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The -SiH Vibrational Stretch as an Indicator of the Oxidation State of Silicon in a Cometary or Asteroidal Regolith

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Spectral features due to -SiH functional groups are observed to be extremely sensitive to the oxidation state of the "silicate" in which it is bound, ranging from 4.4 μm in highly oxidized grains to 4.74 μm in silicon carbide. Solar wind ions have been shown to chemically reduce exposed surfaces on the moon and it seems reasonable that such processes should also act on asteroidal surfaces, albeit at a reduced rate. If H-atoms in the solar wind are implanted in asteroidal surfaces undergoing solar wind sputtering, then the strength and position of the -SiH fundamental stretch could be used as an indicator of the relative age of the regolith. Observations to test this hypothesis could prove to be very exciting.

1. INTRODUCTION

The surfaces of comets and asteroids are continuously exposed to solar wind ions impacting at a velocity which varies between about 300 and 700 km/sec. Silicate minerals on such surfaces will therefore undergo ion-sputtering and ion-implantation at relatively low energies, e.g., 1–5 keV for H^+ ions and 4–20 keV for He^+ ions as well as higher energy heavy ions at considerably lower flux. Yin, Ghose, and Adler (1972a,b) have shown that solar wind sputtering of lunar surface materials leads to the chemical reduction of minerals in the lunar regolith due to the higher relative sputter-loss cross section of oxygen compared to that of heavier elements such as silicon or iron. Studies of the hydrogen (Epstein and Taylor 1971) or nitrogen (Kerridge 1989) content of lunar soils have demonstrated conclusively that solar wind ions are implanted in the lunar regolith. Similar processes should occur on exposed cometary and asteroidal surfaces, although the magnitude of the effects will depend upon the oribital history of the object and the age of the particular surface in question. In this paper we will demonstrate that there should be observable consequences of these processes, e.g., -SiH groups should be formed in the exposed silicates. It may be possible to use the -SiH signature to establish the relative ages of individual asteroidal surfaces.

We have measured the infrared spectra of amorphous silicate grains and films formed in a variety of laboratory experiments and have found that the energy of the -SiH fundamental vibration is extremely sensitive to the chemical environment of the grain in which the silicon is bound (Moore *et al.* 1991). The wavelength of this stretching vibration varies from a high of 4.39 μm in oxidized grains to 4.74 μm in a reduced solid. We have previously (Moore *et al.* 1991) suggested that -SiH may be an important diagnostic indicator of the chemical state of interstellar grains and here suggest that the position of the -SiH fundamental could serve a similar function for asteroidal and cometary surfaces.

Laboratory studies of the ion-implantation of H^- and D^+ into silicon at energies between 70 and 2500 keV showed the development of infrared features between 4.5–5.5 and 6.2–7.5 μm due to the formation of -SiH and –SiD groups, respectively (Stein 1975, Gerasimenko *et al.* 1978, Mukashev *et al.* 1985). Although these energies are considerably higher than those of the solar wind, Stein (1975) has shown that the H^- ion energy does not affect the position of the SiH features (e.g., see his Fig. 3) but does affect the depth to which the hydrogen is implanted and the ion damage profile within the crystal. Using his results one would predict that solar wind hydrogen ions

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(1–5 keV) would be implanted to depths of several hundred to a thousand angstroms in exposed asteroidal or cometary silicates. Of course, in the case of a comet, it is possible that -SiH groups may already be present in relatively pristine interstellar materials which become exposed at the surface due to the sublimation of water ice and the formation of a crust (Saunders *et al.* 1986) without the need for solar wind processing. In what follows we will briefly describe our experimental results and their application to the surfaces of planetesimals in the Solar System.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Silicon oxide smokes were prepared from a mixture of $SiH_4 + O_2$ in a hydrogen flow at temperatures ranging from 500 up to 1400 K in an experimental apparatus described by Nelson *et al.* (1987) and Nuth *et al.* (1988). In this system electronic grade silane (Air Products) is introduced into a flow of hydrogen (technical grade) then mixed with a stream of oxygen (technical grade) inside an alumina-lined, resistively heated, graphite furnace. Combustion of the silane and hydrogen occurs both inside the one-inch diameter, three-inch long alumina furnace tube and after the gas exits the furnace into a region nominally at room temperature. Smoke particles are collected on polished aluminum substrates and the infrared absorbance spectra of these smokes are obtained using a Mattson Polaris FTIR. Some of these samples were then exposed to either water vapor or vacuum at elevated temperatures and the changes in their infrared spectra were monitored at periodic intervals over many weeks (Tanabé and Nuth 1992) as the particles oxidized and lost hydrogen from the evolving silicate structure.

The infrared spectra of amorphous silicate grains condensed after combustion of SiH_4 and O_2 in hydrogen at a variety of furnace temperatures from 1370 to 470 K or exposed to various metamorphic influences have been published elsewhere (Moore *et al.* 1991). We generally find that the -SiH absorption feature in higher temperature grains occurs at shorter wavelengths than in grains condensed at lower temperatures. Exposure of the samples to air at room temperature, to water vapor at 370 K, and to mild vacuum at 370 K over a period of several months results in a slight shift of the -SiH peak to longer wavelength and a dramatic reduction in the intensity of the absorption.

Figure 1 shows the diffuse reflectance spectrum of a fresh silicate smoke sample (diluted in KBr) over the wavelength range from 2 to 5 μm (5000–2000 cm^{-1}) obtained using a Harrick Diffuse Reflectance Attachment and the Mattson FTIR. This sample was produced at a furnace temperature of ~1000 K. The strongest feature in this spectrum occurs at 4.4 μm with a secondary peak near 4.55 μm and a weak shoulder at 4.74 μm. It has been suggested (Cruickshank, private communication) that it would be observationally easier to detect the overtone of the SiH stretch (near 2.2 μm) rather than the fundamental, if the overtone were a strong transition. Unfortunately, the overtone does not appear to be a strong transition since no feature is evident above the background at 2.2 μm and the background from ~2.1 to 2.4 μm is relatively flat. We estimate that the strength of the overtone can be no more than a few percent of that of the fundamental.

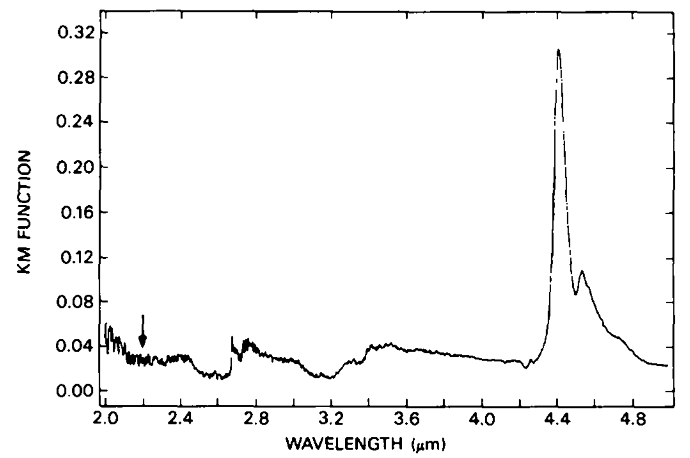

FIG. 1. Diffuse reflection spectrum of an Si_2O_3 smoke diluted in KBr over the wavelength range between 2 and 5 μm. The arrow indicates the expected position of the SiH overtone transition.

III. DISCUSSION

It is obvious from the work reported by Moore *et al.* (1991) that the wavelength of the -SiH fundamental is sensitive to the chemical environment in which the silicon atom resides; the higher the electronegativity of the surroundings, the shorter the wavelength of the fundamental. In the case of smokes condensed by the combustion of silane and oxygen in hydrogen, the smokes formed at the highest temperatures and which therefore should be most completely oxidized, all have very strong absorption near 4.4 μm. Smokes formed at lower temperatures and which are more likely to remain at least partially reduced, exhibit not only the strong absorption near 4.4 μm, but also weaker components near 4.52, 4.55, and 4.60 μm and possibly a very broad component near 4.76 μm. It is interesting that as these samples are oxidized in air at room temperature, features at longer wavelength are observed to be destroyed more rapidly than those at shorter wavelength.

Recent airborne and groundbased spectrophotometry of Comet Halley revealed the 10-μm emission band identified with the silicate material in cometary dust (Bregman *et al.* 1987). Spectra in the 2.5–5 μm region of Halley were obtained by the IKS-Vega instrument during its flyby through the coma of the comet. Several small and as yet unidentified features were reported in the 4.4–4.6 μm region which would be consistent with the position of the -SiH groups. Unfortunately no firm conclusions can be reached from these observations due to the poor signal-to-noise ratio of these small features (Moroz *et al.* 1987). However, if -SiH groups are incorporated into icy interstellar grains (Nuth and Moore 1988) or if a silicate regolith were exposed to the solar wind for many orbital periods, then one would expect to observe this feature in cometary materials.

In the case of asteroids we do not know of any observations of an asteroidal spectral feature in the wavelength range between 4.4 and 4.8 μm. However, due to the great difficulty in observing asteroidal reflectance spectra at these wavelengths it may not be surprising that the -SiH feature has remained undiscovered. Because it may prove to be possible to use the strength and position of this feature both as an indicator of the chemical state of an asteroidal regolith and as an indicator of the exposure age of the asteroidal surface (discussed below) we suggest that it may be worthwile to carry out an observational search for the -SiH stretch in the spectra of near-Earth and possibly even main-belt asteroids.

In the case of near-Earth asteroids and the lunar surface, where the blackbody temperature is on the order of 300 K or so, most of the energy in the 4–5 μm bandpass should be thermal emission. This is of course particularly true on the lunar nightside where there can be no interference from reflected sunlight. In these instances the SiH feature will appear in emission. Main-belt asteroids and Jupiter's Trojan population are much colder than either the lunar surface or the near-Earth asteroids and most of the 4–5 μm flux from these bodies will be reflected sunlight. The -SiH group should be observable as an absorption feature in these objects. -SiH should also appear in absorption in comets which have not yet developed a coma. Comets with comae present a much more complicated problem (Chyba and Sagan 1987) especially if -SiH groups are present in small grains in the coma. Blackbody temperatures of such grains can be considerably higher than the temperature of the cometary nucleus (Chyba *et al.* 1989). According to the study by Chyba *et al.* (1989) features near 5 μm should be prominent in emission at perihelion distances in the range 1.5–3 AU. At closer approach to the sun, emission features in this region become swamped by the continuum emission from the small grains in the coma.

It is interesting to note that no infrared reflection spectra are available in the literature for fresh lunar soils or rocks in the 4–5 μm region (C. Pieters, personal communication). Spectra should be obtained on materials which have never been exposed to the atmosphere if one would hope to observe the -SiH feature; our preliminary experiments show that exposure to the air or to water vapor results in a significant loss of SiH on timescales of months. If such a feature were to be observed in several lunar soils or rocks then it might be possible to calibrate the exposure age derived from the position of the -SiH feature with other measures of exposure age such as solar wind nitrogen or the intensity of ferromagnetic resonance. Such results might be scaled to provide semiquantitative ages for asteroidal surfaces.

The intensity of the solar wind varies over the solar cycle and as a function of heliocentric distance. However, quantitative calculations of the average rate at which an asteroidal surface becomes chemically reduced should be possible provided that its orbit is well determined and that suitable experimental studies of hydrogen implantation and solar wind reduction are undertaken. Even without laboratory calibration experiments it might be possible to use spectral comparisons of the 4.4–4.8 μm -SiH feature in asteroidal reflectance spectra as measurements of the relative exposure ages of bodies in similar orbits by determination of the intensity and position of the -SiH feature: a more intense, longer wavelength -SiH feature in a rocky asteroid would be indicative of an older surface. In a similar fashion if time-resolved spectra of slowly rotating asteroids are obtained over this wavelength range it would be possible to measure the relative age of individual asteroidal surfaces on several asteroidal bodies. Because of the difficulty of observing asteroidal surfaces over this wavelength range from the ground, such measurements may require spacebased observations to obtain the required signal-to-noise level in short enough times to spatially resolve spectral features such as the -SiH stretch on individual surfaces.

V. SUMMARY

We have experimentally shown that the position of the -SiH fundamental vibrational stretch is very sensitive to the chemical environment surrounding the silicon atom. In particular, silicon in an oxidizing environment will exhibit an -SiH feature near 4.4 μm, whereas silicon in a reducing grain could be responsible for a feature at 4.74 μm. As an oxidized grain is reduced, the -SiH fundamental shifts to longer wavelengths through a series of intermediate bands. Based on our laboratory experiments and the assumption that most silicon will initially reside in highly oxidized environments in chondritic asteroids, we predict that when observations are possible over the entire region between 4 and 5 μm, a feature due to -SiH should be observed near 4.4–4.8 μm. Furthermore, it is possible that a number of additional features could be observed due to SiH in a variety of more reducing, and therefore older, environments. Observations of both asteroids and comets between 4 and 5 μm could be extremely informative and should be carried out at the first available opportunity.

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