

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 (that at 100ºC) for which we calculate a value for s of 6 x 10^{10} s^{-1}. This peak has a mean life of 16 min at room temperature and 1 year in a freezer at -20ºC. These E and s values correspond to an equilibration temperature of about 30ºC. Note that T_{eq} is well below the TL peak temperature of 100ºC.
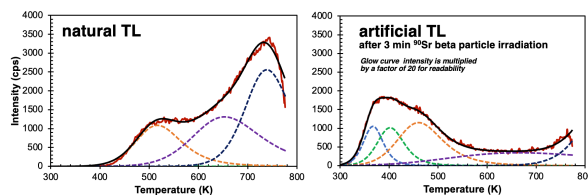

Fig. 3. Glow curves for Apollo 17 regolith sample 70004 in the natural state (left) and after draining the TL and irradiating with ^{90}Sr beta radiation (right).

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 liquid nitrogen temperature (-196 ºC) to 250ºC (Fig. 4). A strong peak at -100ºC is probably present in most silicates, such as lunar regolith.
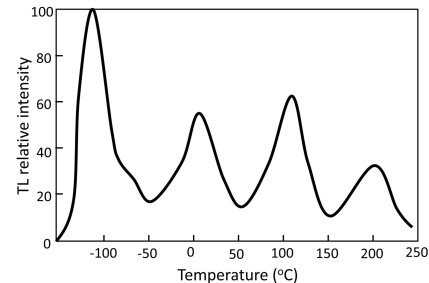

Fig. 4. A glow curve covering a temperature range of -196ºC (liquid nitrogen temperatures) to 250ºC for an aubrite (pyroxene-rich) meteorite [6].

If we assume an activation energy of 0.5 eV for a TL peak at -100ºC then we calculate an s value of 5.31×10^{14} s^{-1}. Referring to Fig. 2 this suggests an equilibration temperature around 100 K. In other words, the presence of a -100ºC peak indicates that the sample was stored at ≤100 K for a considerable time, i.e. the time it takes for the TL to reach equilibrium, which is on the order of 2×10^5 years. It could be a location for the storage of water and other volatiles.

These kinetics correspond to a mean life of 0.1 s in the best scientific freezer (-90ºC) but the TL would be infinitely stable (~1.2×10^{14} years) at liquid nitrogen temperatures (-196ºC). Thus, Durrani's arguments for low-temperature storage of lunar samples are even stronger if samples are returned from the permanently shadowed regions of the Moon [13].

References: [1] Durrani S.A. et al. (1976) *LPSC VII Proc.* 1157-1177. [2] Durrani, S.A. (1972). *Nature 240* 96-97. [3] Hayne, P.O. et al. (2021). *Nature Astronomy 5*, 169-175. [4] Sehlke A. et al. (2021). *NASA SSERVI ESF*. [5] Sehlke and Sears (2022) 53rd LPSC Abstract #1257 [6] Garlick G.F.J. (1949). *Luminescent Materials*. [7] Zhang S. et al. (2020). *Science Advances*, 6 (39), p.eaaz1334. [8] Malla, R.B. and Brown, K.M. (2015). *Acta Astronautica 107*, 196-207. [9] Paige, D.A. et al. (2010). S*cience 330,* 479-482. [10] Paige, D.A., et al. (2010). *AGU Fall Meeting Abstracts* (P31E-04). [12] Schorghofer, N. and Taylor, G.J. (2007). *JGR-Planets 112* (E2). [12] Sun K.H and Gonzales J.L. (1966) *Nature 212*, 23-25. [13] Mitchell J.L. et al. (2021). *52nd LPSC* (abs #1214).