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Is ozone a reliable proxy for molecular oxygen?

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Molecular oxygen (O2) paired with a reducing gas is regarded as a promising biosignature pair for atmospheric characterization of terrestrial exoplanets. In circumstances when O2 may not be detectable in a planetary atmosphere (for instance, at mid-IR wavelengths) it has been suggested that O3, the photochemical product of O2, could be used as a proxy to infer the presence of O2. While O3 is not directly produced by life, it plays an important role in habitability as the ozone layer is the primary source of UV shielding for surface life on modern Earth. However, O3 production is known to have a nonlinear dependence on O2, as well as being strongly influenced by the UV spectrum of the host star. To evaluate the reliability of O3 as a proxy for O2 we used Atmos, a 1D coupled climate/photochemistry code, to study the O2-O3 relationship for "Earth-like'' habitable zone planets around a variety of stellar hosts (G0V-M5V) for O2 abundances from 0.01%-150% of the Present Atmospheric Level (PAL) on modern Earth. We studied how O3 emission features for these planetary atmospheres varied for different O2 and O3 abundances using the radiative transfer code PICASO. Overall we found that the O2-O3 relationship differed significantly around different stellar hosts, with different trends for hotter stars (G0V-K2V) than cooler stars (K5V-M5V). Planets orbiting hotter host stars experience an increase in O3 when O2 levels are initially decreased from the present atmospheric level, with maximum O3 abundance occurring at 25-55% PAL O2. Although this effect may seem counterintuitive, it is due to the pressure dependency on O3 production, as with less atmospheric O2 incoming UV photons capable of O2 photolysis are able to reach lower (denser) regions of the atmosphere to spark O3 formation. This effect is not present for planets orbiting our cooler host stars (K5V-M5V), as the weaker incident UV flux (especially FUV flux) does not allow O3 formation to occur at dense enough regions of the atmosphere such that the faster O3 production outweighs a smaller source of O2 from which to create O3. As a result, for cooler host stars the O3 abundance decreases as O2 decreases, albeit nonlinearly. Interpretation of O3 emission spectral features was found to require knowledge of the atmosphere's temperature profiles -particularly the temperature differences between the planetary surface and stratospheric temperature- which are highly influenced by the amount of stratospheric O3. Planets experiencing higher amounts of incident UV have more efficient O3 production and UV absorption leading to larger stratospheric temperature inversions, and therefore shallower emission features. Overall it will be extremely difficult (or impossible) to infer precise O2 levels from an O3 measurement, however, with information about the UV spectrum of the host star and context clues, O3 will provide valuable information about potential surface habitability of an exoplanet.