Long-Term Water Vapor Weathering of Taurus Littrow Orange Soil: A Pore Structure Analysis by D. A. Cadenhead, Department of Chemistry, State University of New York at Buffalo, Buffalo N.Y. 14214 and R. Sh. Mikhail, Department of Chemistry, Ain Shams University, Cairo.

In a previous publication [Cadenhead and Stetter (1974)] following outgassing at 150° and 300°C a sequence of water vapor adsorption-desorption cycles were described for sample 74220,46. The sample showed extensive changes in surface area presumably accompanied by changes in pore structure. The present study concerns two important aspects of this subsequent work:

1. A detailed pore structure analysis of all data obtained with this sample.
2. A study of the effects of a long-term (6 months) exposure to water vapor at low relative pressures.

The pore structure analysis was carried out initially by obtaining volume adsorbed verses statistical thickness of the adsorbed layer, \((V_x-t)\) plots [Lippens et.al (1964)]. From such a plot it is possible to deduce the existence of micro-(4-20\(\text{Å}\)) radius) and meso-(20-500\(\text{Å}\)) radius) pore structure. Subsequently, the data was further analysed to provide a "core" size distribution in accordance with the "model-less" method of Brunauer et.al. (1967). This distribution utilizes a hydraulic radius (volume:surface ratio) and plots the rate of change of core volume (capillary volume less the adsorbed layer) with change in hydraulic radius, as a function of the hydraulic radius. Finally, using the total volume and total surface area as criteria, a fit may be made to an actual pore distribution when a selection is made of a pore-shape model. This treatment has been applied to the data of Cadenhead and Stetter (1974) as well as to new data obtained by us following a lengthy (6 month) exposure to water vapor. For the sake of clarity we will refer here to the sample as "fresh"
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[data of Cadenhead and Stetter (1974)] or "aged" [new data].

Following the outgassing of the fresh sample at 150°C only wide (meso-) pores could be detected during the initial adsorption isotherm. However, after exposure to water vapor at saturation vapor pressure, the subsequent desorption and resorption isotherms clearly reflect the presence of both meso- and macropores. The new micropores would appear to be predominately parallel plate pores. If the adsorption and resorption isotherms reflect true equilibrium, the micropores would appear to have a hydraulic radius of about 3 to 3.5Å. Heating the fresh sample to 300°C during outgassing appears to leave the mesopores essentially unchanged, however, the number of micropores (of the same radius) was substantially increased.

With the aged sample (exposed for six months) both the surface area and the total volume adsorbed underwent a decrease. Compared to the fresh sample [Cadenhead and Stetter (1974)] the irreversibility of the isotherm (hysteresis) is very much reduced and is confined to higher relative pressures. A stable structure appears to have formed which consists primarily of micropores. In addition, aging appears to have widened the wider (meso) pores and narrowed the micropores [the average hydraulic radius was reduced to approximately 2.5Å]. The stability of the structure was indicated by the fact that essentially the same pore-size distribution was obtained when the sample was outgassed at 150°C and 300°C.

The analysis clearly indicates that exposure of 74220 to water vapor has resulted in significant changes in the pore-size distribution. In particular, we observe the appearance of large numbers of micropores, which in turn results in corresponding changes in the sample surface area. These pores are apparently produced by exposure of the sample to high relative pressures of
water vapor, suggesting the fracturing has occurred forming pores of approximately 10Å diameter. Outgassing at higher temperatures with the fresh sample, enhanced the number of micropores indicating that the higher temperature was required to remove "water" blocking these fine pores. Based on the change of the isotherm in the low pressure region [Cadenhead and Stetter (1974)], at least part of the water removed must have been originally present as hydroxyl groups. The stability of the aged sample suggests that any hydroxyl groups now formed are more stable since 300°C was not a high enough temperature to remove them. The widening of the wide pores and the narrowing of the narrow pores is suggestive of a process of surface diffusion. In addition to narrowing the radius of the micropores, clearly, this process of surface diffusion could result in pore blocking and explain the observed decrease in surface area and adsorbate volume. It may be that eventually the entire aging process would result in a total elimination of all the micropore region created at higher relative pressures, and would reproduce the original low surface area sample possessing only mesopores. Finally the fracturing process referred to presumably relates to the partially crystalline nature of this sample.

References