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## Interactive comment on "The observation of chemiluminescent NiO<sup>\*</sup> emissions in the laboratory and in the night airglow" by W. F. J. Evans et al.

## Anonymous Referee #3

Received and published: 1 June 2011

This paper reports that emission from electronically excited NiO can be observed in the earth's nightglow by limb-viewing spectrometers on satellites. If correct, this would represent an important new discovery. However, the first two reviewers have raised a number of valid concerns which need to be addressed by the authors. Here I want to focus on the apparent ratio of the NiO/FeO airglow emission intensities. The authors compare this ratio to the meteoritic abundances of these elements (Ni/Fe = 6%), which is roughly what is observed with one set of measurements (Osiris), and then hypothesise that when the ratio of the spectral emission is around 3:1 (GLO measurements) this is due to an influx of Ni-rich meteoroids. There are a whole host of problems with this section of the paper:

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1. The kinetics of the reactions of Fe + O3 and FeO + O have been measured (by John Plane's group) and are fast, essentially gas kinetic. The kinetics of the analogous reactions of Ni (R2 and R3 in the paper) have not been measured, so the recycling efficiency is not known (NiO is likely to recombine with O2 and H2O, and react with O3, so if R3 is a bit slower than gas kinetic then Ni will be quickly converted to potentially stable reservoirs).

2. Even if we assume that R2 and R3 are fast (which is likely to be the case), the quantum yield(s) to produce electronically excited NiO in the light-emitting state(s) is (are) not known. Indeed, there is a serious question as to whether the laboratory estimate of a 2% yield for Fe + O3 producing the FeO orange arc band emission can account for the observed FeO emission in the nightglow. Thus, taking the ratio of two emission intensities produced by mechanisms with essentially unknown quantum yields is almost meaningless.

3. A final assumption (unstated in the paper) is that both Fe and Ni ablate with the same efficiency from incoming meteoroids, which have a huge mass range and velocity distribution. Given that differential ablation is now a well-established phenomenon (explaining the very small quantity of atomic Ca in the upper mesosphere, for example), the authors need to explain why they consider that these two metals will ablate with equal efficiency. No other metals of those which are observable by lidar (Na, K, Fe and Ca) appear to ablate in their meteoritic ratios (see papers by von Zahn, Murad and Plane).

4. The authors should also note that although there have been plenty of attempts to see evidence of individual meteor showers affecting the background metal layers in the upper mesosphere, there is no conclusive evidence that meteor showers add much more material to the atmosphere, even on a timescale of less than a day, than the continuous input of sporadic meteoroids (see, e.g., papers by Grebowsky).

For these reasons I would suggest removing much of the discussion relating the air-

glow emission ratios to the meteoroid metal ratios. Instead, the paper should focus on showing more evidence that this residual emission really could be from NiO. For instance, it is stated that the emission has a similar altitude profile to the FeO emission – it would be useful to see this evidence in more detail.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 11839, 2011.

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