Meteor-ablated Aluminum in the Mesosphere-Lower Thermosphere

John Maurice Campbell Plane¹, Shane Daly¹, Wuhu Feng¹, Michael Gerding², and Juan Carlos Gomez Martin³

¹University of Leeds ²Leibniz-Institute of Atmospheric Physics ³Instituto de Astrofísica de Andalucía

November 23, 2022

Abstract

The first global atmospheric model (WACCM-Al) of meteor-ablated aluminum was constructed from three components: the Whole Atmospheric Community Climate Model (WACCM6); a meteoric input function for Al derived by coupling an astronomical model of dust sources in the solar system with a chemical meteoric ablation model; and a comprehensive set of neutral, ion-molecule and photochemical reactions relevant to the chemistry of Al in the upper atmosphere. The reaction kinetics of two important reactions that control the rate at which Al⁺ ions are neutralized were first studied using a fast flow tube with pulsed laser ablation of an Al target, yielding $k(AlO^+ + CO) = (3.7 \pm 1.1) \times 10^{-10}$ and $k(AlO^+ + O) = (1.7 \pm 0.7) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 294 K. The first attempt to observe AlO by lidar was made by probing the bandhead of the B² Σ^+ (v' = 0) - X² Σ^+ (v" = 0) transition at $\lambda_{air} = 484.23$ nm. An upper limit for AlO of 57 cm⁻³ was determined, which is consistent with a night-time concentration of ~5 cm⁻³ estimated from the decay of AlO following rocket-borne grenade releases. WACCM-Al predicts the following: AlO, AlOH and Al⁺ are the three major species above 80 km; the AlO layer at mid-latitudes peaks at 89 km with a half-width of ~5 km, and a peak density which increases from a night-time minimum of ~10 cm⁻³ to a daytime maximum of ~60 cm⁻³; and that the best opportunity for observing AlO is at high latitudes during equinoctial twilight.

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6 7	John M.C. Plane ¹ , Shane M. Daly ¹ , Wuhu Feng ^{1,2} , Michael Gerding ³ and Juan Carlos Gómez Martín ⁴
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9	¹ School of Chemistry, University of Leeds, United Kingdom.
10	² NCAS, University of Leeds, United Kingdom.
11	³ Leibniz Institute of Atmospheric Physics, Kühlungsborn, Germany.
12	⁴ Instituto de Astrofísica de Andalucía, CSIC, 18008, Granada, Spain
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14	Corresponding author: John Plane (j.m.c.plane@leeds.ac.uk)
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17	Key Points:
18 19	• experimental study of the reactions of AlO ⁺ with O and CO provides closure for the neutral and ion-molecule chemistry of meteor-ablated Al
20	
21 22	• atmospheric model of Al is constructed by adding this chemistry and an Al meteoric source function to the WACCM chemistry-climate model
23	
24 25 26	 the model predicts a nighttime AlO density of ~10 cm⁻³, consistent with an AlO upper limit of 57 cm⁻³ determined from a lidar campaign

27 Abstract

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- 29 from three components: the Whole Atmospheric Community Climate Model (WACCM6); a
- 30 meteoric input function for Al derived by coupling an astronomical model of dust sources in the
- 31 solar system with a chemical meteoric ablation model; and a comprehensive set of neutral, ion-
- 32 molecule and photochemical reactions relevant to the chemistry of Al in the upper atmosphere.
- 33 The reaction kinetics of two important reactions that control the rate at which Al^+ ions are
- neutralized were first studied using a fast flow tube with pulsed laser ablation of an Al target, yielding $k(AlO^+ + CO) = (3.7 \pm 1.1) \times 10^{-10}$ and $k(AlO^+ + O) = (1.7 \pm 0.7) \times 10^{-10}$ cm³ molecule⁻¹
- 35 yielding $k(AIO^+ + CO) = (3.7 \pm 1.1) \times 10^{-10}$ and $k(AIO^+ + O) = (1.7 \pm 0.7) \times 10^{-10}$ cm³ molecule⁻¹ 36 s⁻¹ at 294 K. The first attempt to observe AIO by lidar was made by probing the bandhead of the
- 37 $B^2\Sigma^+(v'=0) \leftarrow X^2\Sigma^+(v''=0)$ transition at $\lambda_{air} = 484.23$ nm. An upper limit for AlO of 57 cm⁻³
- 38 was determined, which is consistent with a night-time concentration of $\sim 5 \text{ cm}^{-3}$ estimated from
- 39 the decay of AlO following rocket-borne grenade releases. WACCM-Al predicts the following:
- 40 AlO, AlOH and Al^+ are the three major species above 80 km; the AlO layer at mid-latitudes
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- 44
- 45

46 **1 Introduction**

- 47 The ablation of cosmic dust particles entering the Earth's atmosphere injects a range of metals
- 48 into the mesosphere/lower thermosphere (MLT) region between 80 and 120 km, giving rise to
- 49 layers of metal atoms and ions [*Plane et al.*, 2015]. A recent estimate of the global mass input
- 50 rate of dust is 28 ± 16 t d⁻¹ [*Carrillo-Sánchez et al.*, 2020]. The relative mass abundance of Al in
- 51 cosmic dust should be around 1.4%, based on the Carbonaceous Ivuna (CI) chondritic abundance
- 52 [*Asplund et al.*, 2009] (the CI ratio is regarded as the closest in composition to interplanetary dust
- 53 [*Jessberger et al.*, 2001]). However, Al is present in the dust as a highly refractory oxide, so that
- 54 only 14% of the incoming Al ablates, mostly from high speed dust particles which originate from 55 Helley Tyme Compte [Carrillo Sánchez et al. 2020]
- 55 Halley Type Comets [*Carrillo-Sánchez et al.*, 2020].
- 56 Ablated Al atoms will then react rapidly with O₂ to form AlO [*Gómez Martín et al.*, 2017]:

57
$$Al + O_2 \rightarrow AlO + O$$
 $\Delta H^{\circ} = -14 \text{ kJ mol}^{-1}$ (R1)

58 with a time constant of $\sim 300 \,\mu s$ at 85 km. Thus, unlike the major meteoric metals Fe, Mg and Na 59 which occur as layers of neutral metal atoms between about 80 and 105 km, aluminum is likely 60 to occur predominantly as a layer of AlO. There are two reasons for this conjecture. First, atomic 61 Si is the only other major meteoric species which undergoes a fast bimolecular reaction with O_2 , 62 and a detailed model of silicon chemistry predicts that this element occurs as a layer of SiO 63 rather than Si in the MLT [Plane et al., 2016]. Second, solar-pumped fluorescence from the 64 AlO($B^2\Sigma^+$ - $X^2\Sigma^+$) band has been observed when tri-methyl aluminum (TMA) is released in the 65 MLT during twilight [Rosenberg et al., 1964; Johnson, 1965; Golomb et al., 1967]. Emission 66 from the same AlO band was also observed during entry of the very bright Benešov bolide over 67 the Czech Republic [Borovička and Berezhnoy, 2016].

- 68 The only aluminum species which has so far actually been observed in the background
- atmosphere is the ²⁷Al⁺ ion, measured using rocket-borne mass spectrometry [Krankowsky et al., 69
- 1972; Kopp, 1997; Grebowsky and Aikin, 2002]. The Al⁺/Fe⁺ ratio between 90 100 km was 70
- 71 found from a series of rocket flights to be 0.022 ± 0.005 [Daly et al., 2019], which is reasonably
- 72 close to the estimated Al/Fe meteoric ablation ratio of 0.037 [Carrillo-Sánchez et al., 2020]. We
- 73 have recently carried out a study of the kinetics of the pertinent neutral [Gómez Martín et al.,
- 74 2017; Mangan et al., 2020] and ion-molecule [Daly et al., 2019] reactions that aluminum is
- 75 likely to undergo in the MLT. These studies, along with electronic structure theory calculations
- 76 to elucidate likely reaction pathways, has enabled the chemical network shown in Figure 1 to be
- 77 constructed. The reactions that we have measured previously are indicated with blue arrows.
- 78 In terms of ion-molecule chemistry, Al^+ mostly reacts with O_3 in the MLT (Figure 10 in Daly et
- 79 al. [2019]) to produce AlO⁺. In Section 2.1 of the present paper we describe an experimental
- 80 study to measure the rate coefficients for the reactions of the AlO⁺ ion with O and CO (red
- 81 arrows in Figure 1):

 $AlO^+ + O \rightarrow Al^+ + O_2$ $\Delta H^{\Theta} = -372 \text{ kJ mol}^{-1}$ 82 (R22)

83
$$AlO^+ + CO \rightarrow Al^+ + CO_2$$
 $\Delta H^{\Theta} = -406 \text{ kJ mol}^{-1}$ (R23)

84 (note that the reaction numbering follows the complete list of reactions in Table 1). These two

highly exothermic reactions (the reaction enthalpies are calculated using the electronic structure 85

- 86 method discussed in Section 2.2) control the balance between ionized and neutral aluminum 87 because they reduce AlO⁺ to Al⁺, which can only undergo slow dielectronic recombination with
- 88 electrons (see Figure 1).
- 89 In terms of neutral chemistry, the measured reaction kinetics indicate that AlO will initially form
- 90 OAlO₂ and AlCO₃ (see Figure 11 in Mangan et al. [2020]). However, AlCO₃ may then react 91 exothermically with O₂ to form OAlO₂, which in turn is likely to react with H to produce AlOH,
- 92 as shown in Figure 1. Unlike other metal hydroxides such as FeOH [Self and Plane, 2003],
- 93 NaOH [Gómez-Martín et al., 2017] and CaOH [Gómez-Martín and Plane, 2017], AlOH is stable
- 94 with respect to reaction with H and O atoms [Mangan et al., 2020] and is therefore likely to be a
- 95 major Al reservoir. In Section 2.2 we use electronic structure theory calculations to explore
- 96 these pathways for converting AlO to AlOH.

 \rightarrow AlO + H

- In fact, it appears that the only process which can recycle AlOH to AlO directly is photolysis. 97
- 98 The excited electronic states of AlOH have been studied in some detail by Trabelsi and
- 99 Francisco [2018] (in order to explain the observed ratio of AlO to AlOH in the interstellar
- 100 medium). Using high level coupled cluster theory calculations, they showed that the two
- 101 photolysis channels:

$$102 \qquad AlOH + hv \rightarrow Al + OH \tag{R17a}$$

103

(R17b)

104 should have almost identical thresholds around 225 nm. Note that any Al produced via channel 105 R17a will immediately be oxidized to AlO via reaction R1. In Section 2.3 the photodissociation

106 rate of AlOH in the MLT is estimated.

- 107 In Section 3 we describe a set of lidar observations of the expected AlO layer. The peak
- 108 absorption cross section of AlO in the B-X band at 484.23 nm was measured in our laboratory to
- be $\sigma(298 \text{ K}) = (6.7 \pm 1.6) \times 10^{-15} \text{ cm}^2 \text{ molecule}^{-1}$ [Gómez Martín et al., 2017]. This cross section 109

- 110 is unusually large for a molecular diatomic transition, and is only a factor of 80 smaller than the
- 111 cross section for atomic Fe at 372 nm used for lidar measurements of the Fe layer in the MLT. It
- 112 is worth emphasizing that although chemiluminescence from FeO and NiO has been observed in
- the nightglow spectrum [*Evans et al.*, 2011; *Saran et al.*, 2011], no molecular metallic species
- has been actively detected by resonance lidar. The lidar results are then compared with an
- estimate of the AlO peak density determined from the lifetime of the AlO trails produced by
- 116 TMA releases.
- 117 In Section 4 we incorporate into a whole atmosphere chemistry-climate model the aluminum
- 118 chemistry network shown schematically in Figure 1, together with a meteoric input function for
- 119 Al [Carrillo-Sánchez et al., 2020]. The model simulations are then compared with observations
- 120 of Al^+ and AlO.
- 121



- 123 Figure 1. Schematic diagram of meteor-ablated Al chemistry in the MLT. Ionized and neutral Al
- 124 species are contained in blue and green boxes, respectively. Blue arrows indicate reactions
- 125 measured previously, and the red arrow shows the reactions measured in the present study.

126 2 Underpinning laboratory and theoretical work

127 2.1 Experimental study of AlO⁺ reaction kinetics

128 Reactions R22 – R23 were studied in a stainless-steel fast flow tube which has been described in

detail previously [*Daly et al.*, 2019; *Bones et al.*, 2020]. At the upstream end of the tube, a pulsed

130 Nd:YAG laser (Continuum Surelite) was used to ablate Al^+ ions from a rotating Al rod, which 131 were then entrained in a carrier gas flow of He (mass flow rate ranging from 3.3 - 3.5 standard

- 131 were then entrained in a carrier gas flow of He (mass flow rate ranging from 3.3 3.5 standard 132 liters min⁻¹). O₃ was added at a fixed injection point 19 cm downstream of the Al rod to produce
- AlO^+ via reaction R21 [*Daly et al.*, 2019]. Atomic O or CO was then added further downstream
- 134 via a sliding injector. At the downstream end of the flow tube, after a reaction time of several
- 135 milliseconds, Al⁺ ions were detected with a quadrupole mass spectrometer (Hiden Analytical,
- 136 model HPR60) operating in positive ion mode. A roots blower backed by a rotary pump provided
- 137 a range of flow velocities from $48 76 \text{ m s}^{-1}$, at the constant pressure of 1.0 Torr which was used
- in these experiments. The resulting reaction times after injection of O or CO ranged from 7.5 8.0 ms. All experiments were conducted at 204 K
- 139 8.0 ms. All experiments were conducted at 294 K.
- 140 O_3 was generated by passing O_2 through a high voltage corona discharge in a commercial

141 ozonizer, with its concentration measured spectrophotometrically at 253.7 nm (provided by a Hg

142 pen lamp) in a 19 cm pathlength optical cell. The O_3 absorption cross section used was $1.16 \times$

143 10⁻¹⁷ cm² molecule⁻¹ [*Molina and Molina*, 1986]. Atomic O was generated through microwave

- 144 discharge of N₂ (McCarroll cavity, Opthos Instruments Inc.), followed by titration with NO
- before injection into the flow tube through the sliding injector [*Self and Plane*, 2003]. The
- 146 concentration of O at the point of injection was measured by using the mass spectrometer in
- 147 neutral mode to determine the amount of NO required to titrate the O. The (first-order) loss rate
- of O to the walls of the flow tube was measured by observing the relative change in the concentration of O ([O]) as the flight time was varied by changing the carrier gas flow rate at
- 145 concentration of O ([O]) as the fight time was varied by changing the carrier gas flow rate at 150 constant pressure. Relative [O] was monitored by adding NO downstream and recording the
- relative intensity of the chemiluminescence (at $\lambda > 550$ nm) produced by reaction between NO
- 152 and O [*Self and Plane*, 2003].
- 153 Materials: carrier gas He (99.995%, BOC gases) was purified through a molecular sieve at 77 K
- before flow tube entry; N_2 (99.9999%, Air products), O_2 (99.999%, Air products) and CO
- 155 (99.5% pure, Argo International) were used without further purification; NO (99.95%, Air
- 156 products) was purified via 3 freeze-pump-thaw cycles before dilution in He.
- 157

158 $2.1.1 Reaction of AlO^+ + CO$

AlO⁺ was produced by reaction with O_3 by injecting $[O_3]$ at a fixed point, and CO was then

added from a sliding injector 0.5 cm downstream of the O_3 injection point. This gave a 7.5 ms

reaction time from the sliding injection point to the mass spectrometer skimmer cone. k_{23} was

162 measured by varying [CO] at a fixed $[O_3]$ of 2.73×10^{11} molecule cm⁻³, and recording the 163 fractional recovery of $[A1^+]$, where this is defined with respect to the $[A1^+]$ before O_1 is added

163 fractional recovery of $[Al^+]$, where this is defined with respect to the $[Al^+]$ before O₃ is added. 164 Figure 2 illustrates how this fraction increases as a function of [CO], due to R23 converting AlO⁺

- 165 back to Al^+ .
- 166 The flow tube kinetics are complicated by the additional reactions of AlO^+ with O_3 and O_2 [*Daly*

167 et al., 2019], as well as diffusional loss of the ions to the flow-tube walls. A kinetic model of the

168 flow tube was therefore used to determine the rate coefficient k_{23} . The model uses a set of

- 169 Ordinary Differential Equations (ODEs) to describe the time-dependent variation of Al⁺, AlO⁺
- and AlO_2^+ down the length of the flow tube. The model is described in detail elsewhere [*Bones et*]
- 171 *al.*, 2020]. The first-order wall loss rate (k_{diff}) for Al⁺ was measured to be 655 ± 15 s⁻¹ at 294 K
- and 1 Torr [*Daly et al.*, 2019]. k_{diff} for AlO⁺ and AlO₂⁺ were calculated to be 650 and 649 s⁻¹,
- respectively, from the long-range ion-induced dipole forces between these ions and the He bath
- 174 gas [*Bones et al.*, 2020]. The rate coefficients and branching ratios for the reactions of Al^+ and
- 175 AlO⁺ with O_2 and O_3 have been measured previously by *Daly et al.* [2019], and are listed in
- 176 Table 1.
- 177 A value for k_{23} was obtained by independently fitting the model to each experimental data point
- 178 in Figure 2, and then calculating an overall mean value and standard deviation of $k_{23} = (3.7 \pm$
- 179 1.1 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 294 K. The model run using this result is shown as the solid line
- 180 in Figure 2 (the dashed lines indicate the uncertainty in k_{23}), and clearly provides a satisfactory
- 181 fit to the experimental data.



Figure 2. Fractional recovery of $[Al^+]$ plotted against the ratio of $[CO]/[O_3]$ in the flow tube. The solid points are the experimental data and the model fit is the solid black line, with the dashed lines illustrating the $1.1 \pm 0.04 \text{ K}$

- lines illustrating the $\pm 1\sigma$ uncertainty in k_{23} . Conditions: 1 Torr, T = 294 K.
- 186

187
$$2.1.2 \text{ Reaction of } AlO^+ + O$$

This reaction was studied by again adding O_3 to produce AlO^+ , and then injecting a constant [O] through the sliding injector. The reason for keeping [O] constant is that this reactant is more difficult to make, requiring titration of the N₂ discharge with NO and then measuring [O] at the point of injection (see above). Unlike our previous recent work on NiO⁺ + O [*Bones et al.*, 2020], the reaction of the Al⁺.N₂ cluster ion with O did not have to be accounted for in the model (the source of N₂ is the microwave discharge) because the reaction between Al⁺ and N₂ is very slow

194 [*Daly et al.*, 2019]. Figure 3 shows the Al⁺ signal as a function of $[O_3]$ (varied from $(0.4 - 3.4) \times$

- 195 10^{11} molecule cm⁻³), with [O] either fixed at 1.36×10^{13} molecule cm⁻³ (open circles) or turned
- 196 off (solid circles). The flow tube kinetic model now also requires the wall loss rate for atomic O,

- 197 which was measured to be 500 ± 45 s⁻¹. The model fit (solid lines) is in good agreement with the
- 198 experimental data both in the presence and absence of O, yielding $k_{22}(294 \text{ K}) = (1.7 \pm 0.7) \times$
- 199 10^{-10} cm³ molecule⁻¹ s⁻¹. The dashed lines illustrate the model fit with k_{22} set to its upper and
- 200 lower limits at the 1σ uncertainty level.
- 201





Figure 3. [Al⁺] as a function of $[O_3]$ in the presence of O (open circles, $[O] = 1.36 \times 10^{13}$ molecule cm⁻³) and with the O discharge switched off (solid circles). The solid lines are model fits through the experimental data, and the dashed lines denote the ±1 σ uncertainty in k_{22} .

- 206 Conditions: 1 Torr, T = 294 K.
- 207
- 208 2.2 Neutral Al Chemistry

In order to explore the likely balance between AlO and AlOH in the MLT, we examine here the pathways from $OAlO_2$ and $AlCO_3$ to AlOH (Figure 1). H and H_2O have similar concentrations

between 80 and 90 km [*Plane et al.*, 2015], and so direct conversion of OAlO₂ to AlOH (R10),

and indirect conversion via $Al(OH)_2$ (R11 + R12), need to be considered:

213	$OAlO_2 + H \rightarrow AlOH + O_2$	$\Delta H^{\Theta} = -264 \text{ kJ mol}^{-1}$	(R10)
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214
$$OAlO_2 + H_2O \rightarrow Al(OH)_2 + O_2 \qquad \Delta H^{\Theta} = -96 \text{ kJ mol}^{-1}$$
 (R11)

215
$$Al(OH)_2 + H \rightarrow AlOH + H_2O$$
 $\Delta H^{\Theta} = -168 \text{ kJ mol}^{-1}$ (R12)

Although these reactions are highly exothermic, it is important to determine whether there are any substantial energy barriers on the potential energy surfaces (PES) which link the reactants to the products. Electronic structure calculations were used to do this. The geometries of the Alcontaining molecules were first optimized at the B3LYP/6-311+g(2d,p) level of theory within the Gaussian 16 suite of programs [*Frisch et al.*, 2016], and then more accurate energies determined using the Complete Basis Set (CBS-QB3) method [*Montgomery et al.*, 2000]. The potential energy surfaces for R10, R11 and R12 are illustrated in Figure 4, which also shows the geometries of the

- 223 stationary points on each surface. The Cartesian coordinates, rotational constants, vibrational
- frequencies and heats of formation of the relevant molecules are listed in Table S1 (Supporting Information).







All three reactions exhibit deep wells on their potential energy surfaces, corresponding to very stable intermediates. However, at the low pressures of the MLT these intermediates will not be producing by collisional quenching with air molecules. There are also no barriers above the energy of the reactant entrance channels. Hence, the rate coefficients for these reactions should all be close to their collision frequencies, with small temperature dependences. Interestingly, the reaction between OAlO₂ and H can take place on surfaces of either singlet or triplet spin multiplicity. Although the singlet surface has a deeper well corresponding to singlet HOAlO₂, spin conservation means that this species will dissociate to $AIOH(^{1}A')$ and electronically excited O₂($^{1}\Delta_{g}$).

In the case of AlCO₃, the most likely reaction is with O_2 to form OAlO₂, although reaction with H to make AlOH directly, or indirectly with H₂O via Al(OH)₂, are also exothermic:

241 AlCO₃ + O₂
$$\rightarrow$$
 OAlO₂ + CO₂ $\Delta H^{\circ}(0 \text{ K}) = -61 \text{ kJ mol}^{-1}$ (R14)
242 AlCO₃ + H \rightarrow AlOH + CO₂ $\Delta H^{\circ}(0 \text{ K}) = -325 \text{ kJ mol}^{-1}$ (R15)

$$242 \qquad \text{AlCO} + H = AlCOH + CO_2 \qquad \text{All}(0 \text{ K}) = 323 \text{ KJ mol} \qquad (R13)$$

243
$$AlCO_3 + H_2O \rightarrow Al(OH)_2 + CO_2 \qquad \Delta H^{\circ}(0 \text{ K}) = -158 \text{ kJ mol}^{-1}$$
 (R16)

The potential energy surfaces for these three reactions (Figure S1-S3 in the Supporting Information) show that there are no barriers, so these reactions should also be close to their collision frequencies. In order to assign rate coefficients to R10 – R12 and R14 – R16, we assume a typical collision frequency of 2×10^{-10} cm³ molecule⁻¹ s⁻¹ (*T*/300)^{1/6} cm³ molecule⁻¹ s⁻¹, and multiply this by a statistical factor if the combination of reactant spins leads to a multiplicity of potential energy surfaces which exceeds that of the products [*Smith*, 1980]. For example, for R15 the products are both singlets, and the reactants are both doublets, so the statistical factor is

- 251 $(1 \times 1)/(2 \times 2) = 0.25$. These rate coefficients are listed in Table 1.
- 252
- 253 2.3 Photochemistry of AlOH

We have shown previously that the observed growth of Fe on the underside of the mesospheric

- Fe layer at sunrise is most probably due to the photolysis of the reservoir species FeOH, which has a relatively large photolysis rate in the MLT of $J(\text{FeOH}) = (6 \pm 3) \times 10^{-3} \text{ s}^{-1}$ [*Viehl et al.*,
- 257 and a relatively large photolysis rate in the WE1 of $J(reOff) = (0 \pm 3) \times 10^{-5}$ s [*vient et al.*, 257 2016]. Here we use the quantum chemistry method that we used previously for FeOH [*Viehl et al.*,
- *al.*, 2016] and NiOH [*Daly et al.*, 2020] to estimate *J*(AlOH). First, the geometry of AlOH was
- optimized at the B3LYP/6-311+g(2d,p) level of theory [*Frisch et al.*, 2016]. Second, the vertical
- 260 excitation energies and transition dipole moments for transitions from the AlOH ground state to
- 261 the first 50 electronically excited states were calculated using the time-dependent density
- 262 function theory (TD-DFT) method [Bauernschmitt and Ahlrichs, 1996].



263



266 The resulting absorption spectrum is plotted in Figure 5, which shows that the threshold for

267 photodissociation occurs close to the peak of a strong near-UV absorption band peaking at 229

268 nm. If absorption at wavelengths shorter than 225 nm causes photodissociation to either AI + OH

or AlO + H [*Trabelsi and Francisco*, 2018], then convolving the AlOH cross section up to this threshold with the solar actinic flux from the semi-empirical SOLAR2000 model [*Tobiska et al.*,

271 2000] (averaged over a solar cycle), yields $J(AlOH) = 3.3 \times 10^{-3} \text{ s}^{-1}$ in the MLT.

- 272
- 273 2.4 Al ion-molecule chemistry

274 The ionization energies of AlO and AlOH are 9.82 eV [*Clemmer et al.*, 1992] and 8.89 eV

275 [Sikorska and Skurski, 2009], respectively. These are both lower than the ionization energy of O₂

276 (12.07 eV), which means that both AlO and AlOH should charge transfer with ambient E region

- 277 O_2^+ ions (R18 and R19). However, the lower ionization energy of NO (9.26 eV) means that only
- AlOH will charge transfer with ambient NO^+ (R20). The rate coefficients for these reactions are
- set to their Langevin capture rates, increased to account for the significant dipole moments of
- AlO (4.45 D [*Bai and Steimle*, 2020]) and AlOH (0.97 D [*Sikorska and Skurski*, 2009]) using the
- statistical adiabatic model of *Troe* [1985]. These capture rates are then multiplied by a statistical
- factor to take account of the spin multiplicities of reactants and products.
- Al⁺ reacts most rapidly with O₃ (R21 in Table 1) throughout the MLT [*Daly et al.*, 2019]. AlO⁺
- is then most likely to react with O and be reduced back to Al^+ (R22, see Section 2.1). However,
- AlO⁺ can also recombine with N₂ (R33 in Table 1). The rate coefficient k_{33} was calculated using
- the version of Rice Ramsperger Markus Kassel (RRKM) theory described in *Daly et al.* [2019].
- The relevant molecular parameters are listed in Table S4. This reaction is reasonably fast because the AlO^+ .N₂ cluster ion is bound by 106 kJ mol⁻¹. It is then likely to react with O to form
- because the AlO⁺.N₂ cluster ion is bound by 106 kJ mol⁻¹. It is then likely to react with O to form the weakly bound Al⁺.N₂ ion, which can ligand switch with CO₂ and H₂O to form more stable
- $Al^+.CO_2$ and $Al^+.H_2O$ cluster ions [*Daly et al.*, 2019]. Note that all three of these cluster ions can
- also form directly through the recombination of Al⁺ with N₂, CO₂ or H₂O (R27 R29), though
- only the Al⁺ + N₂ reaction is within two orders of magnitude of reaction with O₃ (R21) [*Daly et*
- 293 *al.*, 2019]. The three cluster ions can then be converted to AlO⁺ by reaction with O (R30 R32).
- 294 The rate coefficients of all the relevant bimolecular ion-molecule reactions which have not been
- 295 measured (black arrows in Figure 1) are set to their Langevin capture rates [*Smith*, 1980]. The
- 296 molecular Al-containing ions can all undergo dissociative recombination with electrons (R35).
- 297 These reactions are all set to the rate coefficient measured for FeO⁺ + e^- [*Bones et al.*, 2016],
- 298 based on the observation that dissociative recombination reactions of small molecular ions nearly
- all have rate coefficients within a factor of 2 of 3×10^{-7} cm³ molecule⁻¹ s⁻¹ [*Florescu-Mitchell*
- 300 *and Mitchell*, 2006].

301 2.5 Permanent removal of Al species

- 302 Reaction R36 in Table 1 is a set of polymerization reactions which account for the permanent
- 303 loss of the significant neutral Al-containing molecules AlO, AlOH and, to a lesser extent,
- $Al(OH)_2$ (see Section 4) to form meteoric smoke particles. We have used this type of reaction in
- previous models of the Na [Marsh et al., 2013], K [Plane et al., 2014], Fe [Feng et al., 2013],
- 306 Mg [Langowski et al., 2015], SiO [Plane et al., 2016], Ca [Plane et al., 2018] and Ni [Daly et
- 307 *al.*, 2020] layers. In this case, k_{36} is set to 6×10^{-8} cm³ s⁻¹, which is ~80 times larger than a
- 308 typical dipole-dipole capture rate for these metallic molecules. This factor allows for the Al-

- 309 containing reservoir species to polymerize with other metal-containing molecules produced by
- 310 meteoric ablation (e.g., FeOH and Mg(OH)₂), whose concentration will be around 80 times
- 311 higher because the elemental ablation ratio of Al atoms to the sum of Na + Fe + Mg + Si + Ni +
- 312 Al atoms is 1/81.2 [Carrillo-Sánchez et al., 2020].
- 313

314 **3** Observations of AlO in the MLT

315 3.1 Lidar observations

316 3.1.1 Lidar and calibration cell setup

- The absolute absorption cross section of AlO at the bandhead of the $B^2\Sigma^+(v'=0) X^2\Sigma^+(v''=0)$ 317
- transition at $\lambda_{air} = 484.23$ nm is $\sigma(298 \text{ K}, 1 \text{ hPa}) = (6.7 \pm 1.6) \times 10^{-15} \text{ cm}^2 \text{ molecule}^{-1} (0.003 \text{ nm})$ 318
- 319 resolution) [Gómez Martín et al., 2017]. Because this cross section is unusually large for a
- 320 diatomic molecule, we carried out a lidar campaign to determine if an AlO layer could be
- 321 detected. Soundings were performed at Kühlungsborn, Germany (54°N, 12°E) for 3 nights during
- January 2016 and 3 nights in April 2017, yielding ~20 hours of integration time. Details of the 322
- 323 lidar system are given by Gerding et al. [2019]; the instrument is a modification from an earlier
- 324 twin dye laser design [Alpers et al., 1996; Gerding et al., 2000]. Laser emission at 484.23 nm
- 325 was produced using a XeCl excimer laser at 308 nm (repetition rate = 30 Hz) to pump a dve laser
- 326 with Coumarin 102 dye dissolved in methanol, producing laser radiation over the 455 - 495 nm 327 spectral range.
- 328 A small-scale version of the flow tube used by [Gómez Martín et al., 2017] was installed next to
- 329 the lidar as an AlO calibration cell, both to check the laser wavelength before atmospheric
- 330 measurements and then to avoid drift away from the AlO bandhead during operation. AlO was
- 331 produced in the cell by laser ablation of a rotating Al rod, using 532 nm light that was beam-split
- 332 from a Nd:YAG laser in the co-located Rayleigh-Mie-Raman (RMR) lidar [Gerding et al.,
- 333 2016]. The Al was entrained in a flow of N_2 (total pressure = 2.1 Torr), and a trace of O_2 added
- 334 N2 downstream to make AlO via reaction 1. A quartz fiber was used to guide the 484 nm laser
- 335 light from the AlO lidar to the calibration cell, and laser induced fluorescence detected with a
- 336 photomultiplier orthogonal to the laser beam. The dye laser was scanned in 1 pm intervals to find
- 337 the peak of the AlO bandhead. A flip mirror was used to alternately direct the dye laser to the calibration cell or to the optics in the lidar transmitter.
- 338
- 339 3.1.2 Observations at 484 nm
- 340 Figure 6a shows the integrated lidar backscatter profile at 484.23 nm (blue line), summed over 341 the 3 sounding nights during April 2017. The background noise level, which was determined by 342 averaging the signal from 120 - 150 km (dashed line in Figure 6a), has been subtracted. The
- 343 RMR lidar (green line in Figure 6), which operated simultaneously alongside the AlO resonance
- 344 lidar, was used to provide an off-resonance measurement (at 532 nm) since no off-resonance
- 345 measurements were taken with the resonance lidar (which was set to the AlO bandhead). Both
- 346 profiles showed a monotonic decay of the Rayleigh scatter into the background noise. The 484
- 347 nm Rayleigh scatter was detected well above 80 km where an AlO layer would be expected
- 348 (Figure 6b), based on the metal atom layers [*Plane*, 2003; *Gerding et al.*, 2019].





Figure 6. Integrated backscatter profile of lidar soundings during April 2017 on a log scale. (a) 484 nm lidar (blue line) and RMR lidar (green), after background subtraction. The dashed line is the 484 nm background signal measured between 120 and 150 km. The purple line is the extrapolated Rayleigh backscatter above 80 km. (b) The 484 nm lidar – background (blue line) and the extrapolated Rayleigh signal (purple line) on a linear scale. (c) Residual signal after the background and extrapolated Rayleigh backscatter are subtracted from the 484 nm signal. The red line is the 3σ photon noise level. The altitude resolution is 200 m.

358 The Rayleigh backscatter was then extrapolated from 80 km to higher altitudes (purple lines in 359 Figure 6a and 6b) and subtracted from the backscatter signal to yield the residual signal (black 360 line in Figure 6c). No obvious resonance layer was detected over the observation period; application of Poisson statistics shows that an AlO resonance signal was not present above the 361 362 the 3_o photon noise threshold (red line in Figure 6c) [Gerrard et al., 2001]. Nevertheless, an 363 upper limit for the AlO density can be estimated. A Gaussian profile for the AlO layer was 364 assumed, extending from 85 to 100 km with a peak at 90 km (analogous to other metal layers [Plane, 2003]), and fitted to the residual signal. Adapting the work of Tilgner and von Zahn 365

366 [1988], the upper limit to the AlO density, n_z (AlO), is then given by:

367
$$n_z(AlO) = n_{zr}(air) \frac{\sigma_{Ray}(air)}{\sigma_{res}(AlO)} \frac{z^2(AlO)}{z_r^2} \frac{C(AlO)}{C(air)} \frac{1}{Tr^2(z_r, z)}$$
(I)

368 where $n_{zr}(air)$ is the air density at the reference altitude from NRLMSISE-00 [*Picone et al.*,

369 2002], σ_{Ray} (7.6 × 10⁻²⁷ cm² molecule⁻¹) and σ_{res} ((6.7 ± 1.6) × 10⁻¹⁵ cm² molecule⁻¹ [*Gómez*

370 *Martín et al.*, 2017]) are the Rayleigh and effective resonance AlO cross sections, *z* the altitude

- taken for the AlO peak, z_r the reference altitude of 30 km, C(AlO) and C(air) are the AlO
- resonance and Rayleigh photon counts after the background noise is subtracted, and $Tr(z_r, z)$ is

373 the transmission (assumed to be 1) of the atmosphere between z_r and z at the laser pulse

374 wavelength. This yields an AlO detection limit of 57 cm^{-3} .

- 375
- 376 3.2 Al releases in the MLT
- 377 TMA grenade releases from rocket payloads in the MLT generate visible chemiluminescence
- 378 [*Golomb et al.*, 1967; *Roberts and Larsen*, 2014], which was proposed to arise from the radiative 379 recombination reaction [*Golomb and Brown*, 1976; *Gole and Kolb*, 1981]:
- 380 AlO + O \rightarrow OAlO + hv $\Delta H^{\circ}(0 \text{ K}) = -390 \text{ kJ mol}^{-1}$ (R36)

R36 is sufficiently exothermic to produce emission at wavelengths longer than 306 nm. TheOAIO product is then recycled to AIO by reaction with O:

383 $OAIO + O \rightarrow AIO + O_2$ $\Delta H^{\circ}(O \text{ K}) = -107 \text{ kJ mol}^{-1}$ (R3)

which proceeds close to the capture rate [Mangan et al., 2020], so that AlO is in a large excess 384 385 over OAlO and the intensity of the chemiluminescence is a marker for the AlO concentration. 386 Roberts and Larsen [2014] reported that the chemilumiscence intensity decayed with an e-387 folding lifetime of around 29 min between 90 and 100 km i.e. the first-order removal for AlO into a long-lived reservoir is $\sim 6 \times 10^{-4}$ s⁻¹. The rate of injection of Al atoms into the MLT has 388 recently been estimated to be 3×10^{-3} cm⁻³ s⁻¹ [*Carrillo-Sánchez et al.*, 2020]; since the Al will 389 immediately be oxidized by O₂ to AlO, this represents the injection rate of fresh AlO. Balancing 390 391 injection against removal, the steady-state concentration of AlO should then be ~5 cm⁻³. This is 1 392 order of magnitude lower than the upper limit for AlO determined from the lidar observations in 393 Section 3.1. Note that this estimate of the AlO density is during *night-time*, when these rocket 394 release experiments were conducted.

395

396 4 Model simulations of Al chemistry in the MLT

397 4.1 WACCM-Al set up

398 The Al reactions in Table 1 were imported into the Whole Atmosphere Community 399 Climate Model (WACCM6), which uses the framework developed from the second iteration of 400 the fully coupled Community Earth System Model (CESM2) [Gettelman et al., 2019]. 401 WACCM6 has a vertical extension from the Earth's surface to the lower thermosphere at ~140 402 km. Although the model can be nudged by a reanalysis dataset, as we have done with other 403 meteoric metals where measurements are available for comparison [Plane et al., 2015; Plane et 404 al., 2018], for the present study we used a free-running version of WACCM6 with a reduced tropospheric chemical mechanism. The model has a horizontal resolution of 1.9° latitude $\times 2.5^{\circ}$ 405 406 longitude, and 70 vertical model layers (~3 km vertical resolution in the MLT region). This 407 version of WACCM6 with Al chemistry is termed WACCM-Al. The full set of Fe reactions in WACCM-Fe [Feng et al., 2013; Viehl et al., 2016] was also included in order to compare model 408 409 simulations with measurements of Al⁺ and Fe⁺ in the MLT. The model simulations were 410 performed from 1979 to 2014, using the standard WACCM6 initialization conditions file 411 [Danabasoglu et al., 2020]. Here we focus on a decade of model output from 2004-2014, which 412 is sufficiently long to produce a climatology of the Al species.

No.	Reaction	Rate coefficient ^a
	Neutral reactions	
R1	$Al + O_2 \rightarrow AlO + O$	$k_1 = 1.7 imes 10^{-10} \ (T/300)^{1/6}$ b
R2	$AlO + O_3 \rightarrow OAlO + O_2$	$k_2 = 1.3 imes 10^{-10} \ (T/300)^{1/6} \ c$
R3	$OAlO + O \rightarrow AlO + O_2$	$k_3 = 1.9 \times 10^{-10} \ (T/300)^{1/6} \ c$
R4	$OAlO + CO \rightarrow AlO + CO_2$	$k_4 = 2.6 \times 10^{-11} (T/300)^{1/6}$ c
R5	$AlO + CO \rightarrow Al + CO_2$	$k_5 = 2.0 \times 10^{-12} \ (T/300)^{1/6} \ c$
R6	$AlO + O_2 (+ N_2) \rightarrow OAlO_2$	$log_{10}(k_6) = -35.137 + 6.1052 log_{10}(T) - 1.4089$ $(log_{10}(T))^2$ ^c
R7	$AlO + CO_2 (+ N_2) \rightarrow AlCO_3$	$log_{10}(k_7) = -38.736 + 8.7342log_{10}(T) - 2.0202$ $(log_{10}(T))^2$ c
R8	$OAlO_2 + O \rightarrow OAlO + O_2$	$k_8 = 1.2 \times 10^{-10} (T/300)^{1/6} d$
R9	$OAlO + H \rightarrow AlOH + O$	$k_9 = 2 \times 10^{-10} \ (T/300)^{1/6} \ d$
R10	$OAlO_2 + H \rightarrow AlOH + O_2$	$k_{10} = 2 \times 10^{-10} \ (T/300)^{1/6} \ d$
R11	$OAlO_2 + H_2O \rightarrow Al(OH)_2 + O_2$	$k_{11} = 2 \times 10^{-10} \ (T/300)^{1/6} \ d$
R12	$Al(OH)_2 + H \rightarrow AlOH + H_2O$	$k_{12} = 5 \times 10^{-11} \ (T/300)^{1/6} \ d$
R13	$AlCO_3 + O \rightarrow OAlO + CO_2$	$k_{13} = 4 \times 10^{-11} \ (T/300)^{1/6} \ d$
R14	$AlCO_3 + O_2 \rightarrow OAlO_2 + CO_2$	$k_{14} = 6.6 \times 10^{-11} \ (T/300)^{1/6} \ d$
R15	$AlCO_3 + H \rightarrow AlOH + CO_2$	$k_{15} = 5 \times 10^{-11} \ (T/300)^{1/6} \ d$
R16	$AlCO_3 + H_2O \rightarrow Al(OH)_2 + CO_2$	$k_{16} = 2 \times 10^{-10} (T/300)^{1/6} d$
R17	AlOH $+hv \rightarrow$ AlO $+$ H	$k_{17} = 3.3 \times 10^{-3} e^{-3}$
	Ion-molecule reactions	
R18	$AlO + O_2^+ \rightarrow AlO^+ + O_2$	$4.1 \times 10^{-9} (T/300)^{-0.364} \mathrm{f}$
R19	$AlOH + O_2^+ \rightarrow AlOH^+ + O_2$	$2.3 \times 10^{-9} (T/300)^{-0.165} \mathrm{f}$
R20	$AlOH + NO^{+} \rightarrow AlOH^{+} + NO$	$1.7 \times 10^{-9} (T/300)^{-0.22} \mathrm{f}$
R21	$Al^+ + O_3 \rightarrow AlO^+ + O_2$	1.4×10^{-9} g
R22	$AlO^+ + O \rightarrow Al^+ + O_2$	$1.7 imes 10^{-10}$ h

Table 1. Aluminum chemistry in the MLT

R23	$AlO^+ + CO \rightarrow Al^+ + CO_2$	3.7×10^{-10} h
R24a	$AlO^+ + O_3 \rightarrow OAlO^+ + O_2$	4.1×10^{-10} g
R24b	$AlO^+ + O_3 \rightarrow Al^+ + 2O_2$	8.8×10^{-10} g
R25	$OAlO^{+} + O \rightarrow AlO^{+} + O_{2}$	3.5×10^{-10} f
R26	$AlOH^{+} + H \rightarrow Al^{+} + H_2O$	1.7×10^{-10} f
R27	$Al^+ + N_2 (+N_2) \rightarrow Al^+.N_2$	$log_{10}(k) = -27.9739 + 0.05036log_{10}(T) - 0.60987(log_{10}(T))^2$ g
R28	$Al^+ + CO_2 (+N_2) \rightarrow Al^+.CO_2$	$log_{10}(k) = -33.6387 + 7.0522log_{10}(T) - 2.1467(log_{10}(T))^{2 g}$
R29	$Al^+ + H_2O (+N_2) \rightarrow Al^+.H_2O$	$log_{10}(k) = -24.7835 + 0.018833log_{10}(T) - 0.6436(log_{10}(T))^2 g$
R30	$Al^{+}.N_{2} + O \rightarrow AlO^{+} + N_{2}$	1.2×10^{-10} f
R31	$Al^+.CO_2 + O \rightarrow AlO^+ + CO_2$	1.2×10^{-10} f
R32	$Al^+.H_2O + O \rightarrow AlO^+ + H_2O$	1.2×10^{-10} f
R33	$AlO^{+} + N_2 (+N_2) \rightarrow AlO^{+}.N_2$	$2.7 \times 10^{-27} (T/300)^{-2.31}$ i
R34	$AlO^+.N_2 + O \rightarrow Al^+.N_2 + O_2$	3×10^{-10} f
R35	$Al^+.X + e^- \rightarrow Al + X$	$3 \times 10^{-7} (T/300)^{-0.5 \text{ j}}$
	Sink polymerization reactions	
R36	$AlX + AlY \rightarrow Al_2XY$ (X, Y = O, OH, (OH) ₂)	$5.8 \times 10^{-7 \text{ k}}$

^a Units: s⁻¹ for photolysis reactions; cm³ molecule⁻¹ s⁻¹ for bimolecular reactions; cm⁶ molecule⁻² s⁻¹ for termolecular reactions. ^b *Gómez Martín et al.* [2017]. ^c *Mangan et al.* [2020]. ^d set to a collision frequency of $2 \times 10^{-10} (T/300)^{1/6}$ cm³ molecule⁻¹ s⁻¹, scaled by a statistical electronic branching factor (see text). ^e Calculation from electronic structure theory, this study. ^f Set to the Langevin collision frequency, scaled by a statistical electronic branching factor (see text). ^g *Daly et al.* [2019]. ^h Measured, this study. ⁱ RRKM calculation (see text). ^j Set to the measured rate coefficient for FeO⁺ + e⁻ [*Bones et al.*, 2016]. ^k See text.

422

423 4.2 Al meteoric input function

424 The global average injection profiles of Al and Fe are illustrated in Figure 7. These Meteoric

425 Input Functions (MIFs) were estimated by combining the new version of the Chemical ABLation

426 MODel (CABMOD-3), which simulates the ablation of the major meteoric elements from an

427 individual dust particle [Carrillo-Sánchez et al., 2020], with the Zodiacal Cloud Model (ZoDY)

428 which provides the mass, velocity and radiant distributions of particles entering Earth's

429 atmosphere from Jupiter Family Comets, the asteroid belt, and long-period Halley-Type comets

430 [*Nesvorný et al.*, 2011]. The contributions from these different sources are weighted using the

431 procedure in *Carrillo-Sánchez et al.* [2016].

432 Note that both injection profiles in Figure 7 have been reduced by a factor of 5 from the profiles

433 in *Carrillo-Sánchez et al.* [2020]. This accounts for the fact that global models such as WACCM

underestimate the vertical transport of minor species in the MLT, because short wavelength
gravity waves are not resolved on the current horizontal grid scale of the model (~220 km).

435 gravity waves are not resolved on the current nonzontal grid scale of the model (~220 km). 436 These sub-grid waves contribute to vertical chemical and dynamical transport of constituents

437 while dissipating, and this can exceed transport driven along mixing ratio gradients by the

- 438 turbulent eddy diffusion produced once the waves break [*Gardner et al.*, 2017]. Because these
- 439 additional vertical transport mechanisms are underestimated, the MIF of each metal needs to be
- 440 reduced in order to correctly simulate the observed *absolute* metal density [*Plane et al.*, 2018].
- 441 The Al MIF in WACCM is then set to vary with season and latitude in the same way as the Fe
- 442 MIF [*Feng et al.*, 2013] i.e. an autumnal maximum and vernal minimum, increasing from
- 443 essentially no variation at the equator to $\pm 30\%$ at the pole, with the same annual average input at 444 all latitudes.



445



447 profiles from [*Carrillo-Sánchez et al.*, 2020] have been divided by factor of 5.0.

448

449 4.3 Model results

450 Figure 8 shows the annual average vertical profiles of the major Al species at 54°N, the latitude

451 of the lidar observations. As expected, Al⁺ is the dominant species above 95 km. AlO and AlOH

then occur in layers that peak around 89 and 86 km, respectively. Al(OH)₂ is also significant

453 below 80 km once the atomic H concentration decreases significantly [*Plane et al.*, 2015], so that

454 reaction R12 becomes very slow. Below 92 km, most of the Al is tied up as Al-containing

455 polymers, which represent a surrogate for meteoric smoke particles (MSPs) (see Section 2.5).



457 Figure 8. Annual average profiles of the major Al-containing species, simulated by WACCM-Al
458 at 54°N between 2004 and 2014. MSP = meteoric smoke particle.

456

460 Figure 9 (left panel) compares the vertical profile of Al⁺ simulated by WACCM-Al with the

461 geometric mean profiles from a set of eight mid- to high-latitude rocket-borne mass

462 spectrometric measurements by Kopp and co-workers [*Meister et al.*, 1978; *Kopp et al.*, 1984;

463 *Kopp et al.*, 1985a; *Kopp et al.*, 1985b; *Kopp*, 1997]. Details of these flights are provided in

464 Table S5. The model results are the annual average simulated Al^+ profile at 0 LT for 54°N. The

do bserved Al⁺ layer peaks around 92 - 94 km, with a geometric mean density of 40 cm^{-3} and

466 geometric standard deviation from 20 - 100 cm⁻³. The modeled layer peaks at 93 km, with a

467 density close to 100 cm⁻³. Given the paucity of observations, this level of agreement is

468 satisfactory. Because the reaction of AlO^+ with O (R22) is relatively fast (Section 2.1.2) and O is 469 a major species above 84 km, Al^+ is the major Al-containing ion by 2-5orders of magnitude

470 between 85-110 km. Figure 9 (right panel) shows that the rocket-measured Fe⁺:Al⁺ ratio is also

471 satisfactorily modeled between 86 and 104 km. The ratio is very close to the CABMOD-ZoDy

472 estimate of the relative meteoric inputs, which is a factor of 2.8 larger than the CI ratio of the two

- 473 metals.
- 474
- 475





477 Figure 9. Left-hand panel: annual mean altitude profile of Al⁺ at 0 LT, simulated by WACCM-Al for Kühlungsborn (54°N, 12°E) (dotted line). The solid black line with open circles is the 478 479 geometric mean profile of Al⁺, with the geometric standard deviation (1σ error limits, thin black lines lines), for the eight rocket flights listed in Table S5. Right-hand panel: mean altitude profile 480 481 of the modeled Fe⁺:Al⁺ ratio (dotted line), compared with the measured ratio (solid black line 482 with open circles; geometric 1σ standard deviation shown by thin black lines lines). The Fe:Al 483 ablation ratio predicted by the CABMOD-ZoDY model and the CI ratio are shown by the 484 vertical lines on the plot.

- 486 Figure 10 shows the diurnal variation of Al⁺, AlO and AlOH as a function of height during April
- 487 at 54°N, in order to compare with the lidar measurements described in Section 3.1. The diurnal
- 488 variation of the vertical column densities of these species is shown in Figure S4. As expected,
- 489 Al⁺ peaks between 13 and 17 UT because of the daytime increase in the concentrations of the
- 490 lower *E* region ions NO⁺ and O_2^+ , which charge transfer with AlO and AlOH (R18 R20).
- 491 More interesting is the diurnal behavior of the neutral species AlO and AlOH, which are
- 492 essentially anti-correlated: AlO peaks during daytime, and AlOH at night. This behavior is
- 493 caused by the photolysis of AlOH (R17) to produced AlO either directly or via Al. The result is
- that AlO varies between 10 and 20 cm⁻³ at night, but it increases to over 60 cm⁻³ between 13 and
- 495 20 UT. The nighttime level is consistent with the upper limit of 57 cm⁻³ determined from the
- 496 lidar observations (Section 3.1), and also with the concentration of $\sim 5 \text{ cm}^{-3}$ that is inferred from
- 497 the Al rocket release experiments (Section 3.2).
- 498





500 Figure 10. Hourly average vertical profiles of Al⁺ (top panel), AlO (middle panel) and AlOH
501 (bottom panel) for 54°N during April (local time is ~1 hour ahead of Universal Time).

- 503 Figure 11 illustrates the variation with latitude and month of the vertical column densities of Al⁺,
- $AIO and AIOH. AI^+$ shows little seasonal variation at low latitudes, but a 3-fold increase between
- 505 winter and summer at mid- to high-latitudes, reflecting the change in ambient lower *E* region
- 506 ionization. AlOH also demonstrates a strong (though opposite) annual cycle at high latitudes,
- 507 increasing by a factor of ~6 from a mid-summer minimum in the continuously sunlit polar region 508 to a mid-winter maximum in polar night. In contrast, AlO exhibits a semi-annual cycle at mid- to
- 508 to a mid-winter maximum in polar night. In contrast, AIO exhibits a semi-annual cycle at mid- to 509 high-latitudes, peaking at the equinoxes. The reason is that after polar night, during which AIO
- 50 is very low because most of the neutral Al is in the form of AlOH, photolysis causes a spring-
- time increase in AlO by a factor of ~ 3 . However, moving into summer the AlO is reduced again
- 512 by increased charge transfer with O_2^+ (R18), causing Al⁺ to peak. The situation then reverses in
- 513 the autumn. Note that the AlO is up to a factor of 2 times higher at the autumnal compared with
- 514 the vernal equinox, because of the autumnal peak in the MIF [*Feng et al.*, 2013].
- 515 Figure S5 illustrates the seasonal/latitudinal variation of the centroid height and root-mean-
- 516 square width of the AlO layer. Although the layer mostly peaks around 90 km, at high latitudes
- 517 during polar night the peak increases to 98 km because AlOH is essentially a sink for neutral Al
- 518 species below this in the absence of sunlight. In contrast, the mid-summer AlO layer at high
- 519 latitudes still peaks around 90 km because now the removal of AlO is via charge transfer at
- 520 higher altitudes. The RMS layer width is on average around 5 km, with a mid-summer minimum
- 521 at polar latitudes of 3.6 km because of the ionization of the top-side of the AlO layer.





Figure 11. Seasonal/latitudinal variations of the column abundances of AlO, AlOH and Al⁺
(units: 10⁷ cm⁻²), averaged from 2004 to 2014.

527 **5 Conclusions**

- 528
- 529 In this study we describe a comprehensive Al chemistry network, constructed from a set of
- neutral and ion-molecule reactions measured previously in our laboratory [*Daly et al.*, 2019;
- 531 Mangan et al., 2020], as well as the reactions of AlO⁺ with O and CO (R22 and R23) reported as
- 532 part of the present study. Additional reaction rate coefficients are estimated by using electronic
- 533 structure theory to explore the relevant potential energy surfaces. The Al reaction network was
- then incorporated into the WACCM chemistry-climate model, along with a new MIF for Al
- 535 [Carrillo-Sánchez et al., 2020].
- 536 We also report the first attempt, to our knowledge, to directly observe the AlO layer in the MLT.
- 537 Although the lidar observations did not detect a layer, an upper limit of only 57 cm⁻³ for the AlO
- 538 density was determined. This sets an important benchmark for future observations. A rough
- estimate for AlO of around 5 cm⁻³ was obtained from the rate of decay of AlO
- 540 chemiluminescence from rocket-borne grenade releases. Both of these types of atmospheric
- 541 measurements apply to nighttime. However, the WACCM-Al model indicates that AlO should
- 542 be a factor of ~6 times higher during daytime, because of photolysis of AlOH, which is the other
- 543 major neutral Al-containing molecule. Of course, this result depends on the accuracy of the
- 544 calculated photolysis rate of AlOH (Section 2.3), and it is essential that this is measured in the
- 545 future. Lidar measurements during twilight, when photolysis of AlOH in the MLT is still
- 546 occurring but the solar terminator is above the troposphere so that the amount of scattered
- 547 sunlight is reduced, would offer the best chance of detecting AlO. This is particularly the case at 548 high latitudes during spring or autumn (e.g. at 69°N, 3 hrs of twilight measurements could be
- made on J112 or J253), when the AlO density should also be highest (Figure 11).
- 550

551 Acknowledgments

- 552 This work was supported by Natural Environment Research Council grant NE/P001815/1.
- 553 S.M.D. was supported by a studentship from the NERC SPHERES Doctoral Training Program.
- 554 The rocket flight data was kindly provided by E. Kopp (University of Bern). The WACCM-Al
- and WACCM-Fe models were performed on the University of Leeds Advanced Research
- 556 Computer (ARC4). There are no conflicts of interest for any author.
- 557

558 Data Availability Statement

- 559 The version cesm2_1_3 model and input data are provided by the National Centre for
- 560 Atmospheric Research (<u>http://www.cesm.ucar.edu/models/cesm2/release_download.html</u>). The
- 561 WACCM-Al and WACCM-Fe models and output are archived in the Petabyte Environmental
- 562 Tape Archive and Library at the University of Leeds via <u>https://petal.leeds.ac.uk/</u>. The data is
- 563 available at <u>http://doi.org/10.5281/zenodo.4066748</u>.
- 564

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- 720

723 Figure Captions

- 724
- Figure 1. Schematic diagram of meteor-ablated Al chemistry in the MLT. Ionized and neutral Al
- species are contained in blue and green boxes, respectively. Blue arrows indicate reactions
- measured previously, and the red arrow shows the reactions measured in the present study.
- Figure 2. Fractional recovery of $[A1^+]$ plotted against the ratio of $[CO]/[O_3]$ in the flow tube. The solid points are the experimental data and the model fit is the solid black line, with the dashed
- Find points are inpermitted and the interval of the solution of the solution
- Figure 3. [Al⁺] as a function of [O₃] in the presence of O (open circles, [O] = 1.36×10^{13}
- molecule cm⁻³) and with the O discharge switched off (solid circles). The solid lines are model fits through the curve in and the decked lines denote the ± 1 supertointy in *k*
- fits through the experimental data, and the dashed lines denote the $\pm 1\sigma$ uncertainty in k_{22} . Conditions: 1 Torr, T = 294 K.
- Figure 4. Reaction potential energy surfaces calculated at the CBS-QB3 level of theory: (a) OAlO₂
 + H; (b) OAlO₂ + H₂O; (c) Al(OH)₂ + H
- **Figure 5.** Absorption cross section of AlOH calculated at the TD-B3LYP//6-311+g(2d,p) level
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- Figure 7. Global annual mean injection rates of Al and Fe from meteoric ablation. The injection
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- Figure 8. Annual average profiles of the major Al-containing species, simulated by WACCM-Al
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- 750 **Figure 9.** Left-hand panel: annual mean altitude profile of Al⁺ at 0 LT, simulated by WACCM-
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- geometric mean profile of Al^+ , with the geometric standard deviation (1 σ error limits, thin black
- lines lines), for the eight rocket flights listed in Table S5. Right-hand panel: mean altitude profile
- of the modeled Fe⁺:Al⁺ ratio (dotted line), compared with the measured ratio (solid black line
- 755 with open circles; geometric 1σ standard deviation shown by thin black lines lines). The Fe:Al
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- 757 vertical lines on the plot.
- Figure 10. Hourly average vertical profiles of Al⁺ (top panel), AlO (middle panel) and AlOH
 (bottom panel) for 54°N during April (local time is ~1 hour ahead of Universal Time).
- Figure 11. Seasonal/latitudinal variations of the column abundances of AlO, AlOH and Al^+ (units: 10^7 cm⁻²), averaged from 2004 to 2014.
- 762
- 763 Tables
- 764 **Table 1.** Aluminum chemistry in the MLT



Journal of Geophysical Research – Space Physics

Supporting Information for

Meteor-ablated Aluminum in the Mesosphere-Lower Thermosphere

John M.C. Plane¹, Shane M. Daly¹, Wuhu Feng^{1,2}, Michael Gerding³ and Juan Carlos

Gómez Martín⁴

¹School of Chemistry, University of Leeds, United Kingdom.

² NCAS, University of Leeds, United Kingdom.

³ Leibniz Institute of Atmospheric Physics, Kühlungsborn, Germany.

⁴ Instituto de Astrofísica de Andalucía, CSIC, 18008, Granada, Spain

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Figure S3. Potential energy surface for the reaction of AlCO₃ and H₂O, calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 2000].

Table S1. Molecular properties and heats of formation (at 0 K) of the stationary points on the $OAlO_2$ + H and H₂O potential energy surfaces. The geometries are illustrated in Figure 4a and 4b in the main paper.

Table S2. Molecular properties and heats of formation (at 0 K) of the stationary points on the $Al(OH)_2$ + H potential energy surface. The geometries are illustrated in Figure 4c in the main paper.

Table S3. Molecular properties and heats of formation (at 0 K) of the stationary points on the AlCO₃ + O₂, H and H₂O potential energy surface. The geometries are illustrated in Figures S1 – S3.

Table S4. Parameters used in RRKM fits to the kinetics of $AIO^+ + N_2$.

Table S5. Rocket-borne mass spectrometric measurements of Al⁺ ions used to construct the Al⁺ profile in Figure 9 (main paper): payload reference number, launch location, launch time/date, and reference.

Introduction

The Figures and Tables in the SI are all referred to individually in the main paper, so please refer to that for further information beyond that contained in the captions and footnotes.



Figure S1. Potential energy surface for the reaction of AlCO₃ and O₂, calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 2000].



Figure S2. Potential energy surface for the reaction of AlCO₃ and H, calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 2000].



Figure S3. Potential energy surface for the reaction of AlCO₃ and H₂O, calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 2000].



Figure S4. Diurnal variation of the vertical column densities of AlO, AlOH and Al⁺ at 54°N and Julian day 90. The variation of solar zenith angle is also plotted (right-hand ordinate axis).



Figure S5. Variation of the zonally-averaged AlO centroid height (upper panel, in km) and RMS width (lower panel, in km), as a function of latitude and month. Averaged data from 2004-2014.

Table S1. Molecular properties and heats of formation (at 0 K) of the stationary points on the $OAlO_2 + H$ and H_2O potential energy surfaces. The geometries are illustrated in Figure 4a and 4b in the main paper.

Molecule	Geometry	Rotational	Vibrational	$\Delta_{\rm f} H^{\rm o}(0 \text{ K})$
(electronic state)	(Cartesian co-ordinates in $Å$) ^a	(GHz) ^a	$(\text{cm}^{-1})^{a}$	(kJ mol ⁻¹) ⁰
OAlO ₂ (² A ₂)	Al, 0., 0., -0.394 O, 0., -0.684, 1.318 O, 0., 0.685, 1.318 O, 0., 0., -1.994	33.702 4.0970 3.6530	189, 192, 454, 556, 1109, 1157	-148
HOAlO ₂ (¹ A)	Al, -0.046, -0.015, -0.284 O, -0.113, 0.049, -1.950 O, 0.071, 0.809, 1.194 O, -0.029, -0.824, 1.210 H, -0.184, -0.648, -2.603	23.110 4.3503 3.6612	205, 210, 229, 517, 570, 768, 773, 1103, 3946	-433
HOAlO ₂ (³ A)	Al, 0.320, -0.595, 0.004 O, 1.744, 0.341, -0.002 O, -1.244, 0.236, 0.678 O, -1.244, 0.228, -0.680 H, 1.791, 1.300, -0.008	17.173 4.2521 4.2511	147, 202, 247, 402, 529, 613, 842, 1160, 3892	-269
AlOH $(^{1}\Sigma)$	Al, 0., 0., -0.050 O, 0., 0., 1.638 H, 0., 0., 2.592	15.492	132, 132, 819, 3982	-196
OAlO ₂ -H ₂ O	Al, -0.822, 0.809, 0.341 O, 0.693, -0.259, 0.346 O, 0.971, 0.998, -0.111 O, -2.378, 1.023, -0.041 O, -0.878, 1.544, 2.136 H, -0.339, 2.244, 2.532 H, -1.812, 1.835, 2.033	6.3241 3.4177 2.5610	71, 127, 204, 207, 307, 425, 441, 533, 553, 725, 1035, 1145, 1557, 3536, 3796	-500
TS from OAlO ₂ - H ₂ O to Al(OH) ₂ -O ₂ (TS1)	Al, -0.182, -0.403, -0.008 O, 1.498, -0.052, 0.678 O, 1.473, 0.088, -0.681 O, -1.508, -1.343, -0.087 O, -1.306, 1.150, 0.132 H, -1.426, 1.862, -0.512 H, -1.996, 0.398, 0.008	7.0458 3.2233 2.5548	-139 <i>i</i> , 121, 199, 209, 402, 419, 452, 560, 651 889, 1042, 33 1146, 1474, 2853, 3800	-500
Al(OH) ₂ -O ₂	Al,0,-0.259, 0.007, 0.0 O, 0,1.46,-0.062, 0.682 O, 1.463, -0.065, -0.682	5.44625 3.96904 2.65445	148, 206, 215, 262, 288, 305,	-779

	O, -1.080, -1.470, 0.001 O, -1.083, 1.485, -0.002 H, -0.685, 2.356, 0.0126 H, -2.035, -1.554, 0.004		455, 550, 629, 636, 835, 941, 1151, 3935, 3938	
Al(OH) ₂	Al, -0.652, 0.487, 0.110 O, 0.610, -0.630, 0.381 H, 1.148, -0.639, 1.178 O, -0.996, 1.664, 1.309 H, -1.687, 2.326, 1.234	39.607 6.5199 5.5983	214, 301, 332, 602, 620, 752, 881, 3878, 3913	-483

^a Calculated at the B3LYP/6-311+g(2d,p) level of theory [*Frisch et al.*, 2016]. ^b Calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 2000] with JANAF reference values for $\Delta_{\rm f} H^{\rm o}({\rm Al}) = 327.3$ kJ mol⁻¹, $\Delta_{\rm f} H^{\rm o}({\rm O}) = 246.8$ kJ mol⁻¹, $\Delta_{\rm f} H^{\rm o}({\rm CO})$ = -113.8 kJ mol⁻¹, $\Delta_{\rm f} H^{\rm o}({\rm CO}_2) = -393.2$ kJ mol⁻¹ and $\Delta_{\rm f} H^{\rm o}({\rm H}_2{\rm O}) = -238.9$ kJ mol⁻¹ at 0 K; and $\Delta_{\rm f} H^{\rm o}({\rm AlO}) = 70.3$ kJ mol⁻¹ [*Mangan et al.*, 2020].

Table S2. Molecular properties and heats of formation (at 0 K) of the stationary points on the $Al(OH)_2 + H$ potential energy surface. The geometries are illustrated in Figure 4c in the main paper.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) ^a	Rotational constants (GHz) ^a	Vibrational frequencies (cm ⁻¹) ^a	$\frac{\Delta_{\rm f} H^{\rm o}(0 \text{ K})}{(\text{kJ mol}^{-1})^{\text{ b}}}$
Al(OH)2	Al, -0.652, 0.487, 0.110 O, 0.610, -0.630, 0.381 H, 1.148, -0.639, 1.178 O, -0.996, 1.664, 1.309 H, -1.687, 2.326, 1.234	39.60725 6.51988 5.59832	214, 301, 332, 602, 620, 752, 881, 3878, 3913	-483
HOAl(H)OH	Al, 0.004, -0.466, 0.252 O, 1.507, 0.309, 0.094 H, 1.615, 1.226, -0.164 O, -1.406, 0.436, -0.064 H, -2.299, 0.094, -0.007 H, -0.016, -1.971, 0.678	29.507 6.6458 5.4241	235, 348, 386, 507, 577, 635, 693, 787, 912, 2004, 3918, 3927	-624
TS from HOAl(H)OH to AlOH + H ₂ O	Al, -0.195, -0.843, -0.094 O, 1.363, 0.131, -0.097 H, 1.692, 0.883, 0.431 O, -1.602, 0.131, -0.061 H, -2.514, -0.166, -0.061 H, 1.460, -1.146, 0.294	30.776 6.1249 5.1493	-1482 <i>i</i> , 182, 262, 302, 386, 544, 597, 779, 852, 1651, 3650, 3918	-328
AlOH (¹ Σ)	Al, 0., 0., -0.050 O, 0., 0., 1.638 H, 0., 0., 2.592	15.49171	132, 132, 819, 3982	-196

^a Calculated at the B3LYP/6-311+g(2d,p) level of theory [*Frisch et al.*, 2016].

^b Calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 2000] with JANAF reference values for $\Delta_f H^o(Al) = 327.3 \text{ kJ mol}^{-1}$, $\Delta_f H^o(O) = 246.8 \text{ kJ mol}^{-1}$, $\Delta_f H^o(CO) = -113.8 \text{ kJ mol}^{-1}$, $\Delta_f H^o(CO_2) = -393.2 \text{ kJ mol}^{-1}$ and $\Delta_f H^o(H_2O) = -238.9 \text{ kJ mol}^{-1}$ at 0 K; and $\Delta_f H^o(AlO) = 70.3 \text{ kJ mol}^{-1}$ [*Mangan et al.*, 2020].

Table S3. Molecular properties and heats of formation (at 0 K) of the stationary points on the AlCO₃ + O₂, H and H₂O potential energy surface. The geometries are illustrated in Figures S1 - S3.

Molecule	Geometry	Rotational	Vibrational	$\Delta_{\rm f} H^{\rm o}(0 \ {\rm K})$
(electronic state)	(Cartesian co-ordinates in	constants	frequencies	(kJ mol ⁻¹) ^b
	Å) ^a	(GHz) ^a	$(cm^{-1})^{a}$	``´´´
AlCO ₃	Al, 0.0, -1.589, 0.	12.789	189, 500,	-480
$({}^{3}B_{1})$	O, -1.111, -0.219, 0.	4.1025	577, 658,	
	C, -0.0, 0.605, 0.	3.1061	794, 862,	
	O, 0.0, 1.792, 0.0		911, 1016,	
	O, 1.111,-0.219, 0.		1862	
O ₂ AlCO ₃	Al, 0.141, -1.466, -0.002	9.2502	100, 112,	-751
	O, -0.947, -0.195, -0.471	1.4019	154, 262,	
	C, 0.007, 0.696, 0.003	1.3123	412, 500,	
	0, -0.0657, 1.878, 0.006		529, 686,	
	O, 1.065, -0.074, 0.472		739, 793,	
	0, -0.044, -3.173, 0.618		886, 961,	
	0, 0.535, -3.134, -0.622		1062, 1139,	
			1886	
OAlO ₂	Al, 0., 0., -0.394	33.702	189, 192,	-148
$(^{2}A_{2})$	0, 0., -0.684, 1.318	4.0970	454, 556,	
	0, 0., 0.085, 1.318	3.6530	1109, 1157	
	0, 0., 0., -1.994			
HAlCO ₃	Al, 1.367, 0.0, 0.0	12.847	185, 479,	-613
	O, 0.014, 1.109, -0.0	3.8539	496, 543,	
	C, -0.816, 0.0, 0.0	2.9646	583, 682,	
	0, 0.014, -1.109, -0.0		800, 883,	
	0, -2.002, -0.0, 0.0		921, 1073,	
	H, 2.917, 0.0, 0.0		1877, 2072	
TS from	Al, 1.483, 0.089, 0.017	11.951	-1346 <i>i</i> , 158,	-330
HAlCO ₃ to	0, 0.013, 1.104, -0.040	3.8142	346, 538,	
$AIOH + CO_2$	C, -0.803, 0.030, -0.025	2.9373	575, 601,	
	0, 0.029, -1.107, -0.162		794, 819,	
	H 1.086 -1.263 0.904		8/8, 1066,	
			1040, 1802	
AlOH	AI, 0., 0., -0.050	15.49171	132, 132,	-196
$(^{1}\Sigma)$	0, 0., 0., 1.038		819, 3982	
	11, 0., 0., 2.372			
AlCO ₃ -H ₂ O	Al, -0.620, 0.121, 1.541	6.5976	96, 105, 203,	-809
	O, -0.914, 0.973, -0.008	2.1681	218, 367,	
	C, 0.001, 0.127, -0.591	2.0178	382, 490,	
	0, 0.337, 0.132, -1.736		544, 639,	
	O, 0.464, -0.704, 0.393		670, 808,	

	O, 0.386, 1.682, 2.291 H, 0.269, 2.067, 3.170 H, 0.401, 2.391, 1.625		853, 931, 1073, 1609, 1834, 3699, 3836	
TS from AlCO ₃ - H ₂ O to Al(OH) ₂ + CO ₂	Al, -0.959, 0.723, 0.384 O, 0.181, -0.780, 0.729 C, 1.147, -0.121, -0.074 O, 2.226, -0.554, -0.314 O, 0.595, 1.036, -0.463 O, -1.767, -0.711, -0.502 H, -2.627, -1.116, -0.348 H, -0.794, -1.187, 0.018	6.5151 2.4560 2.0973	-1257 <i>i</i> , 129, 200, 382, 410, 479, 534, 588, 716, 739, 806, 817, 913, 1139, 1398, 1819, 1871, 3865	-772
Al(OH) ₂	Al, -0.652, 0.487, 0.110 O, 0.610, -0.630, 0.381 H, 1.148, -0.639, 1.178 O, -0.996, 1.664, 1.309 H, -1.687, 2.326, 1.234	39.60725 6.51988 5.59832	214, 301, 332, 602, 620, 752, 881, 3878, 3913	-483

^a Calculated at the B3LYP/6-311+g(2d,p) level of theory [*Frisch et al.*, 2016] ^b Calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 2000], with JANAF reference values for $\Delta_f H^o(Al) = 327.3 \text{ kJ mol}^{-1}$, $\Delta_f H^o(O) = 246.8 \text{ kJ mol}^{-1}$, $\Delta_f H^o(CO) = -$ 113.8 kJ mol⁻¹, $\Delta_f H^o(CO_2) = -393.2 \text{ kJ mol}^{-1}$ and $\Delta_f H^o(H_2O) = -238.9 \text{ kJ mol}^{-1}$ at 0 K; and $\Delta_f H^o(AlO) = 70.3 \text{ kJ mol}^{-1}$ [*Mangan et al.*, 2020].

Table S4. Parameters used in RRKM fits to the kinetics of $AlO^{+} + N_2 (+ N_2)$

AlO ⁺	Rotational constant = 16.724 GHz			
	Vibrational frequency = 787 cm^{-1} a			
N ₂	Rotational constant = 60.730 GHz			
	Vibrational frequency = 2447 cm^{-1} a			
AlO ⁺ .N ₂	Rotational constant = 2.4664 GHz			
	Vibrational frequencies: 49 (×2); 228 (×2); 304; 1098; 2424 cm ⁻¹			
$\langle \Delta E \rangle_{\rm down} = 330 \ (T / 300)^{0.0} \ {\rm cm}^{-1}$				
7(410+1) $(52.10+10-10-3)$ $(52.10+10-10-3)$ $(52.10+10-10-10-1)$				

 $Z(AlO^+.N_2 + N_2) = 5.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ b}; k_{\infty} = 7.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

^a Calculated at the B3LYP/6-311+g(2d,p) level of theory [*Frisch et al.*, 2016]

 b Collision frequency between the adduct and N_{2}

^c High pressure limiting recombination rate coefficient, calculated from Langevin theory.

Table S5. Rocket-borne mass spectrometric measurements of Al⁺ ions used to construct the Al⁺ profile in Figure 9 (main paper): payload reference number, launch location, launch time/date, and reference.

Payload reference	Location	Time/date	Reference
18.1006	Wallops Islands	12-Aug-1976	Meister et al.
	(37.8° N, USA)	11:58 LT	[1978]
18.1008	Wallops Islands	01-Jan-1977	Meister et al.
	(37.8° N, USA)	14:03 LT	[1978]
S26/1	Kiruna	30-Jul-1978	<i>Kopp et al.</i> [1985b]
	(67.8° N, Sweden)	01:32 LT	
S26/2	Kiruna	13-Aug-1978	<i>Kopp et al.</i> [1985b]
	(67.8° N, Sweden)	01:38 LT	
33.010	Kiruna	16-Nov-1980	<i>Kopp et al.</i> [1985a]
	(67.8° N, Sweden)	05:50 LT	
S37/P	Kiruna	03-Aug-1982	<i>Kopp et al.</i> [1984]
	(67.8° N, Sweden)	01:32 LT	
18.1020	Red Lake	24-Feb-1979	[Kopp, 1997]
	(50.9° N, Canada)	10:52 LT	
18.021	Red Lake	26-Feb-1979	[Kopp, 1997]
	(50.9° N, Canada)	11:55 LT	

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