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Benna, M, Mahaffy, PR, Grebowsky, JM et al. (2015) Metallic ions in the upper atmosphere of Mars from the passage of comet C/2013 A1 (Siding Spring). *Geophysical Research Letters*, 42 (12). 4670 - 4675. ISSN: 0094-8276

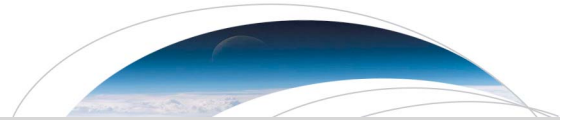
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RESEARCH LETTER

10.1002/2015GL064159

Key Points:

- Metal ions were identified for the first time in the upper atmosphere of Mars
- Metal ions result from cometary dust ablation in the atmosphere of Mars
- Metal ions were depleted with respect to the Cl abundance of Na⁺

Supporting Information:

- Texts S1 and S2, Figures S1–S3, and Table S1
- Data Set S1

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Citation:

Benna, M., P. R. Mahaffy, J. M. Grebowsky, J. M. C. Plane, R. V. Yelle, and B. M. Jakosky (2015), Metallic ions in the upper atmosphere of Mars from the passage of comet C/2013 A1 (Siding Spring), *Geophys. Res. Lett.*, 42, doi:10.1002/2015GL064159.

Received 9 APR 2015

Accepted 27 APR 2015

Metallic ions in the upper atmosphere of Mars from the passage of comet C/2013 A1 (Siding Spring)

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Abstract We report the first in situ detection of metal ions in the upper atmosphere of Mars resulting from the ablation of dust particles from comet Siding Spring. This detection was carried out by the Neutral Gas and Ion Mass Spectrometer on board the Mars Atmosphere and Volatile Evolution Mission. Metal ions of Na, Mg, Al, K, Ti, Cr, Mn, Fe, Co, Ni, Cu, and Zn, and possibly of Si, and Ca, were identified in the ion spectra collected at altitudes of ~185 km. The measurements revealed that Na⁺ was the most abundant species, and that the remaining metals were depleted with respect to the Cl (type 1 carbonaceous Chondrites) abundance of Na⁺. The temporal profile and abundance ratios of these metal ions suggest that the combined effects of dust composition, partial ablation, differential upward transport, and differences in the rates of formation and removal of these metal ions are responsible for the observed depletion.

1. Introduction

The close passage of comet Siding Spring (C/2013 A1, CSS) [McNaught *et al.*, 2013] provided a unique opportunity to observe the close interaction between the dusty coma of a comet and a dense planetary atmosphere. Traveling on a highly inclined, hyperbolic orbit, the comet encountered Mars on 19 October 2014 at 18:29 UTC from a closest approach distance of ~134,000 km and with a relative velocity of 56 km s⁻¹ [Farnocchia *et al.*, 2014]. During this event, the Mars Atmosphere and Volatile Evolution Mission (MAVEN) spacecraft [Jakosky, 2014] was ideally located and equipped to measure the response of the upper atmosphere of Mars to a strong and rapid cometary mass and energy disposition, and to assess the mechanisms by which the atmospheric system returns to equilibrium [Yelle *et al.*, 2014]. It also offered the rare opportunity for direct characterization of cometary material being freshly delivered into the upper atmosphere and ionosphere of Mars. Of particular interest was the potential formation of metal ions from the ablation of cometary dust particles streaming through the atmosphere.

As on Earth and Jupiter, the presence of metal ions at high altitudes provides unequivocal signatures of the exogenic nature of the supplied material [Hughes, 1978; Grebowsky, 1981]. The formation of metal ions and their associated ionospheric layers by the ablation of meteoroids has been extensively observed in Earth's upper atmosphere, and metal ions such as Mg⁺, Fe⁺, Na⁺, Al⁺, Ca⁺, and Ni⁺, have been detected in the ionosphere [Kopp, 1997; Grebowsky *et al.*, 1998]. Several models mapped the chemical pathways by which these metal ions are recycled and ultimately removed [Molina-Cuberos *et al.*, 2008, and references herein]. Similar mechanisms were predicted to form metal ions in the Martian ionosphere as the result of the sporadic meteor background [Pesnell and Grebowsky, 2000; Molina-Cuberos *et al.*, 2003; Whalley and Plane, 2010]. Although the formation of transient ionospheric layers below 120 km at Mars was observed by Mars Express and Mars Global Surveyor [Pätzold *et al.*, 2005; Withers *et al.*, 2008], meteoric metal ions had not yet been directly detected. Radio occultation detects layers of electrons, and the corresponding positive ions in these low-lying layers are assumed to be metal ions. Predictions for the cometary dust flux into the Mars atmosphere were concerned primarily with impact hazard to spacecraft [Tricarico *et al.*, 2014; Ye and Hui, 2014; Kelley *et al.*, 2014; Farnocchia *et al.*, 2014] and predicted an input dust flux comparable to the sporadic background with a maximum occurring on 19 October 2014 at 20:08 UTC. Withers [2014] pointed out that the high velocity of CSS dust implied the formation of a more robust ionosphere than formed in sporadic layers, which might be detectable by spacecraft. Such detection is important because it has the potential to validate models of ion transport, recycling, and removal mechanisms in the atmosphere of Mars, as well as allowing

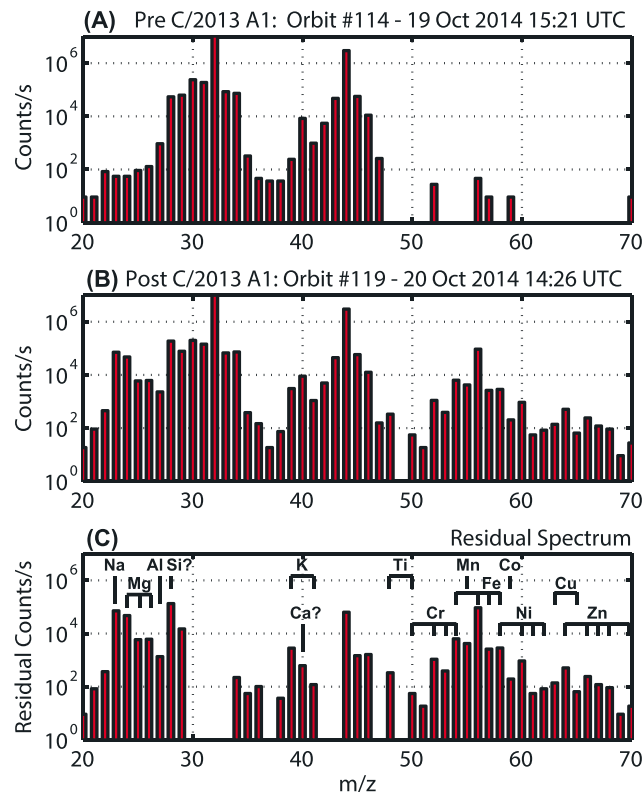


Figure 1. Comparison between two spectra collected (a) 5 h prior to and (b) 19 h following the time of maximum dust flux of CSS. (c) The residual spectrum (plotted to show only m/z channels that registered a signal increase following the passage of CSS) reveals the emergence of 14 spectral lines characteristic of Na^+ , Mg^+ , Al^+ , Si^+ , K^+ , Ca^+ , Ti^+ , Cr^+ , Mn^+ , Fe^+ , Co^+ , Ni^+ , Cu^+ , and Zn^+ . Positive residuals in $m/z = 20\text{--}22$, $34\text{--}36$, and $45\text{--}47$ are due to variations of atmospheric Ne^+ , CO_2^{2+} , O_2^+ , Ar^+ , CO_2^+ , HCO_2^+ , and their isotopes.

encounter with the planet. During this campaign, NGIMS carried out 19 sets of special observations (also called activities). This special observation sequence devoted the majority of the instrument's observing time to a select set of atmospheric neutrals and ions but included 10 ion "survey" scans that were conducted at various altitudes. Each survey scan covered the full 2–90 Da mass range at a unit mass resolution. The NGIMS activities were conducted at regularly spaced intervals (orbits #108–128), interrupted only by a 10 h period at the peak of the cometary dust flux, when the instrument was temporarily turned off to minimize risk to the hardware. The NGIMS instrument operated when the spacecraft altitude was below 500 km. During the days that preceded and followed the encounter with CSS, the orbit of the MAVEN spacecraft remained nearly the same with respect to the Mars Solar Orbital Frame, with a periapsis located at 42° north latitude and 14:58 local mean solar time, a periapsis altitude of 185 km, and an orbital period of 4.6 h. However, due to the planet's rotation, the position of the spacecraft's tracks relative to the predicted region of cometary dust impacts was changing through the orbits (see Figure S1 in the supporting information for additional details).

The changes in the spectral signatures of ions in the upper atmosphere of Mars after the passage of CSS are depicted in two ion survey spectra collected at the same altitude (185–189 km). The first spectrum (Figure 1a) was captured on orbit #114, ~5 h prior to the peak dust flux of CSS, while the second (Figure 1b) was captured on orbit #119, ~19 h after the comet's peak dust flux. The difference between these two spectra (Figure 1c) reveals the emergence of several mass peaks that are characteristic of metal ions in the few hours that followed the CSS encounter. These ions were identified as Na^+ , Mg^+ , Al^+ , K^+ , Ti^+ , Cr^+ , Mn^+ , Fe^+ , Co^+ , Ni^+ , Cu^+ , and Zn^+ , and possibly Si^+ , and Ca^+ . The identity of most of these species (Mg^+ ,

the direct characterization of the refractory content of CSS. Compositional information of CSS will be valuable as it may provide the evidence that some of the Oort cloud comets come from the protoplanetary disks of other stars [Levison *et al.*, 2010].

In this paper, we report the definitive detection of 12 metal ions of cometary origin and tentative detection of two additional ions in the upper atmosphere of Mars by the Neutral Gas and Ion Mass Spectrometer (NGIMS) in the hours that followed the close passage of CSS. The NGIMS instrument is a quadrupole mass spectrometer that utilizes a dual ion source designed to measure both surface reactive and inert atmospheric neutrals, and ion species in the mass range of 2–150 Da [Mahaffy *et al.*, 2014]. Carried by the MAVEN spacecraft, this instrument aims to contribute to the mission goals of measuring the rate of atmospheric escape to space by characterizing the composition and the dynamics of neutrals and thermal ions in the upper atmosphere of Mars.

2. Detections of Metal Ions

Data of neutrals and ions were collected by NGIMS from 18 October to 22 October 2014 as part of the MAVEN Siding Spring observation campaign that took place immediately before and after the comet's

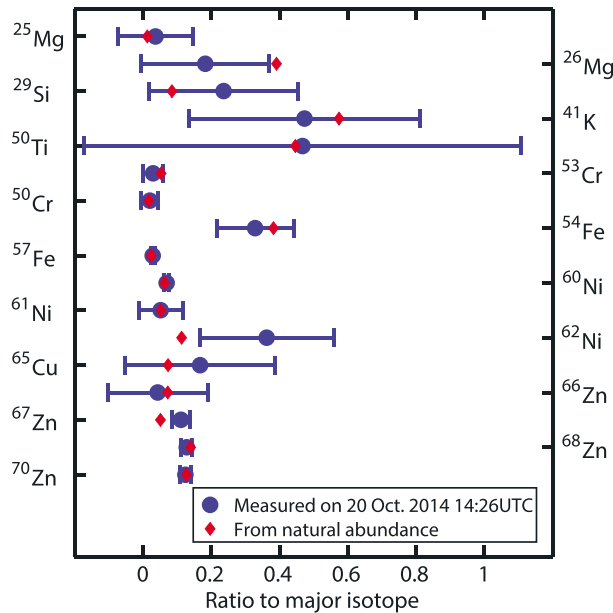


Figure 2. Isotope ratios of detected metal ions. These isotope ratios (blue) were derived from the spectrum acquired by NGIMS on 20 October 2014 14:26 UTC at 185 km altitude. Ratios are reported relative to the major isotopes (²⁴Mg, ²⁸Si, ³⁹K, ⁴⁸Ti, ⁵²Cr, ⁵⁶Fe, ⁵⁸Ni, ⁶³Cu, and ⁶⁴Zn). Error bars reflect the 3 x standard deviation due to counting statistics. These isotope ratios are compared to the ones derived from natural abundance as established by NIST.

3. Temporal Evolution and Spatial Variation

All detected metal ions display comparable temporal evolution during the 48 h leading and following the passage of CSS (Figure 3 for Mg⁺, and figures in the supporting information for the rest of the species). None of these metal ions were found prior to the arrival of the comet. All were detected during the first NGIMS activity that followed the comet’s passage (initiated on orbit #117, 20 October 2014 05:02 UTC), and their highest recorded abundances occurred 19 h following the peak of dust flux (orbit #119). Although the measured abundances decayed exponentially afterward, metal ions were still detectable for 2.5 days

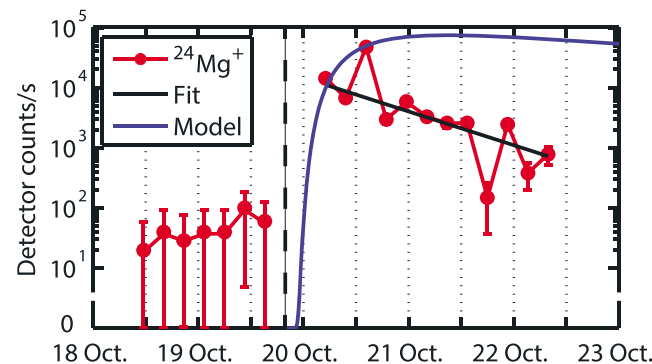


Figure 3. Temporal evolution of the measured abundances of Mg⁺ at periapsis from 18 October to 23 October 2014. The exponential decay can be fitted by a time constant of 1.8 days. All metal ions follow similar temporal profiles as Mg⁺ (see figures in the supporting information). The dashed line marks the predicted time of maximum dust flux. Predicted signal levels were derived by a 1-D model (see text). Error bars reflect 3 x standard deviation of the sampled data due to counting statistics. Instrument background is 10–100 c/s.

K⁺, Ti⁺, Cr⁺, Fe⁺, Ni⁺, Cu⁺, and Zn⁺) was established unambiguously by comparing measured isotope ratios to their relevant natural relative abundances established by the National Institute of Standard and Technology (NIST) (Figure 2).

Although it is possible to attribute the variability of the observed residuals at $m/z=27, 28, 29,$ and 40 to atmospheric ions (HCN⁺, CO⁺/N₂⁺, and Ar⁺, to cite a few), their similar temporal evolution when compared to Mg⁺, Fe⁺, and Zn⁺ strongly support Al⁺, Si⁺, and Ca⁺ as being the originators of these spectral signatures. These NGIMS observations are also supported by concurrent detection of Mg⁺ and Fe⁺ reported by MAVEN’s Imaging Ultraviolet Spectrograph (IUVS) [Schneider *et al.*, 2015], and of a transient dense ionospheric layer reported by the Mars Advanced Radar for Subsurface and Ionospheric Sounding (MARSIS) instrument on MEX and the Shallow Subsurface Radar (SHARAD) instrument on the Mars Reconnaissance Orbiter (MRO) [Gurnett *et al.*, 2015; Restano *et al.*, 2015].

after CSS passage. Previous models of metallic ions in the Martian atmosphere [Pesnell and Grebowsky, 2000; Molina-Cuberos *et al.*, 2003; Whalley and Plane, 2010] have shown that sporadic meteors which enter with relatively low velocities (<15 km s⁻¹) ablate around 80 km. However, the CSS dust particles enter with velocities of 56 km s⁻¹. Assuming that these are low-density cometary dust particles with densities of less than 1000 kg m⁻³, the chemical ablation model CABMOD [Vondrak *et al.*, 2008] predicts ablation around 115 km. A 1-D model for Mg⁺ [Whalley and Plane, 2010] shows that a combination of eddy and then ambipolar ion diffusion will transport ions from 115 km to 185 km fast enough to account for the abundance level measured by NGIMS

Table 1. Abundance of Metal Ions as Derived From the NGIMS Measurements of 20 October 2014 14:26 UTC (Orbit #119) at 185 km Altitude

Ion	Abundance (cm ⁻³)	Ion	Abundance (cm ⁻³)
Na ⁺	201.2 ± 10.2	Cr ⁺	1.0 ± 0.1
Mg ⁺	153.6 ± 7.5	Mn ⁺	3.0 ± 0.2
Al ⁺	2.8 ± 0.4	Fe ⁺	69.0 ± 3.3
Si ⁺	318.2 ^a	Co ⁺	0.13 ± 0.03
K ⁺	3.4 ± 1.4	Ni ⁺	2.8 ± 0.2
Ca ⁺	2.0 ^a	Cu ⁺	0.12 ± 0.03
Ti ⁺	0.38 ± 0.07	Zn ⁺	0.62 ± 0.09

^aUpper limit value.

(diffusion speeds of ~1 m s⁻¹), as shown in Figure 3. However, the model predicts a decay time constant ~8 days compared to the 1.8 days inferred by a fit to the data. This deviation can be explained by the effect of rapid redistribution of the metals by atmospheric winds, nonaccounted for yet in this preliminary model. These atmospheric winds were predicted to reach speeds of 160–260 m/s relative to the surface at 120–210 km altitude [Bougher et al., 1999, 2015]. Rapid redistribution by atmospheric winds would also explain the fact that the temporal evolution of the measured abundances seemed to be independent of the spacecraft location relative to the initial metal deposition region. At the predicted speeds, the winds can drag the outer envelope of the deposit hemisphere more than 90° in less than 10 h, which would tend to “dilute” and homogenize the metal distribution around the planet. The measured deviations on orbit #119 and #125 may reflect localized heterogeneities in the atmosphere as the redistribution was taking place.

The absolute abundances of the metal ions during their observed peak on 20 October 2014 14:26 UTC (orbit #119) are compiled in Table 1. Of all the “survey” scans, only data collected for Na⁺, Mg⁺, K⁺, and Fe⁺ on the first NGIMS activity following the comet’s passage exhibit signals above 200 km with levels high enough to permit the extraction of altitude profiles. Figure 4 shows the detector signal for each of the four species on that first NGIMS activity (orbit #117), revealing an interesting asymmetry between the inbound and the outbound leg. During the inbound leg, only K⁺ and Fe⁺ were detectable above 300 km. This is a surprising observation given that these are relatively heavy ions compared with Na⁺ and Mg⁺, which are below detection at this altitude. In contrast, none of the Na⁺ or Mg⁺ could be detected above 216 km, and the first indication of the presence of these two species was obtained near periapsis. During the outbound leg, the abundances of all four species decayed asymptotically to ~1/15 of their peak value at periapsis and remained at that level until the last measurement was acquired at ~425 km.

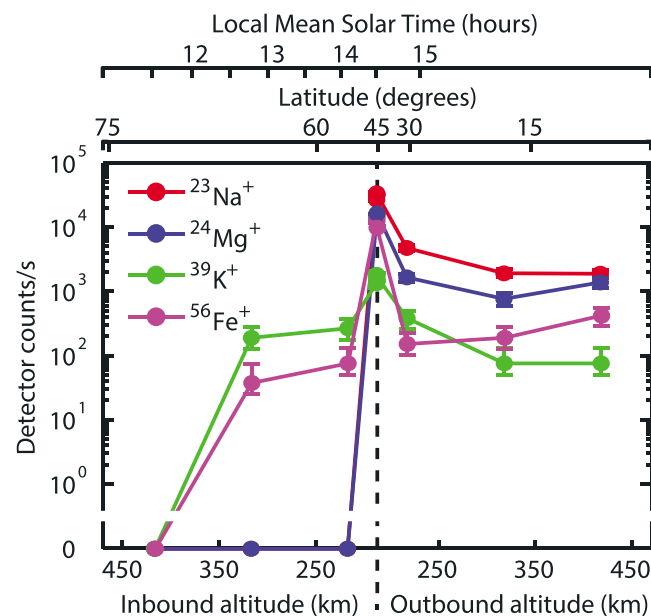


Figure 4. Altitude profile of Na⁺, Mg⁺, K⁺, and Fe⁺ measured during the NGIMS activity of 20 October 2014 05:02 UTC (orbit #117). The inbound and outbound portions of the activity are separated by the passage through periapsis at 185 km (depicted by the dashed line). Error bars reflect 3 x standard deviation of the sampled data due to counting statistics.

With the sparse sampling and limiting spatial information available, we cannot determine whether the apparent asymmetry is due to temporal variations in the metal ion densities or spatial variations along the track.

4. Ion Diffusion and Transport Effects

Figure 5 compares the relative NGIMS ion abundances to those in primitive CI carbonaceous chondrites [Lodders et al., 2009], both normalized to Na⁺. Note that all the elements are depleted with respect to the CI abundance of Na⁺. In view of the high signal-to-noise ratio for Fe⁺ and Mg⁺, and the fact that the chemical rates of formation and removal of these ions as well as those of Na⁺ have been measured [Plane, 2002; Whalley and Plane, 2010], we now focus on possible reasons for the depletions of Fe⁺ and Mg⁺ by factors of 44 and 24, respectively.

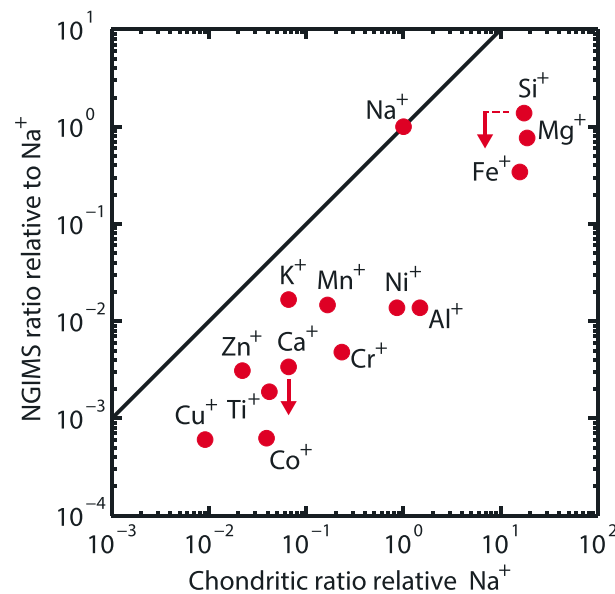


Figure 5. Comparison between relative NGIMS ion abundances and those of primitive CI carbonaceous chondrites [Plane, 2002]. All abundances were normalized to that of Na^+ . The relative abundances of Si^+ and Ca^+ reflect upper limit values.

(note that photoionization is a comparatively slow process) [Whalley and Plane, 2010]. The rate coefficient for charge transfer with Na is about 2.5 times faster than for Fe or Mg [Plane, 2002; Whalley and Plane, 2010]. Since the O_2^+ concentration in the dayside ionosphere is typically $7 \times 10^4 \text{ cm}^{-3}$, the lifetime of Na against ionization is only ~ 1.5 h. Third, neutralization of the metal ions involves clustering with CO_2 , followed by dissociative recombination with electrons [Whalley and Plane, 2010]. The rates of these clustering reactions increase by a factor of ~ 3 from Na to Fe [Plane, 2002; Whalley and Plane, 2010]. Another factor which would cause Fe^+ to be even more depleted than Mg^+ is its significantly larger mass, causing its vertical diffusive transport rate above the homopause (~ 140 km) to be ~ 1.35 times slower. Slower diffusive transport may also explain the relative depletion of K^+ to Na^+ by a factor of ~ 3 , since both alkali elements should ablate and ionize with very similar efficiencies [Vondrak et al., 2008]. Finally, the very low relative abundances of Ca and Al, which are depleted by ~ 2 orders of magnitude, are consistent with the partial ablation of these highly refractory elements even at a meteoroid entry velocity of 56 km s^{-1} [Vondrak et al., 2008].

5. Conclusions

The identification of metal ions in the ionosphere of Mars following the passage of CSS is a first-of-its-kind measurement conducted on another planet of the solar system. The characterization of the metal content in the CSS dust particles that ablated in the Martian atmosphere will require untangling the effects of the various mechanisms that interplayed to produce the signatures of metals observed by NGIMS. However, the large number of metal ion species detected by NGIMS along with published estimates that the dust fluxes from Siding Spring are comparable to the sporadic flux [Tricarico et al., 2014; Ye and Hui, 2014; Kelley et al., 2014; Farnocchia et al., 2014] suggests that the larger sporadic events are detectable at the MAVEN periapsis altitude. These measurements can place useful constraints on exogenic input to Mars.

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Acknowledgments

The MAVEN/NGIMS investigation was supported by NASA. Instrument testing and calibrations were completed at the Planetary Environment laboratory of NASA's Goddard Space Flight Center. We are grateful for the engineering/technical support especially from T. King (Instrument Manager), E. Weidner, E. Lyness, K. Patel, (Instrument Operations), and E. Raaen and M. Elrod (Calibration). J.M.C.P. acknowledges funding from the European Research Council (project 291332-CODITA). The NGIMS data supporting this article are provided in the supporting information Dataset S1.

The Editor thanks two anonymous reviewers for their assistance in evaluating this paper

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