ABSTRACT. The survival of spacecraft payloads during hypersonic, high temperature atmospheric entry is largely dependant on the presence of a carbon-phenolic composite thermal protection system (TPS), which reduces heat transferred to the vehicle wall via ablation and pyrolysis. Recent findings have shown that in-depth reactions of the phenolic release highly absorbing gases, eventually leaving the carbon preform exposed to its high enthalpy environment, where internal radiation dominates at high temperatures. This work evaluates the changes in radiative properties of two TPS material samples before and after pyrolysis by solving the homogenised radiative transfer equations (RTEs) using Monte Carlo techniques in the limit of geometric optics. The effective radiative properties required in the homogenised RTEs are determined by Monte Carlo techniques utilising the real 3D geometries of the samples obtained by high resolution synchrotron computerised tomography. The samples chosen are a medium density carbon phenolic and a high density graphite, each composed of semi-transparent solid and fluid phases. Pyrolysis gas evolution is seen to significantly affect the absorption behaviour of the TPS samples. The absorptance during pyrolysis increases from 0.77 to 0.81 for carbon-phenolic and from 0.76 to 0.78 for graphite.