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MEASUREMENT OF THE DECAY RATE OF THE SiH FEATURE AS A FUNCTION OF TEMPERATURE. Joseph A. Nuth III¹ and George F. Kraus^{1,2} (1. Code 691, NASA-GSFC, Greenbelt, MD: 2, Physical Sciences Dept., Charles County Comm. Col., LaPlata, MD)

We have previously suggested that the SiH fundamental stretch could serve as a diagnostic indicator of the oxidation state of silicate surfaces exposed to the solar wind for prolonged periods.¹ We have now measured the primary decay rate of SiH in vacuo as a function of temperature and find that the primary rate constant for the decay can be characterized by the following equation: $k \text{ (min}^{-1}) \approx 0.186 \exp(-9/RT) \text{ min}^{-1}$, where $R = 2 \times 10^{-3} \text{ kcal deg}^{-1} \text{ mole}^{-1}$. This means that the half-life for the decay of the SiH feature at room temperature is ~20 yrs, whereas the half-life at a peak lunar regolith temperature² of ~500K would be only ~20 days. At the somewhat lower temperature of ~400K the half-life for the decay is on the order of 200 days. The rate of loss of SiH as a function of temperature provides an upper limit to the quantity of H implanted by the solar wind which can be retained by a silicate grain in a planetary regolith. This will be discussed in more detail below.

Silica smokes were prepared by burning SiH₄ diluted in H₂ with O₂ in a tube furnace at ~750K.³ The resultant product was yellowish-tan SiO_x (where $x \approx 1.5$) and exhibited a relatively strong feature near 4.4 microns attributable to the SiH stretching fundamental in an oxidized silicate. Samples were stored in a dessicator. The smoke was diluted by about a factor of 20 with KBr and placed into the sample cup of a Harrick Environmental Chamber mounted in a Mattson Polaris FTIR spectrometer equipped to yield diffuse reflectance spectra. A background spectrum of pure KBr would have already been obtained in the same apparatus. The environmental chamber was then evacuated to a pressure of less than 1 torr using a mechanical pump and the temperature of the sample cup raised to the desired temperature. Once the temperature had stabilized at the set point an initial spectrum was obtained (A₀) and the system was programmed to obtain subsequent spectra at regular intervals: the mechanical pump was on throughout the experiment. The area under the SiH stretch ratioed to the area under the SiO stretch was then measured as a function of time to obtain the SiH decay rate at a given temperature. Measurements were obtained at 650, 700, 750 and 800 K.

Plots of $\ln[(A(4.6)/A_0(4.6))/(A(10)/A_0(10))]$ versus time for the data obtained at both 650 and 800 K yield simple first order decays. Similar plots for the data obtained at 700 and 750 K show two distinct components to the decay. In each case, the slower, long-lived decay yields a rate consistent with what would be expected by interpolation of the 650 and 800 K data points on an Arrhenius Plot; e.g. a process with an activation energy of approximately 9 kcal/mole. The faster decays yield an activation energy on the order of 60 kcal/mole but are only important at the very beginning of the experiments. If the process were a unimolecular rearrangement of the silicate lattice resulting in the elimination of the SiH bond it should dominate the decay for the entire experiment.

We hypothesize that the initial, fast decay of the SiH feature in these experiments is the result of chemisorbed oxygen atoms diffusing into the lattice of the amorphous silicate and reacting to displace the H atoms. This process would stop with the depletion of the chemisorbed oxygen. The activation energy of the process is consistent with that for the diffusion of oxygen through non-stoichiometric oxides.⁴ A calculation of the rate of the "fast" reaction at 650 K based on an extrapolation of the 700 and 750 K data shows that this process could account for roughly half of the initial loss of SiH before the oxygen is depleted: there is some evidence for this in the data. Unfortunately the signal to noise ratio

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depleted: there is some evidence for this in the data. Unfortunately the signal to noise ratio is too low to definitively separate the two decay processes in this dataset. A calculation of the rate of the "fast" reaction at 800 K indicates that the reaction is probably completed during the sample warmup and before we obtained our first spectra. We are in the process of analyzing data obtained in air and therefore hope to more definitively determine the mechanism for the rapid loss of SiH in the 700 and 750 K datasets.

Thermal decomposition of SiH should be the primary decay process on planetessimals and will set a limit on the quantity of SiH which one would expect to accumulate in regolith grains. Such grains should reach an equilibrium between H-implantation from the solar wind and thermal decomposition of the SiH on a timescale equivalent to a few decay halflives. For the lunar surface this will occur within a period of from several months for the subsolar regolith to several years for cooler regolith materials. Asteroidal regoliths at temperatures of 250, 200 and 150 K will equilibrate on timescales of 350, 27 thousand, and 38 million years, respectively (based on one e-folding timescale). Even considering the inverse square decrease in the density of the solar wind as a function of heliocentric distance, the much longer timescales available for the buildup of SiH bonds in asteroidal regolith grains make such bodies ideal candidates to detect this feature.

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Decay of the SiH Feature at 750K

