Further evidence on the formation of water due to radiolysis is observed in the post irradiation TPD as shown in Figure S1. The boehmite sample was first annealed at 500 K following a controlled temperature ramp of 2 K per min while monitoring the amount of water desorbing into the gas phase with a commercial residual gas analyzer. In order to ensure that no residual water from the chamber was adsorbing onto the surface during cool down, a second annealing was conducted with the same operational parameters. No adsorbed water was observed desorbing from the surface in this temperature range. After the second annealing of the sample up to 500 K and subsequent cooling to room temperature, the sample was irradiated with 200 eV electrons at 5µA for 60 mins while scanning over the boehmite film. Upon which, a standard TPD experiment was conducted with the same established parameters. A subtle but clear peak is observed in the post irradiated TPD at approximately 370 K as shown in the left side of Figure S1 and in the normalized differential plotted on the right side of Figure S1 displayed for sake of clarity. The difference in the TPD profile is most likely attributed to the creation of defects through electron bombardment or reduction of the surface that altered the distribution of binding sites for water.
Figure S1: TPD spectra of the boehmite sample up to 500 K. Black line reveals the small desorption peak of molecular water from the high binding sites at 400 K. Red line shows that no residual water adsorbed onto the surface during cool down under vacuum for 12 hours. Blue line is the post irradiation TPD profile that displays a small peak at 360 K which is attributed to physibound molecular water. The profile is different from the original as deposited sample as electron irradiation most likely produced a surface with defects that changed the distribution of binding energies. On the right is the differential of the TPD for sake of clarity.

Figure S2: Normalized ion counts for D$^+$ (black line) resulting from electron impact dissociation of gas phase D$_2$ plotted with HDO$^+$ (red line) during exposure to deuterated hydrogen. A clear increase in HDO is observed when D$_2$ gas is present. Once the D$_2$ is removed, a slow decay resulting from the stimulated removal of residual bound HDO is observed. A second pulse of D$_2$ gas was introduced into the chamber later with a lower pressure ($1 \times 10^{-7}$ torr) yielding similar results with slightly delayed onset due to the lower collision frequency.

Additionally, shown in Figure S2 are the normalized ion counts for D$^+$ and HDO$^+$ while flooding the chamber with D$_2$ gas. A clear correlation is observed between the HDO$^+$ and D suggesting that water is formed on the surface of boehmite via a reaction between D radicals and the surface hydroxyls. Once the D$_2$ gas is evacuated from the chamber, the HDO$^+$ signal slowly decays.
compared to the immediate reduction in $D_2^+$ signal. This indicates that the HDO signal is from residual bound isotopes of water on the surface of the boehmite and not an artifact of pumping speeds, i.e. $D_2$ is removed relatively instantly while HDO lingers for almost an hour post $D_2$ exposure. A second pulse of $D_2$ gas was introduced into the chamber later at a reduced partial pressure of $1 \times 10^{-7}$ torr. Here, an increase in HDO$^+$ is again observed as well with a slight delay. The delay in the onset is attributed to the reduced collisional frequency and lower D atom density associated with the lesser background pressure. This and the very low $H_2O$ neutral number density allows us to rule out gas-phase ion molecule reactions.