

## **Interactive comment on “Chemical characterization of atmospheric ions at the High Altitude Research Station Jungfraujoch (Switzerland)” by Carla Frege et al.**

**Anonymous Referee #2**

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The review is uploaded as a supplement.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-709/acp-2016-709-RC3-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-709, 2016.

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Review of: “Chemical characterization of atmospheric ions at the High Altitude Research Station Jungfraujoch (Switzerland)” by Frege et al., submitted to *Atmospheric Chemistry and Physics Discussions*

This manuscript reports field observations of atmospheric ions measured with the Atmospheric Pressure interface Time-of-Flight (APITOF) mass spectrometer at Jungfraujoch, Switzerland. Measurements were taken over nine months at high altitude. The authors discuss several classes of ions measured by APITOF during the study, including bisulfate and halogen containing ions. The authors often observed a diurnal cycle for bisulfate containing ions, although they also occasionally observed their presence at nighttime. Halogen ion intensities were observed to be more abundant in the morning and evening, and the authors postulate photochemical degradation pathways as a reason for the low intensities during the daytime. The authors also provide some evidence for a marine or coastal origin of these ions through backward dispersion models.

This work is relevant because very few reports of ion composition at high altitude exist. The manuscript is within the scope of *Atmospheric Chemistry and Physics* and is written clearly with interpretable figures. This manuscript may eventually be publishable in *Atmospheric Chemistry and Physics* if the authors carefully address the comments below.

**Major Comment:** In the discussion of halogenated species (section 3.2, page 8, lines 12-32) the authors postulate explanations for the observations of ions such as Br<sup>-</sup>, IO<sub>3</sub><sup>-</sup>, and CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> at enhanced abundances at sunrise and sunset and during the nighttime (page 8, lines 12-14). The authors suggest that photochemical halogen chemistry may deplete the abundance of these ions during the daytime. Although it is possible this is the case, there appears to be an important assumption underlying the interpretation of the time dependent ion abundances that the authors have not addressed. Sulfuric acid is photochemically created during the daytime and its ion abundance increases substantially during the day. However, sulfuric acid also very effectively competes for the limited charge present in the atmosphere. As a result, and as illustrated in Fig. 2, most non-sulfate-containing ions are anticorrelated with bisulfate/sulfuric acid clusters. This anticorrelation does not necessarily indicate that the total concentration of these species (ion + neutral) is varying, only that the ion abundances are varying, potentially due to charge migrating to sulfuric acid clusters. The discussion of the halogens suggests that the observations of maximum abundances during solar minima are due to photochemistry removing the halogen-containing ions. However, it seems equally plausible that the enhanced abundances of halogen-containing ions are due to an overall decrease in sulfuric acid abundance that results in charge migrating to ions that otherwise could not outcompete sulfuric acid. The authors do very briefly allude to this subject in the discussion of Fig. 2 (page 6, line 25), but the discussion is insufficient. It seems to this reviewer that except for perhaps sulfuric acid it would be extremely difficult to draw any conclusions about chemical processes occurring from the time dependent measurements alone, as ion abundances do not necessarily indicate formation or destruction of chemical species.

**Other Comments:**

1. The explanation of the back trajectories in Fig. 7B and 7D was not clear to this reviewer (page 9, lines 9-11). Does a positive value in the relative footprint back trajectory

**Fig. 1.**

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