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Key Points:
- First in situ detection of the continuous presence of several metal ion species in the upper atmosphere of Mars
- New, non-Earthlike metal ion features discovered due to absence of an intrinsic magnetic field
- Departure of vertical metal ion distributions from anticipated diffusion processes and metal ion track atmospheric gravity waves

Supporting Information:
- Supporting Information S1

Correspondence to:
J. M. Grebowsky,
joseph.m.grebowsky@nasa.gov

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Unique, non-Earthlike, meteoritic ion behavior in upper atmosphere of Mars

J. M. Grebowsky[1], M. Benna[1,2], J. M. C. Plane[3], G. A. Collinson[1,4], P. R. Mahaffy[1], and B. M. Jakosky[5]

[1]NASA Goddard Space Flight Center, Greenbelt, Maryland, USA, [2]CSST, University of Maryland, Baltimore County, Baltimore, Maryland, USA, [3]School of Chemistry, University of Leeds, Leeds, UK, [4]Institute for Astrophysics and Computational Science, The Catholic University of America, Washington, District of Columbia, USA, [5]Laboratory for Atmospheric and Space Physics, University of Colorado Boulder, Boulder, Colorado, USA

Abstract Interplanetary dust particles have long been expected to produce permanent ionospheric metal ion layers at Mars, as on Earth, but the two environments are so different that uncertainty existed as to whether terrestrial-established understanding would apply to Mars. The Mars Atmosphere and Volatile EvolutioN (MAVEN) mission made the first in situ detection of the continuous presence of Na^+, Mg^+, and Fe^+ at Mars and indeed revealed non-Earthlike features/processes. There is no separation of the light Mg^+ and the heavy Fe^+ with increasing altitude as expected for gravity control. The metal ions are well-mixed with the neutral atmosphere at altitudes where no mixing process is expected. Isolated metal ion layers mimicking Earth's sporadic *E* layers occur despite the lack of a strong magnetic field as required at Earth. Further, the metal ion distributions are coherent enough to always show atmospheric gravity wave signatures. All features and processes are unique to Mars.

Plain Language Summary We have extensive knowledge of metal ion layers in the Earth's ionosphere resulting from the atmospheric ablation of interplanetary dust particles. Understanding of potential ionospheric metals in other planetary atmospheres has been based primarily on our terrestrial understanding and the inference of their presence on other planets from radio occultation measurements of low-altitude electron density layers. The ion measurements from the Mars Atmosphere and Volatile EvolutioN (MAVEN) spacecraft, now orbiting Mars, have now corroborated the continual presence of metal ion species in the Mars ionosphere. Further, these metal ion distributions are drastically different from those at Earth because the terrestrial ions are strongly affected by the Earth's intrinsic magnetic field, whereas Mars has no such field. Unique Mars metal ion structures have been encountered that have no counterpart in the Earth's ionosphere.

1. Introduction

The persistence of atomic metal meteoric ion debris from ablated interplanetary dust particles (IDPs) entering at high speed in the upper atmosphere of Earth was first observed in situ via sounding rocket in 1963 [*Istomin*, 1963]. The main metal ion species are Mg^+ and Fe^+ [e.g., *Kopp*, 1997] because of the dominance of their neutral species in the IDP composition [*Anders*, 1989]. The main terrestrial metal ion peak is typically around 95 km with much variability in structure particularly above the peak. The average terrestrial global and seasonal properties of the main metal ion layer have been extensively modeled [e.g., *Plane et al.*, 2015], globally measured remotely from satellites [*Langowski et al.*, 2015], measured in situ from a limited number of sounding rockets [*Grebowsky and Aikin*, 2002], and inferred from extensive ground-based lidar measurements of primarily neutral metal species [*Plane et al.*, 2015]. The metal ions on the topside of the main terrestrial metal ion layer arise primarily from charge exchange of the ablated neutral metal species with the ambient ionosphere ions and/or by upward diffusion from the main ablation region.

Below 130 km, the main loss route for Fe^+ is via production of FeO^+, either by reaction with O_3 or, more importantly, by recombination of Fe^+ and CO_2 followed by reaction with atomic O. The FeO^+ then undergoes dissociative recombination with electrons (Table S1 in the supporting information). Above 130 km, dielectronic recombination of Fe^+ with electrons is faster than the conversion of Fe^+ to Fe via these ion-molecule reactions. Even so, the lifetime of Fe^+ against dielectronic recombination is around 6 days at 130 km and 12 days at 150 km, so that transport by winds and electric fields should dominate over chemistry. They can be

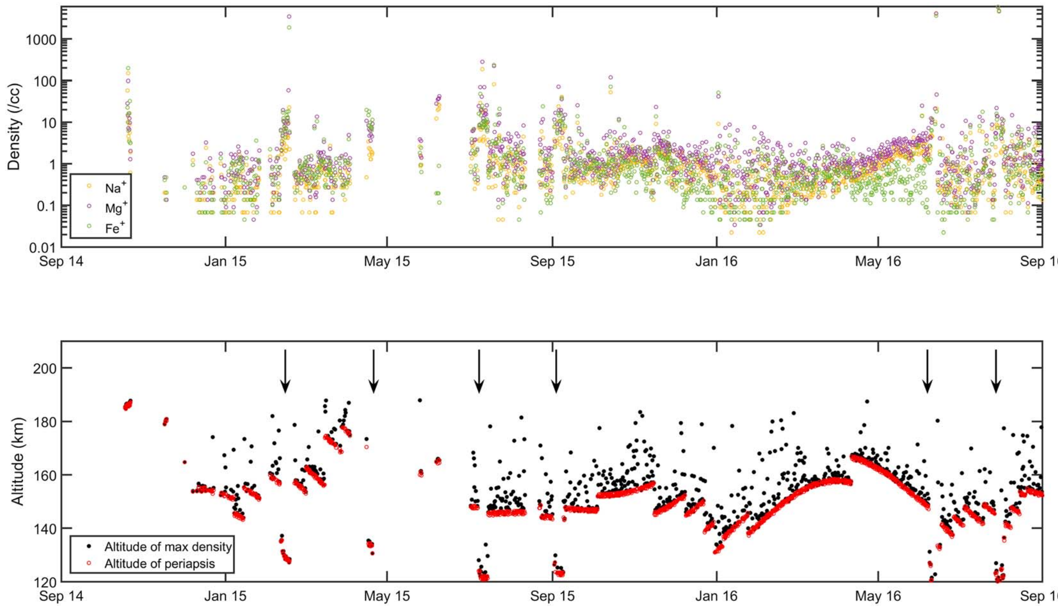

Figure 1. Complete ensemble of metal ion samples. Orbit-by-orbit set of NGIMS measured Mg^+ and Fe^+ maximum concentrations. Data are from the time of Comet Siding Spring encounter in September 2014 until August 2016. The altitude of each orbit's periapsis and the altitude of the maximum metal ion density of each orbit are shown on the bottom. As anticipated for a low-altitude ablation source for the metal ions, higher concentrations are typically observed with decreasing altitude, most notably during the deep-dip campaigns (marked by arrows) to altitudes below 130 km. Note, however, that the maximum concentration is not always observed at the lowest altitudes—evidence of high-altitude sporadic metal layers. The dominance of either Fe^+ or Mg^+ concentrations varies throughout the period with more variability seen in Fe^+ than Mg^+.

transported long distances and have been detected at altitudes as high as 400 km [*Kumar and Hanson*, 1980] and act as good tracers of atmospheric/ionospheric dynamic processes.

The terrestrial metal ion distributions at altitudes above the main chemically controlled metal ion layer are dominated by transport processes that depend on the magnetic field and the neutral wind [*Grebowsky and Aikin*, 2002; *Carter and Forbes*, 1999]. Although well studied, the major characteristics of the topside metal ion layer are its complex structure and temporal variations. Interest in them persists because of the clues and frequent discoveries they provide for exploring meteoric properties, atmospheric dynamics, fundamental chemical processes, and ionospheric structures at low altitudes [e.g., *Plane et al.*, 2015; *Carter and Forbes*, 1999].

It has been commonly accepted that every planet or moon with an atmosphere has upper atmospheric metal ion layers resulting from the high-speed deposition and subsequent ablation of solar system dust particles. Evidence for this is based on planetary spacecraft radio occultation measurements, particularly for Mars and Venus, of isolated electron density layers sometimes seen below the main ionospheric peak [*Pätzold et al.*, 2005, 2009]. These were at altitudes (~75–105 km) consistent with where meteoric ablation should occur [*Molina-Cuberos et al.*, 2008; *Grebowsky et al.*, 2002]. However, definitive proof for the existence of meteoric ions on planets other than Earth did not exist until upper atmospheric ion composition measurements were taken from the Mars-orbiting Mars Atmosphere and Volatile EvolutioN (MAVEN) spacecraft during the close Mars encounter by the comet Siding Spring in 2014. Ionospheric consequences of the dust coma of this high-speed comet were measured in situ by the MAVEN Neutral Gas and Ion Mass Spectrometer (NGIMS) and remotely by the Imaging UltraViolet Spectrograph in the form of metal ion species detected from ~100 km to altitudes above 300 km that persisted for days after the comet departure [*Benna et al.*, 2015; *Schneider et al.*, 2015]. The new NGIMS measurements, to be described below, show for the first time from in situ measurements that the metal ions are indeed a ubiquitous ionospheric feature. Several metal ion species and their isotopes have been, and are, continuously observed by NGIMS at low altitudes on most of MAVEN's orbits, particularly on all specially planned deep-dip orbits when the spacecraft periapsis was as

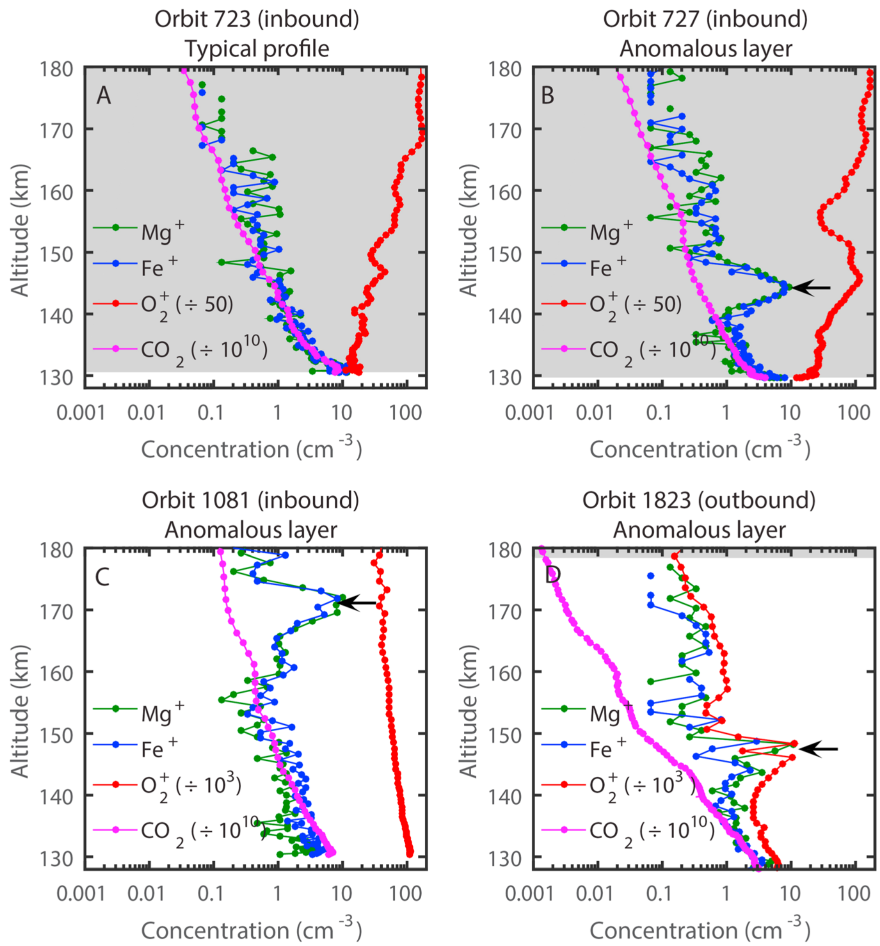

Figure 2. Metal ion profile features. Characteristic structures are shown down to periapsis on four deep-dipping orbits. Relevant measurements of the main ionosphere ion O_2^+ and the major CO_2 neutral species are also shown. The shading indicates measurements in the shadow of the planet. Typical trends include the following: dropoff of the metal ion concentrations follows closely the CO_2 scale heights; isolated high-altitude metal ion peaks are pointed to that are sometimes associated with ambient ionosphere disturbances at night and near the terminator; and oscillations in the metal vertical distributions.

low as 120 km. The question to be explored in this paper is as follows: are the Mars metal ions controlled by the same physical processes as those at Earth or are they uniquely different?

2. Observations and Inferences

Figure 1 depicts the entire ensemble of Mg^+ and Fe^+ measurements from MAVEN. Na^+ is another species detected, but this paper will focus on only the properties of the two most dominant measured species Fe^+ and Mg^+. There is no comparable long-term data set of simultaneous measurement of these species on Earth. As on Earth [e.g., *Grebowsky and Aikin*, 2002] the dominance of Mg^+ or Fe^+ on Mars changes from one measurement campaign to another. At either planet, one might expect Fe^+ to be less dominant with increasing altitude because of the gravitational mass separation anticipated for diffusion processes. On Earth, however, observations made above the main ionospheric metal ion layer are often characterized by complex layers associated with electrodynamic sources, with no clear trend of ordered metal ion concentration decreases with increasing altitude. Figure 1 also shows that there are many MAVEN orbits along which the maximum metal ion concentration was encountered at altitudes above periapsis, indicative of isolated high-altitude layers of the metal ions as at Earth.

Figure 2 shows samples of the metal ion altitude structures observed along orbits from "deep-dip" campaigns (5 day duration and orbital period ~ 4.5 h) when periapsis was below 130 km altitude. Typically, the metal ion concentrations were very low ($<10\,cm^{-3}$), approaching the sensitivity limits of most terrestrial in situ spectrometer measurements. Nevertheless, even at these low concentrations, the Mars ions have an average orderly-like decrease with altitude, as shown in Figure 2a. High-altitude sporadic metal ion layers are also encountered—seen as nearly order of magnitude density enhancements above the altitude decreasing background profiles (see Figures 2b–2d).

At Earth, the generation of isolated metal ion layers, above the main meteoric ion layer, requires the control of ions by neutral winds, or magnetospheric-induced electric fields, in a large magnetic field background [e.g., *Grebowsky and Aikin*, 2002; *Carter and Forbes*, 1999]. However, Mars has no intrinsic global magnetic field and the strength of the Martian surface remanent magnetic fields appears mostly insufficient to support any known terrestrial formation mechanism. Possible formation mechanisms are conjectured: the transport of long-lived metal ions by ambipolar electric fields associated with vertical variations in the ambient ionosphere [*Schunk and Walker*, 1972]; neutral wind shears dragging ions across horizontal ionospheric density gradients; for the highest layers, magnetic fields may come into play as collision frequencies drop off with altitude through the exobase transition; and convergence of the ions by neutral wind shears. It should be noted that neutral winds can drag the layers away from their points of origin, so there may not be local correlation of the layers with magnetic fields in all cases. Lastly, maybe vertical neutral wind velocities have sufficiently large vertical gradients that through drag lead to convergence of the metal ions. Whatever the source is, there is evidence shown in Figure 2 that the metal ion disturbances are sometimes associated with ambient (O_2^+) ionospheric perturbations. These anomalous Martian metal ion layers at first look do not appear to be clearly explainable by established terrestrial metal ion layer physics.

In addition to the transient layer disturbances, the background undisturbed concentration profiles of the metal ions also have unexpectedly non-Earthlike characteristics. Figure 2a is an example where the metal ion concentrations drop off on average monotonically with increasing altitude, unlike at Earth where above the main meteoric peak the metal ion distributions typically show disturbed complex layers and no such orderly concentration decreases with altitude. Another observation to note is that the decay of the Martian metal ion densities with altitude tends to match closely the falloff of the atmosphere (CO_2) concentration. This behavior is also observed during the anomalous layer orbits (Figures 2b–2d), at altitudes above and below the sporadic metal ion layers.

This unexpected correlation with the neutral atmosphere is demonstrated further in Figure 3, which shows the average properties of metal ions and neutral CO_2 for each of the first four deep-dip campaigns. The average decay of the Mg^+ and Fe^+ concentrations with increasing altitude closely matches the falloff rate of the neutral atmosphere density. Since the metal ions are long-lived in the altitude regime region considered (days to a week) [*Whalley and Plane*, 2010], the close similarity of CO_2 and metal ion scale heights indicates a well-mixed atmosphere with the metal ions behaving like inert minor atmospheric species [e.g., *Banks and Kockarts*, 1973]. Such close correlation in scale heights would be expected were these data taken below the homopause, the boundary below which the atmosphere is well mixed through turbulent diffusion. However, these data were taken when MAVEN was well above the homopause, located below 130 km [*Jakosky et al*., 2017]. Thus, such pseudomixing at the higher altitudes is currently a puzzle. Above the homopause, it is expected that molecular diffusion would take over, resulting in a gravity mass separation of the heavy Fe^+ from Mg^+ with increasing altitude (see material). This is clearly not observed. There is no significant departure of the two species' concentrations from one another with increasing altitude.

Other prominent features of the metal ions are seen in Figure 3. First, the average metal ion concentrations and the Mg^+/Fe^+ ratio vary from the location of one deep-dip campaign to another. The largest ion concentrations were seen during the mid-day second campaign (Figure 3b). Mg^+ was the most dominant species for deep-dip campaign 3 (dusk terminator, southern hemisphere, Figure 3c), whereas during deep-dip campaign 2 (subsolar region, Figure 3b), Fe^+ was the most dominant species. The ratio Mg^+/Fe^+ averaged over 130–140 km was 1.54 ± 0.18 for the former and 0.86 ± 0.064 for the latter campaign—the smallest ratio of all the campaigns.

The only published modeling of the Martian metals [*Whalley and Plane*, 2010] using established one-dimensional diffusion physics and measured reaction rate coefficients for the important ion-molecule chemistry involved came to the conclusion that Mg^+ would be dominant. Further details of such modeling appear in the supporting information [*Badnell*, 2006; *Bones et al*., 2016; *Florescu-Mitchell and Mitchell*, 2006;

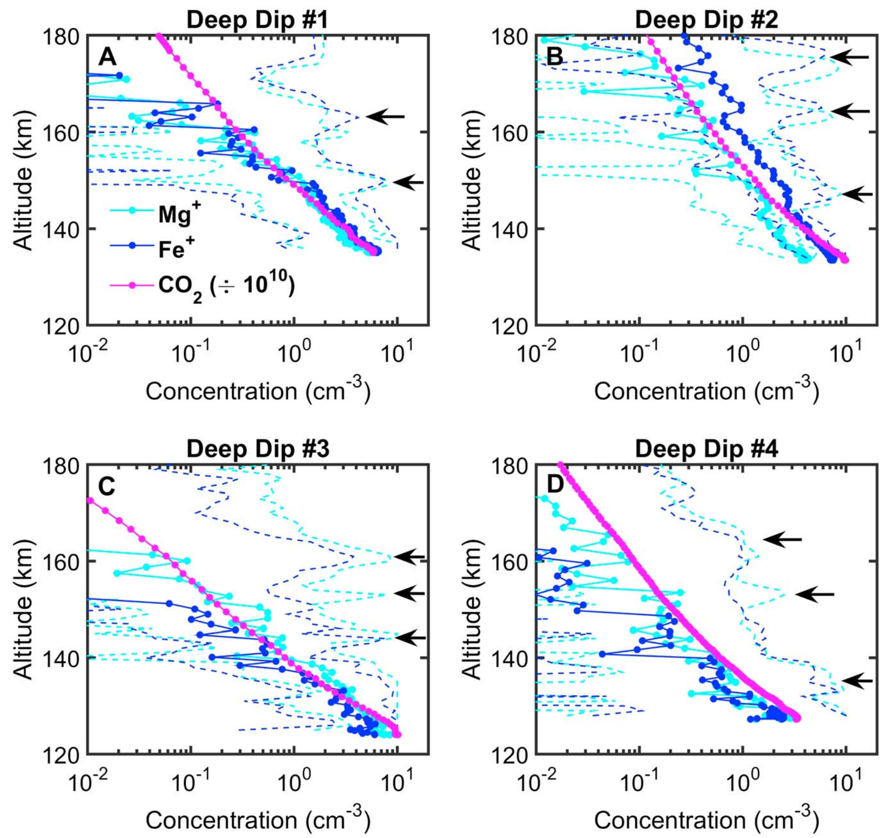

Figure 3. Statistics of Mg^+, Fe^+, and CO_2 concentrations measured on all orbits within each of the first four deep-dip campaigns. The solid lines connect the geometric averages of the concentrations of each of these species in 10 km altitude bins. The dashed lines depict the envelopes of the extrema, i.e., the maximum and minimum values of the measured metal ion concentrations at each sampled altitude. The maximum profiles show distinct localized altitude enhancements—evidence for metal ion concentration layers (indicated by arrows). Consistent with the earlier shown individual profiles, the average CO_2 altitude profiles tend to mimic those of the metal ion concentrations. The relative concentrations of the two metal ion species varied from one campaign to the other, with their highest concentrations seen in the subsolar region (campaign 2). Campaign 1 occurred near the dusk terminator, campaign 3 nightside of dawn, and campaign 4 straddled the dusk terminator.

Izakov, 1978; *Pesnell and Grebowsky*, 2000; *Rodrigo et al*., 1990; *Rollason and Plane*, 1998; *Rosenqvist and Chassefiere*, 1995; *Rowe et al*., 1981; *Rutherford et al*., 1971; *Rutherford and Vroom*, 1972; *Vondrak et al*., 2006; *Whalley and Plane*, 2010; *Whalley et al*., 2011; *Woodcock et al*., 2006]. Hence, either atmospheric/ionospheric sources for the high-altitude metal ions, the physics behind the diffusion, or the transport details of the metals vary from location to location on the planet. One possible consideration is the need to clarify the upper boundary condition for the vertical metal ion flux. The published one-dimensional time-independent metal ion models thus far employed at Earth and Mars simplify the upper altitude boundary condition by assuming a zero flux at infinite altitude. This is likely unrealistic at Mars as collisional diffusion ends at the exobase, where the collisional free path equals neutral atmosphere scale height (below 200 km during the MAVEN mission) [*Jakosky et al*., 2017]. Furthermore, the observance of the same scale heights for the metal ions and CO_2 is consistent with the metal ions acting like a minor species that are diffusing under steady state conditions at the maximum speed possible [*Banks and Kockarts*, 1973]. Hence, either the ions are drifting in the diffusing process so that another transport process needs to be included along with collisional/turbulent diffusion or a new mixing process needs to be defined for the metal ions.

The maximum ion concentration envelopes in the Figure 3 ensemble of measurements clearly show signatures of the prominent isolated layers discussed earlier. Another interesting feature is the offsets in altitude between the Mg^+ and Fe^+ layer peaks, particularly during campaign 2. At Earth, such separations are also seen in metal layers occurring above the main altitude metal ion peak. These are likely due to

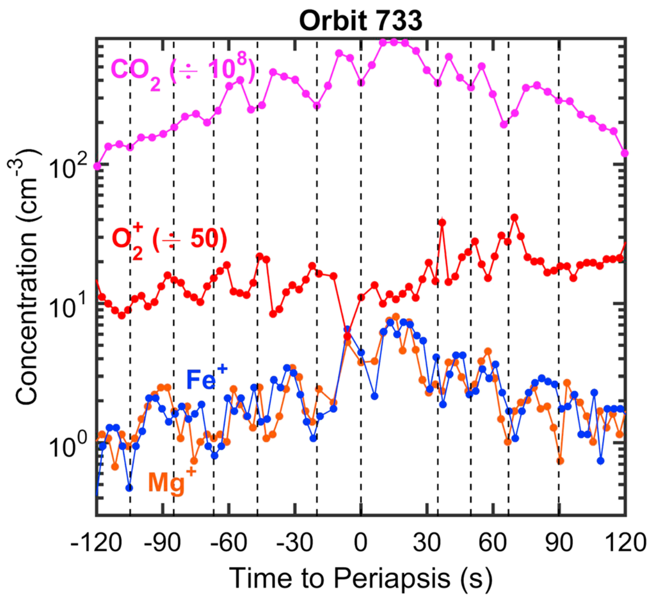

Figure 4. Gravity wave structure. A selected orbit is depicted that illustrates the effect of gravity waves on metal ion distributions. As measured along an orbit, the ion/neutral concentrations have wavelengths of ~80 km. This orbit was selected as a good example for an anticorrelation between the metal ions (which track the atmosphere variations) and the major ion O_2^+ that is taken as direct evidence of gravity wave control of the ions. Neutral gravity waves drag the long-lived metal ions.

electrodynamic transport differences between Mg^+ and Fe^+ whose gyration radii and ion-neutral collision frequencies are different [e.g., *Grebowsky and Aikin*, 2002]. Further study is needed to see what applies at Mars.

The last novel feature of the metal ion observations is the oscillations seen in the metal ion concentration profiles on most orbits. There is compelling evidence that these oscillations reflect the responses of the metal ions to atmospheric gravity waves. The observed waves in the metal concentrations along the MAVEN orbit have periods of the order of 20 s. With MAVEN's ~4.2 km/s orbital speed the structures have wavelengths of ~80 km wavelength projected along the nearly horizontal spacecraft trajectory near periapsis, typical scale lengths for vertically propagating, horizontal gravity waves [*Fritts et al.*, 2006]. Figure 4 shows the time variation of measurements along an orbit selected to clearly demonstrate the presence of high-altitude gravity waves. These data were measured near the terminator during first deep-dip campaign (periapsis 130 km), when MAVEN was below the exobase in the collisionally dominated upper atmosphere. During this observation period, the major ion O_2^+ concentrations are out of phase with the oscillations of the metal ions, whereas the oscillations in CO_2 are in-phase with those of the metal ions. Below the spacecraft the concentrations of metal ions and CO_2 are decreasing with increasing altitude (i.e., average positive vertical scale heights), whereas the O_2^+ concentrations (spacecraft is likely on the bottom side of the ambient ionosphere peak) are increasing with altitude (i.e., negative vertical scale height). Thus, when buoyant neutral atmosphere gravity waves drag metal ions upward from lower altitudes, the CO_2 and metal ion concentration waves will be in-phase but out of phase with the O_2^+ concentrations. This anticorrelation of the ionospheric major ion and neutral concentrations in response to gravity waves has also been observed on Earth [*Earle et al.*, 2008].

The data in Figure 4 were taken near the terminator where the ionosphere is relatively weak and gravity wave activity increases going from day to night [e.g., *Yiğit et al.*, 2015]. Further into daylight where the ionosphere is much stronger, gravity wave control is not very obvious in the MAVEN main ionosphere species O_2^+, but the waves are seen in the metal ion profiles even in the subsolar region—an example is seen in Figure 3c. The effect of enhanced recombination loss of the O_2^+ with increasing electron density will tend to suppress the amplitude swings in the O_2^+. Hence, wave structures in the metal ions are apparently prominent under all conditions, whereas signatures of gravity wave control of the main ionosphere species are only apparent when the ambient ionosphere is somewhat depleted. Such persistent trains of metal ions under gravity wave control have never been identified at Earth.

3. Conclusion

In conclusion, the in situ metal ion measurements at Mars have revealed new facets of how the ablated residues from IDPs can interact with a planetary atmosphere and leave us with several interesting puzzles to unravel: (1) Why is there no gravitational separation of the Mg^+ and the heavier Fe^+ with altitude in the region above the turbopause, where molecular diffusion is prevalent? (2) What are the sources of the observed isolated metal ion layers in the absence of an intrinsic planetary magnetic field that plays a key role in forming such layers at Earth? (3) What are the reasons for the relative changes in the Mg^+/Fe^+ ratio and relative Na^+ (not emphasized in the paper) concentrations as MAVEN's periapsis location precesses during the mission?

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