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Metallic Layers in the Mesosphere

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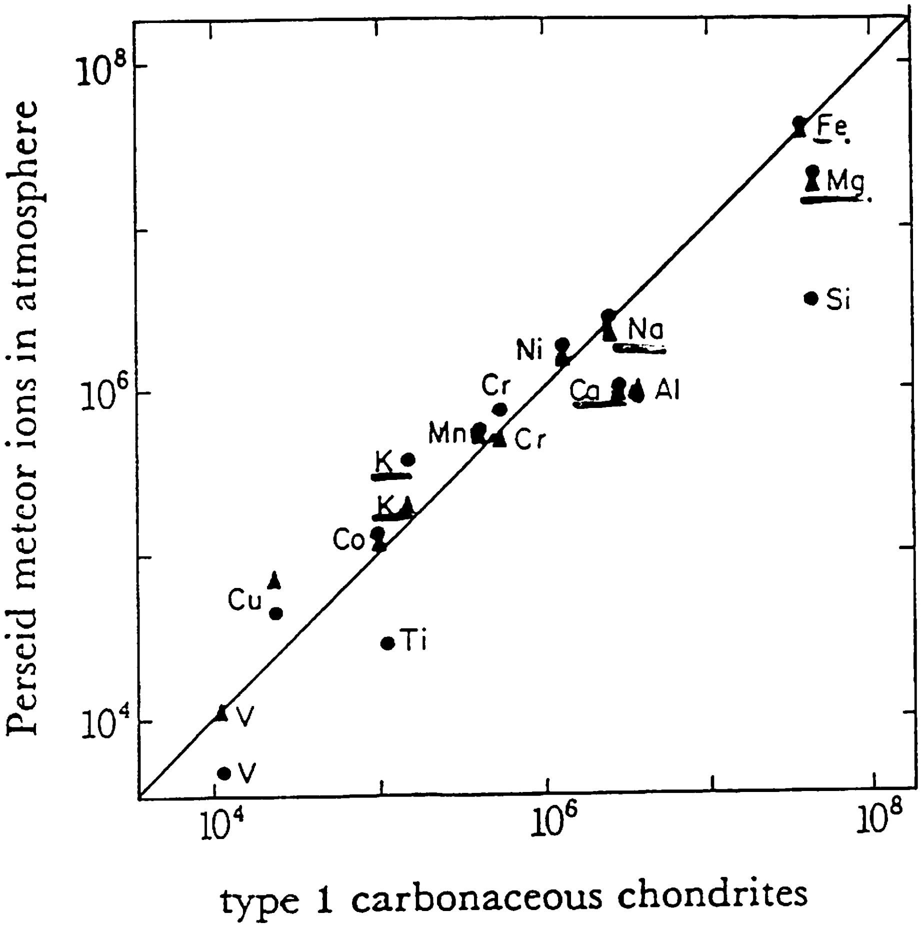
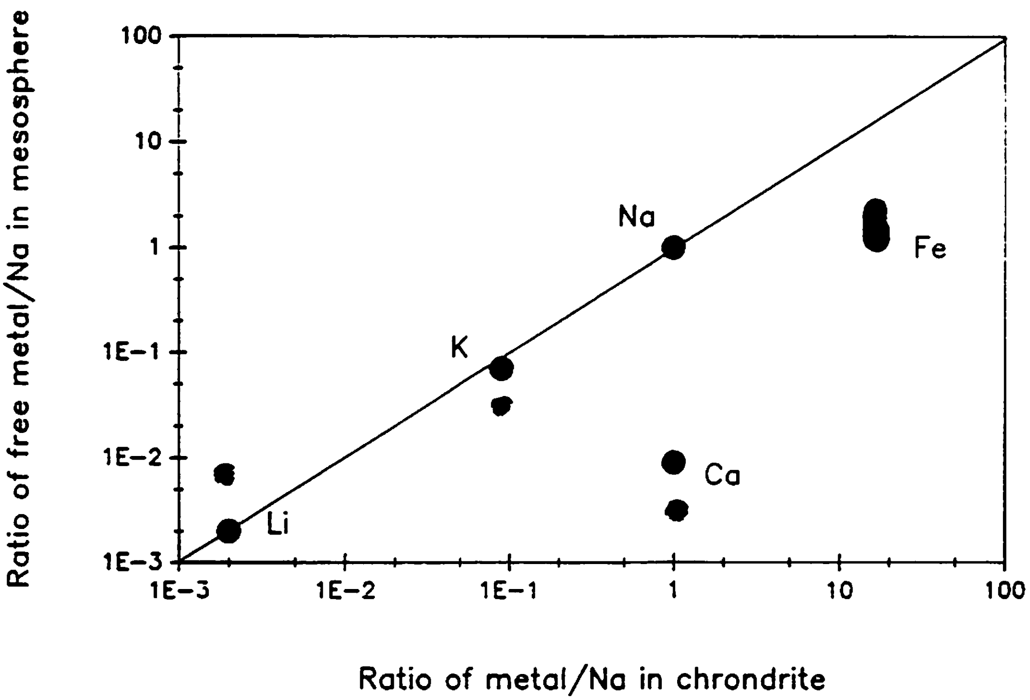
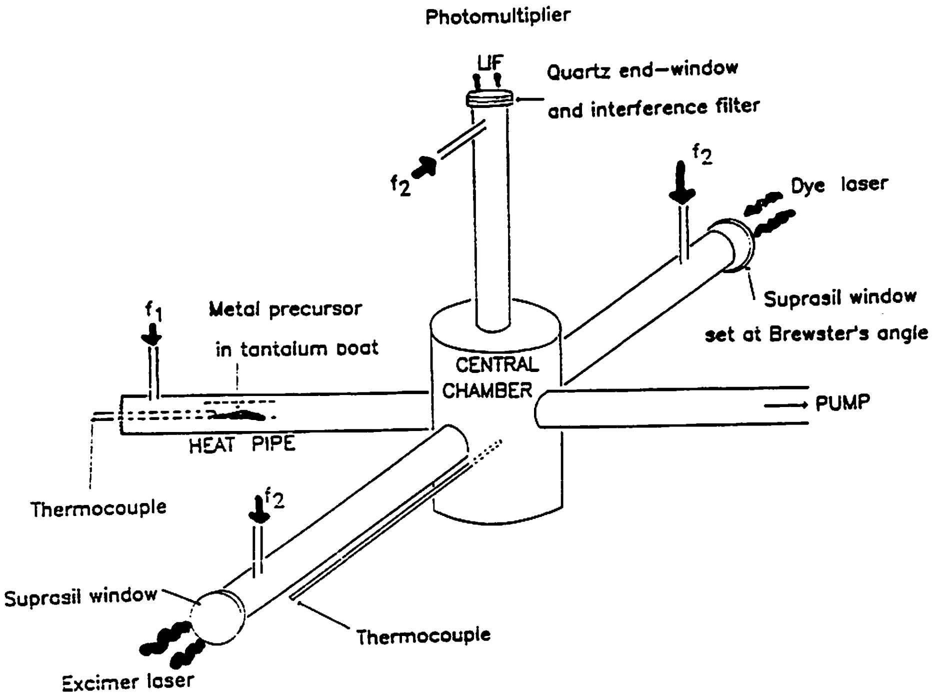
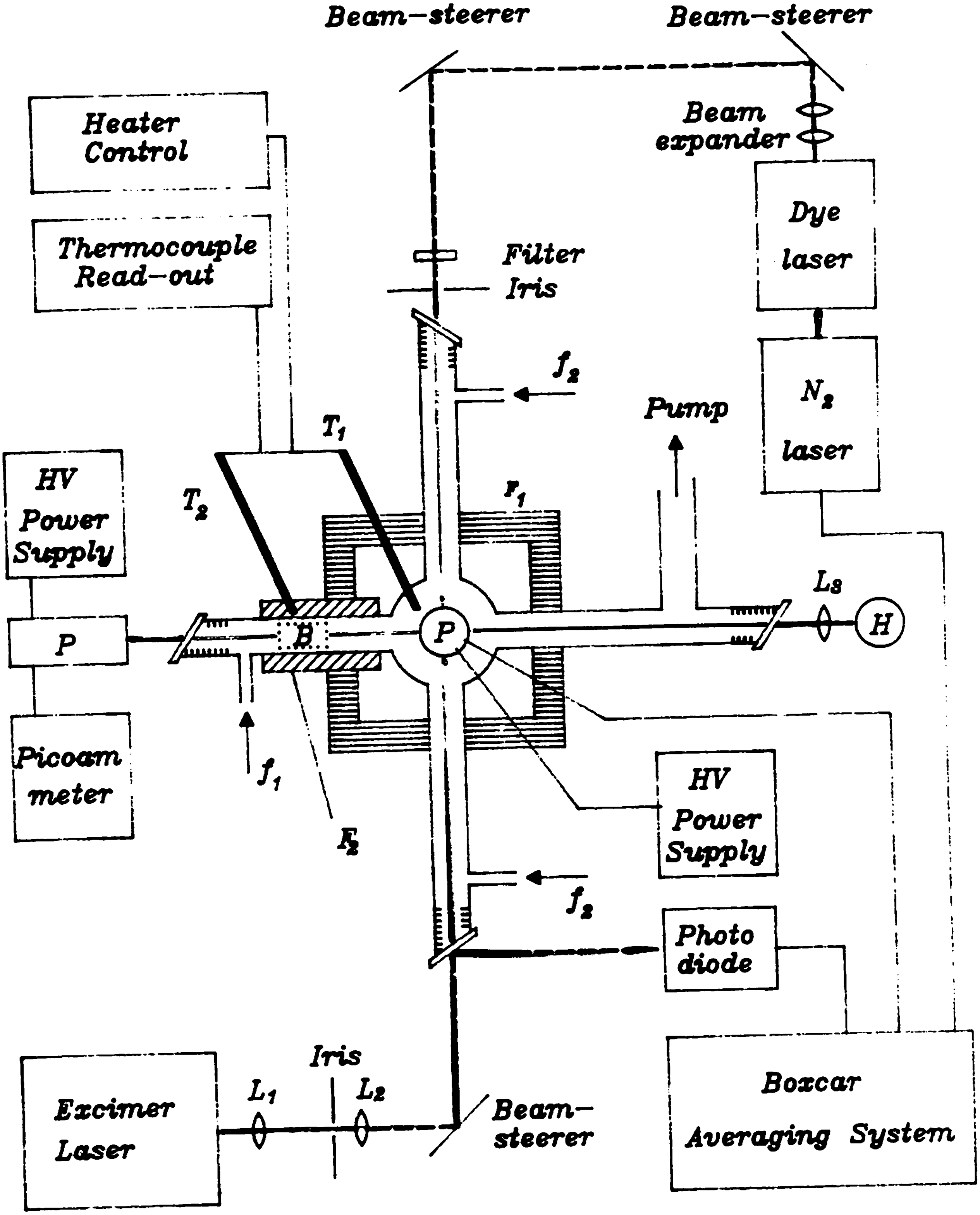

Perseid meteor ions in atmosphere
type 1 carbonaceous chondrites
10^8
10^6
10^4
Fe
Mg
Si
Na
Ni
Ca
Al
Cr
Mn
Cr
K
K
Co
Cu
Ti
V
V



- ● Wintertime relative abundances
- ● Summertime relative abundances

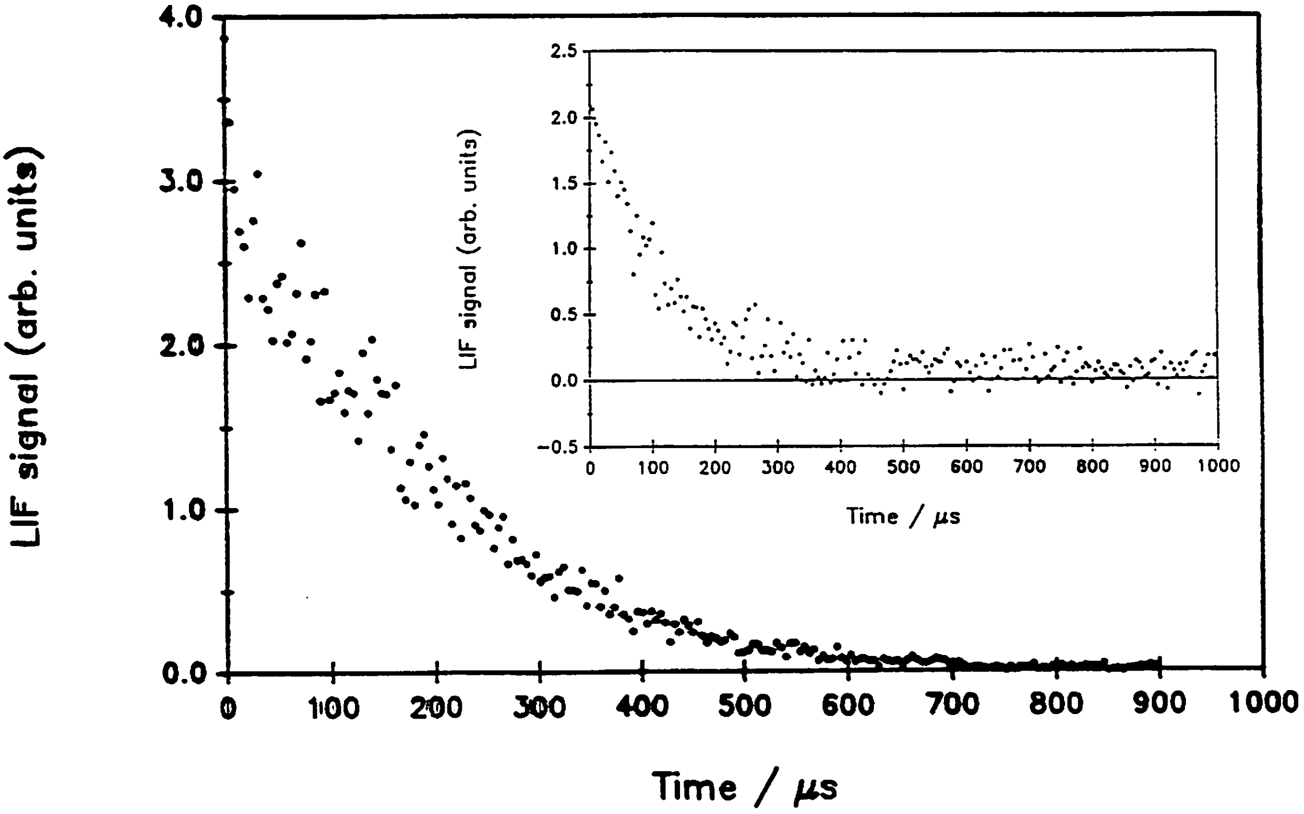

Photomultiplier
LIF
Quartz end–window
and interference filter
f2
f2
Dye laser
Suprasil window
set at Brewster's angle
f1
Metal precursor
in tantalum boat
CENTRAL
CHAMBER
PUMP
HEAT PIPE
Thermocouple
f2
Suprasil window
Excimer laser
Thermocouple


Beam–steerer
Beam–steerer
Heater Control
Thermocouple Read–out
Beam expander
Dye laser
Filter
Iris
f_2
Pump
N_2 laser
T_1
T_2
F_1
HV Power Supply
P
B
P
L_3
H
Picoam meter
f_1
F_2
HV Power Supply
f_2
Photo diode
Iris
L_1
L_2
Excimer Laser
Beam–steerer
Boxcar Averaging System

Precursor: $CaI_2 \xrightarrow[193\ nm]{nh\nu} Ca + 2I$

Temperature: 217 K

LIF at 422 nm $(Ca(^1P_1) - Ca(^1S_0))$

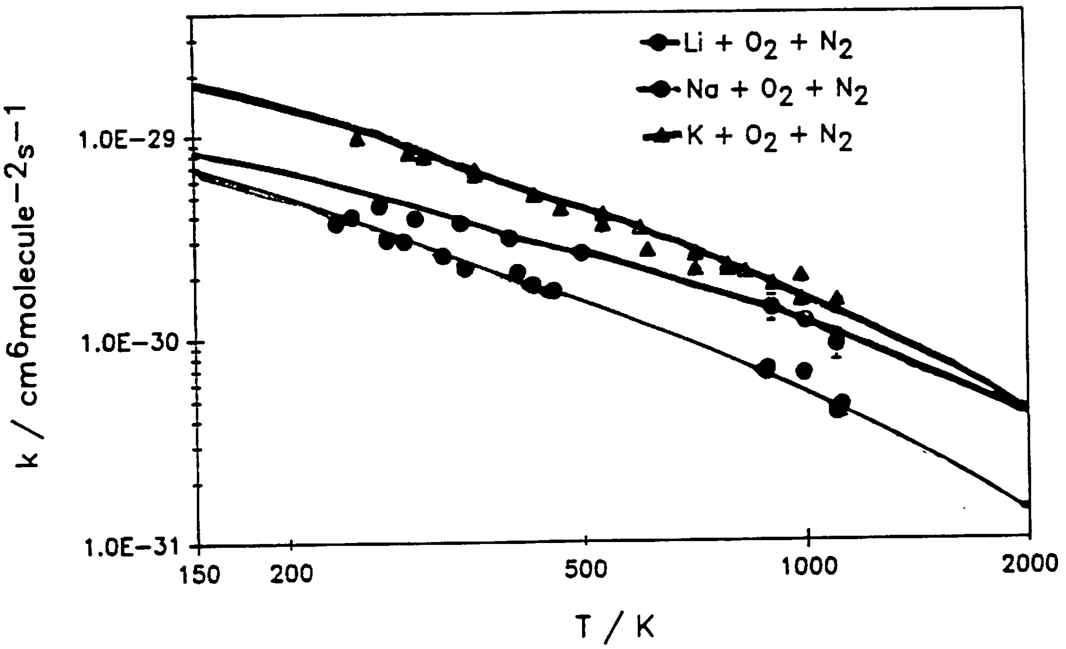


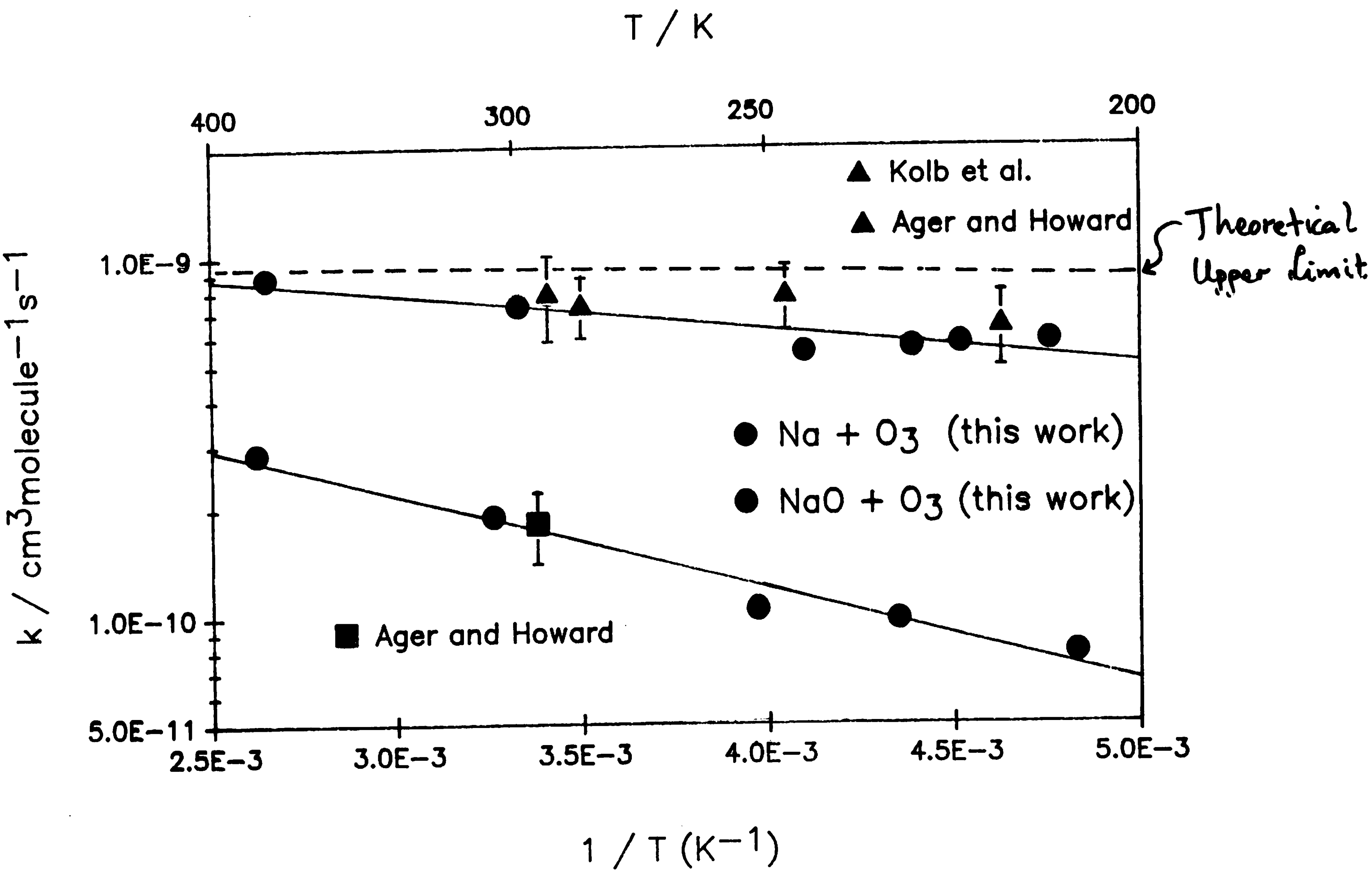
$Ca + O_3 \rightarrow CaO + O_2$ k (rate constant)

$$-\frac{d[Ca]}{dt} = k[O_3][Ca];$$

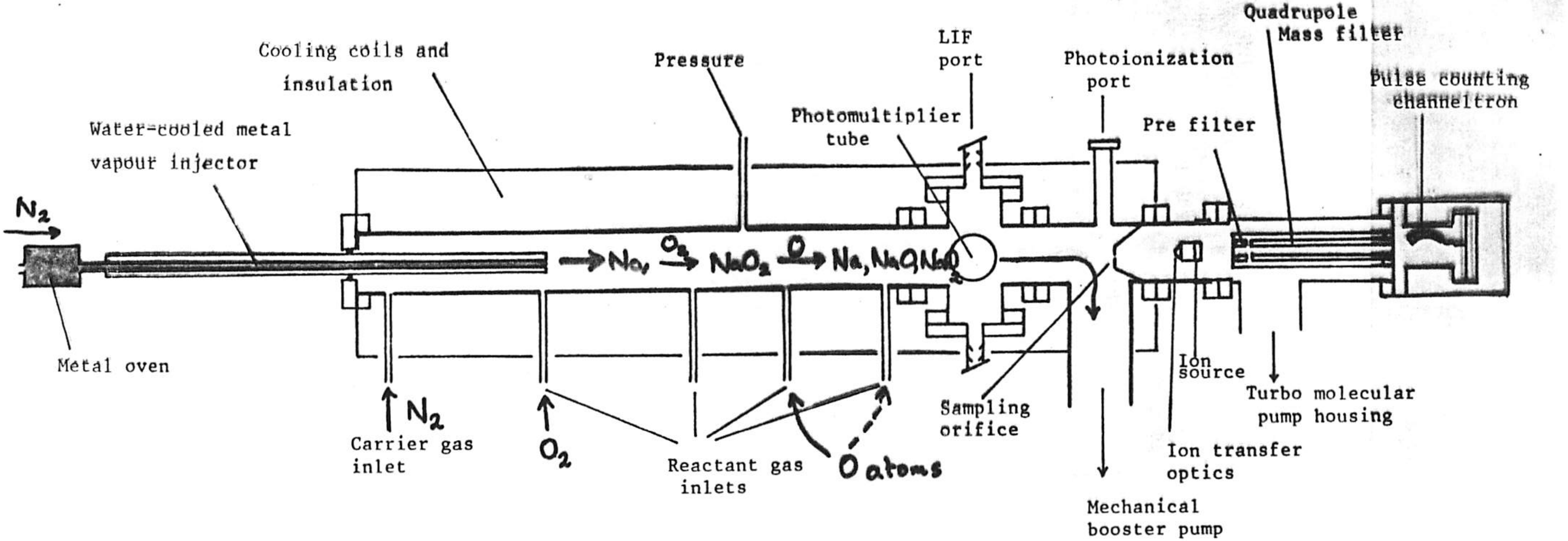
if $[O_3] \gg [Ca]$, then $k' \simeq k[O_3]$

so $[Ca]_t = [Ca]_0 e^{-k't}$: Pseudo First-Order Kinetics


Li + O_2 + N_2
Na + O_2 + N_2
K + O_2 + N_2
1.0E−29
1.0E−30
1.0E−31
k / cm^{6}molecule^{-2}s^{-1}
150
200
500
1000
2000
T / K


T / K
400
300
250
200
▲ Kolb et al.
▲ Ager and Howard
Theoretical Upper Limit
1.0E−9
1.0E−10
5.0E−11
k / cm3molecule−1s−1
● Na + O3 (this work)
● NaO + O3 (this work)
■ Ager and Howard
2.5E−3
3.0E−3
3.5E−3
4.0E−3
4.5E−3
5.0E−3
1 / T (K−1)

$NaO_2 + O \rightarrow NaO + O_2$



$Na + O_2 + N_2 \rightarrow NaO_2 + N_2$ (1)

$NaO_2 + O \rightarrow NaO + O_2$ (2)

$NaO + O \rightarrow Na(^2P, ^2S) + O_2$ (3)

At steady-state,

$$k_2 \simeq \frac{k_1 . [Na][O_2][N_2]}{([Na]_0 - [Na])[O]}$$

$$= (1.6 \pm 0.6) \times 10^{-11} \ \underline{cm^3 s^{-1}}$$

@ 300 K.

Neutral and Ionic Gas-Phase reaction of Na species in the Mesosphere

Neutral Chemistry with Oxygen *only*

No.	Reaction	Rate Coefficient
* 1.	$Na + O_3 \text{ --> } NaO + O_2$	1.5×10^{-9} exp(-220/temp)
* 2.	$NaO + O \text{ --> } Na(^2P,^2S) + O_2$	1.5×10^{-9} exp(-383/temp) (branching ratio[illegible] = 0.2)
* 3.	$Na + O_2 + M \text{ --> } NaO_2 + M$	4.7×10^{-30} $(temp/200)^{-1.22}$
* 4a.	$NaO + O_3 \text{ --> } Na + 2O_2$	3.2×10^{-10} exp(-550/temp)
* 4b.	$NaO + O_3 \text{ --> } NaO_2 + O_2$	1.5×10^{-9} exp(-636/temp)
* 5.	$NaO_2 + O \text{ --> } NaO + O_2$	1.0×10^{-9} exp(-1300/temp)
* 6.	$NaO + O_2 + N_2 \text{ --> } NaO_3 + N_2$	5.3×10^{-30} (200/temp)
* 7.	$NaO_3 + O \text{ --> } NaO + O_2$	3×10^{-10} sqr(temp/290)

Neutral Chemistry with H, O and CO_2

No.	Reaction	Rate Coefficient
* 8.	$NaO + H_2O \text{ --> } NaOH + OH$	8×10^{-10} exp(-374/temp)
* 9a.	$NaO + H_2 \text{ --> } NaOH + H$	1.1×10^{-9} exp(-1100/temp)
* 9b.	$NaO + H_2 \text{ --> } Na + H_2O$	1.1×10^{-9} exp(-1400/temp)
* 10.	$NaO + H \text{ --> } Na + OH$	3×10^{-10} exp(-668/temp)

* measured rate constant

○	11.	$NaO_2 + H$ --> $NaOH + O$	3 x 10^{-10} exp(-2000/temp)
➡	12.	$NaOH + H$ --> $Na + H_2O$	5 x 10^{-10} exp(-1000/temp)
*	13.	$NaO + CO_2 + N_2$ --> $NaCO_3 + N_2$	1.3 x 10^{-27} (200/temp)
○	14.	$NaCO_3 + O$ --> $NaO_2 + CO_2$	1 x 10^{-9} exp(-1400/temp)
○	15.	$NaCO_3 + H$ --> $NaOH + CO_2$	1 x 10-9 exp(-1400/temp)
*	16.	$NaOH + CO_2 + N_2$ --> $NaHCO_3 + N_2$	1.9 x 10^{-28} (200/temp)
➡	17.	$NaHCO_3 + H$ --> $Na + H_2O + CO_2$	1 x 10^{-9} exp(-1800/temp)

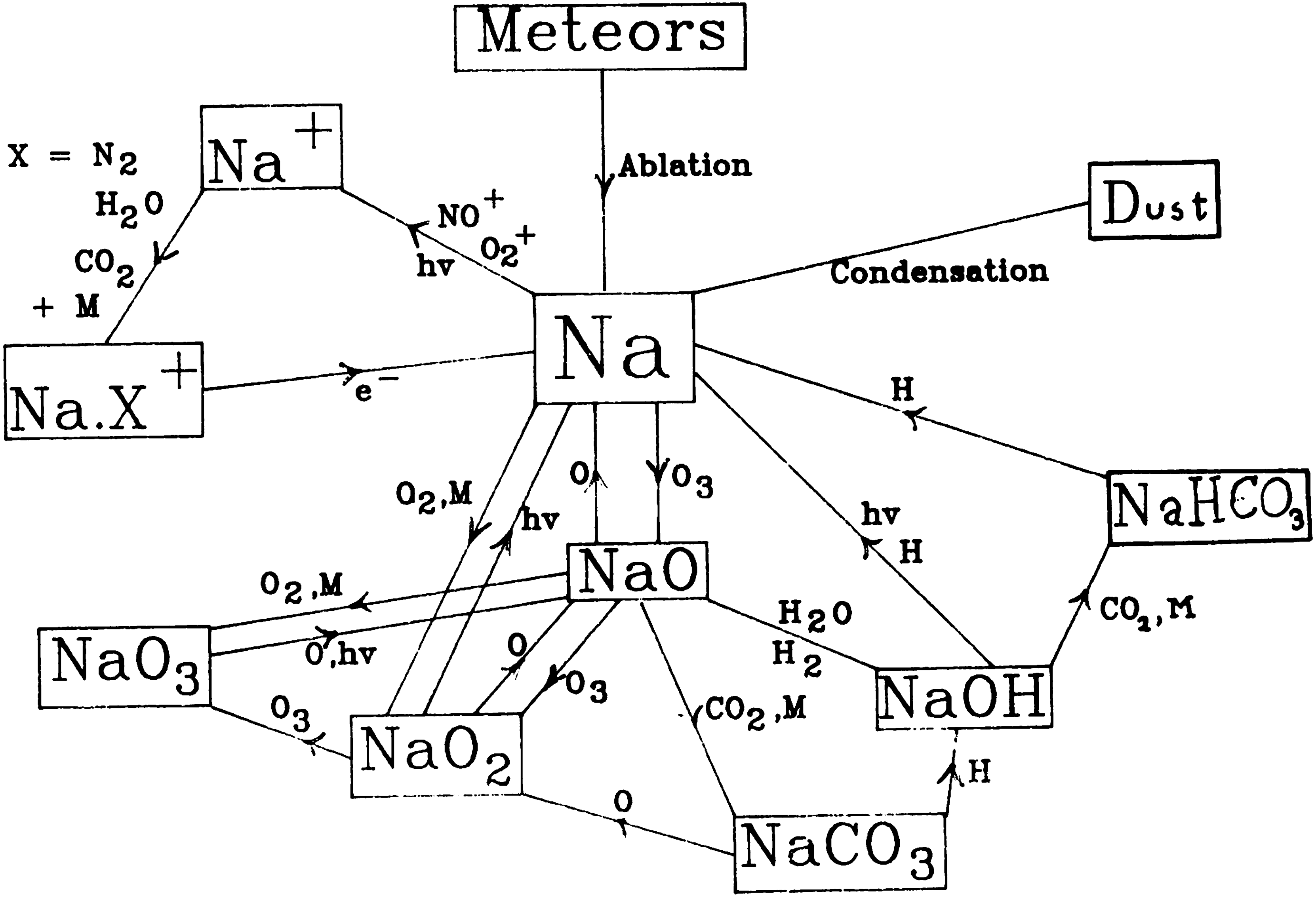
Ionic Chemistry

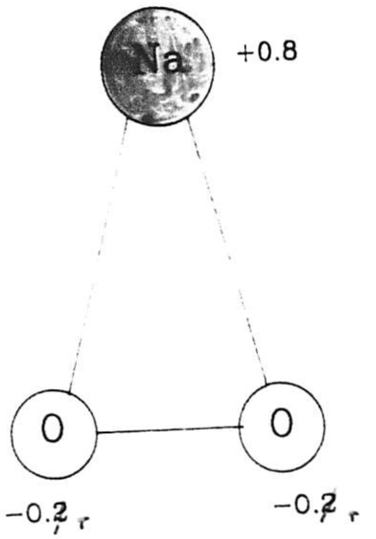
*	18.	$Na + O_2^+$ --> $Na^+ + O_2$	1.4 x 10^{-9}
*	19.	$Na + NO^+$ --> $Na^+ + NO$	1 x 10^{-9}
□	20.	$Na^+ + N_2 + N_2$ --> $Na.N_2^+ + N_2$	2.5 x 10^{-31} $(temp/200)^{-1.6}$
○	21.	$Na.X^+ + e^-$ --> $Na + X$	1 x 10^{-6} $(200/temp)^{1/2}$

Photochemical reactions

*	22.	$NaO_2 + h\varpi$ --> $NaO_2 + O_2$	4 x 10^{-3}
➡	23.	$NaOH + h\varpi$ --> $Na + OH$	1 x 10^{-3}
○	24.	$NaO_3 + h\varpi$ --> $NaO + O_2$	1 x 10^{-4}
*	25.	$Na + h\varpi$ --> Na^+	2 x 10^{-5}

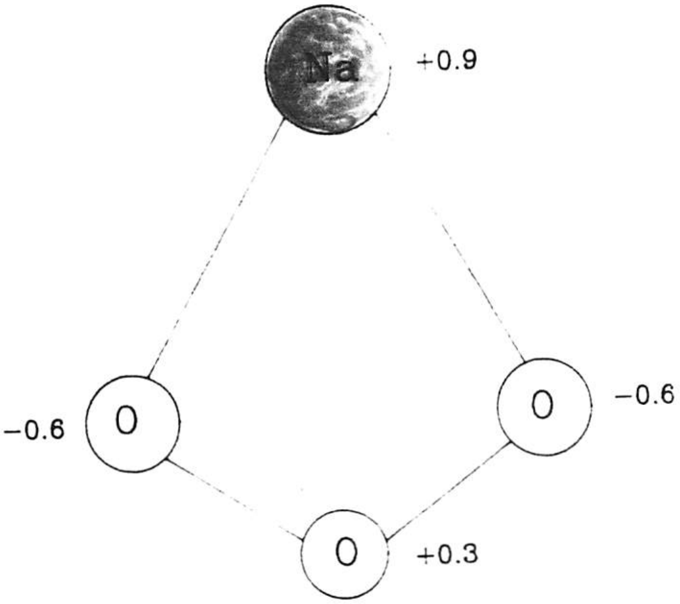
□ calculated theoretically (Helmer and Plane)
○ known approximately or not likely to be important
➡ important unknowns


Meteors
Ablation
Na$^+$
$X = N_2$
H_2O
CO_2
$+ M$
NO^+
O_2^+
hv
Dust
Condensation
Na
Na.X$^+$
e^-
H
$NaHCO_3$
O_2,M
hv
O
O_3
hv
H
NaO
O_2,M
O,hv
NaO_3
O
O_3
H_2O
H_2
NaOH
CO_2,M
O_3
NaO_2
CO_2,M
H
O
$NaCO_3$



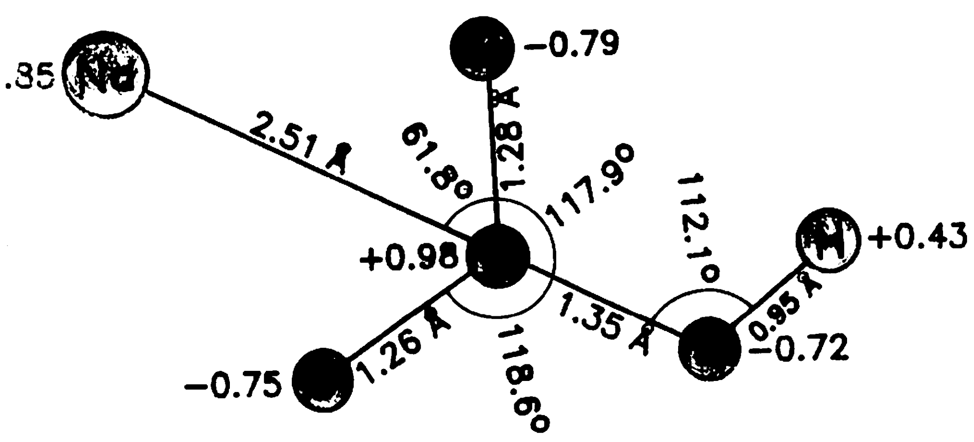
Sodium Superoxide

$^2A_2$

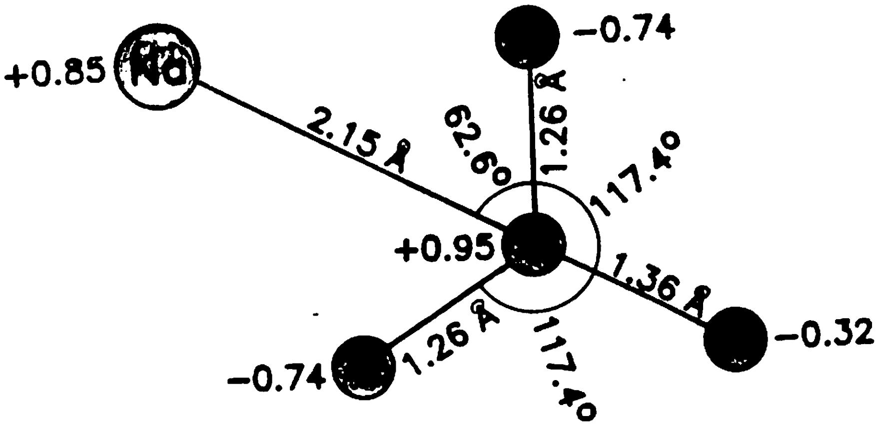


Sodium Ozonide

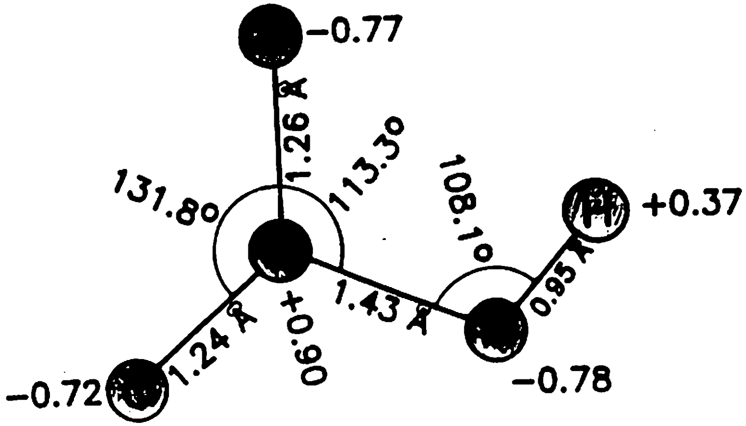
$^2B_1$



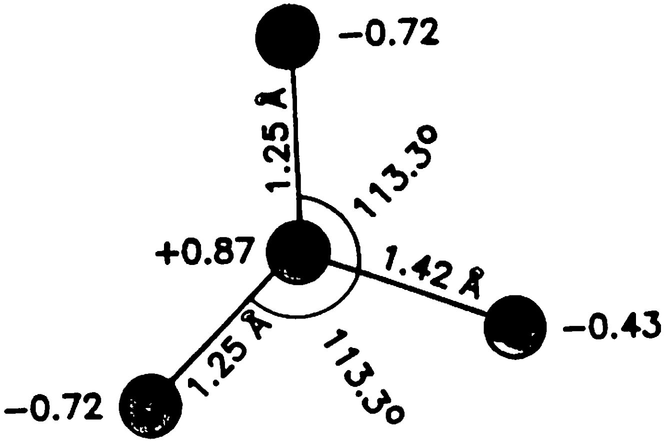
(a) $NaHCO_3$ ($^1A'$)



(b) $NaCO_3$ ($^2A'$)



(c) HCO_3^- ($^1A'$)

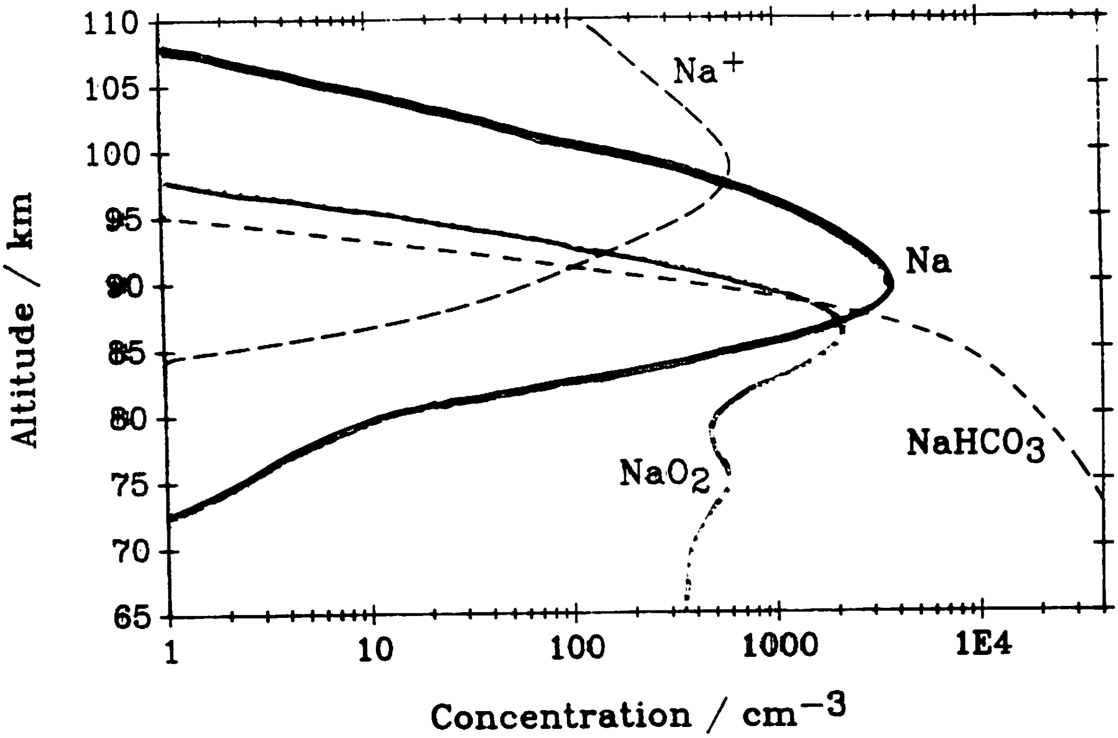


(d) CO_3^- ($^2B_2$)

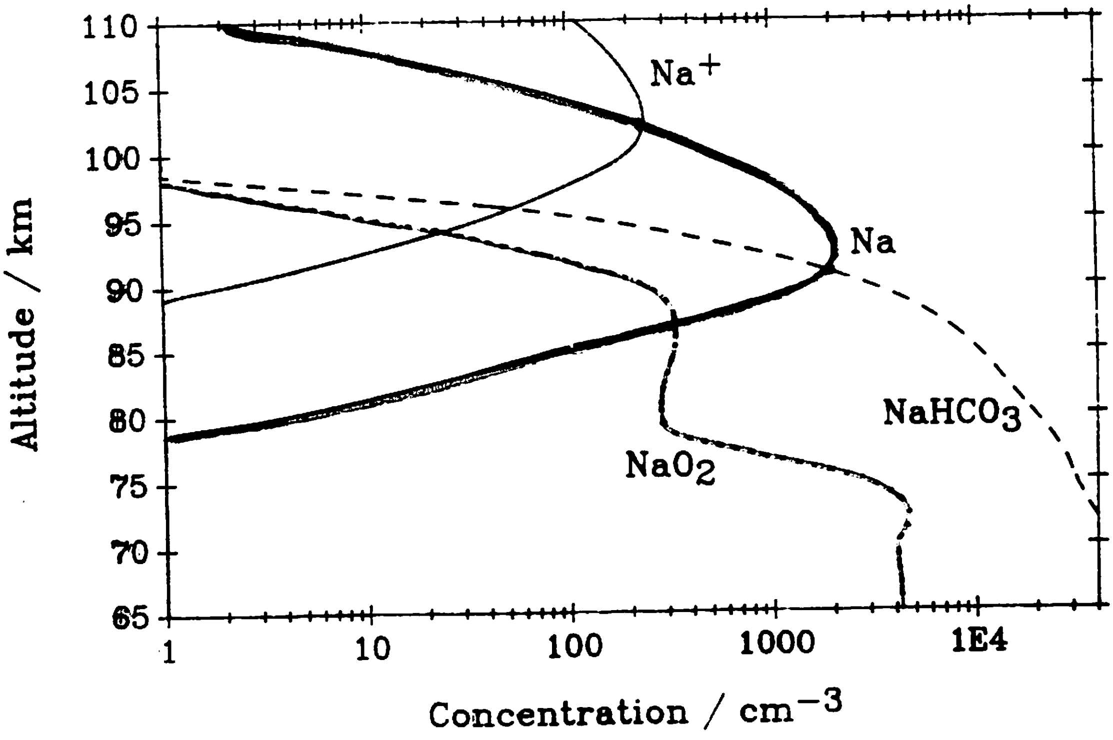
Model of Sodium in the Mesosphere

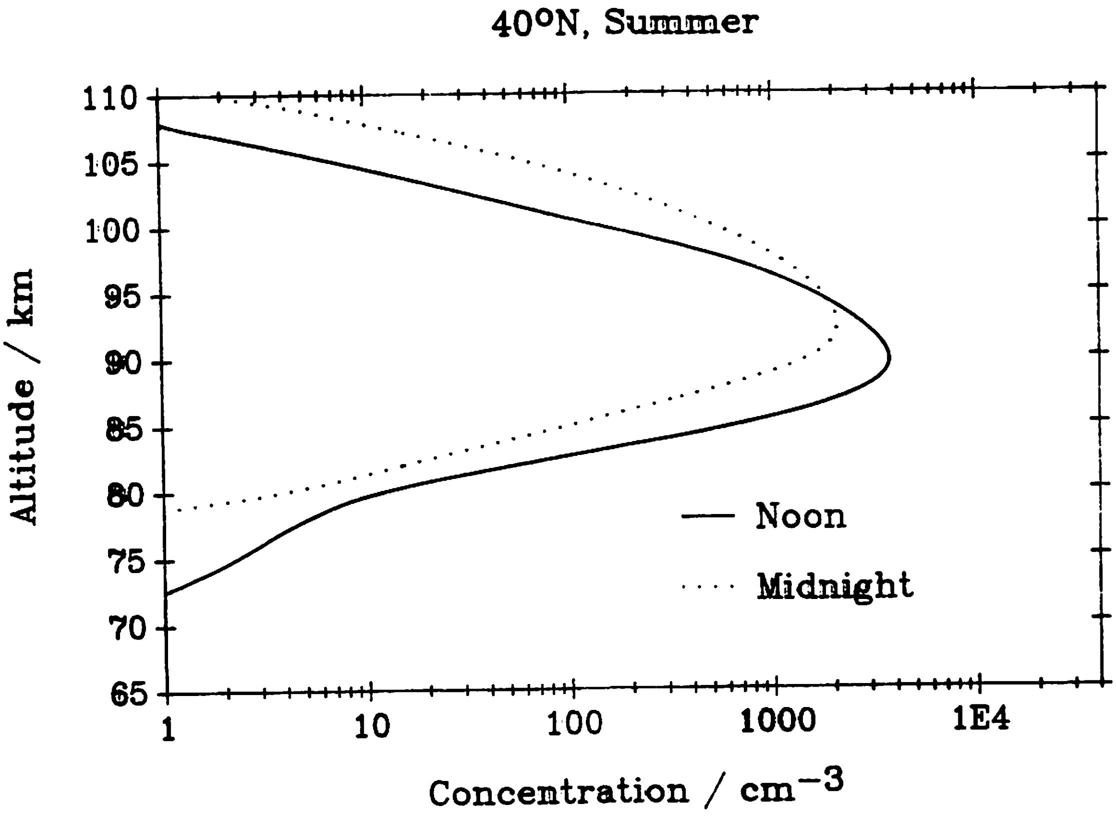
- meteoric input of Na of (1 ± 0.2) x 10^4 atoms $cm^{-2}s^{-1}$ (Hughes, Gadsden)
- ablation profile from Hunten *et al.* (1980)
- assume that at all altitudes sodium is partitioned rapidly on the time-scale of vertical mixing
- since the transport of all sodium constituents is then governed by the same eddy diffusion coefficient, the continuity equation for *total* sodium can then be solved as a function of altitude
- the partitioning of sodium is governed by the *gas-phase* chemistry only
- the seasonal and latitude dependence of temperature, pressure, eddy diffusion coefficient is included
- the seasonal dependence of minor species O, H and O_3 is included
- variable parameters:
  - meteoric input flux
  - total Na at 65 km
  - $k(NaOH + H)$
  - the photolysis cross-section of NaOH
  - $k(NaHCO_3 + H)$

40°N, Summer, Noon



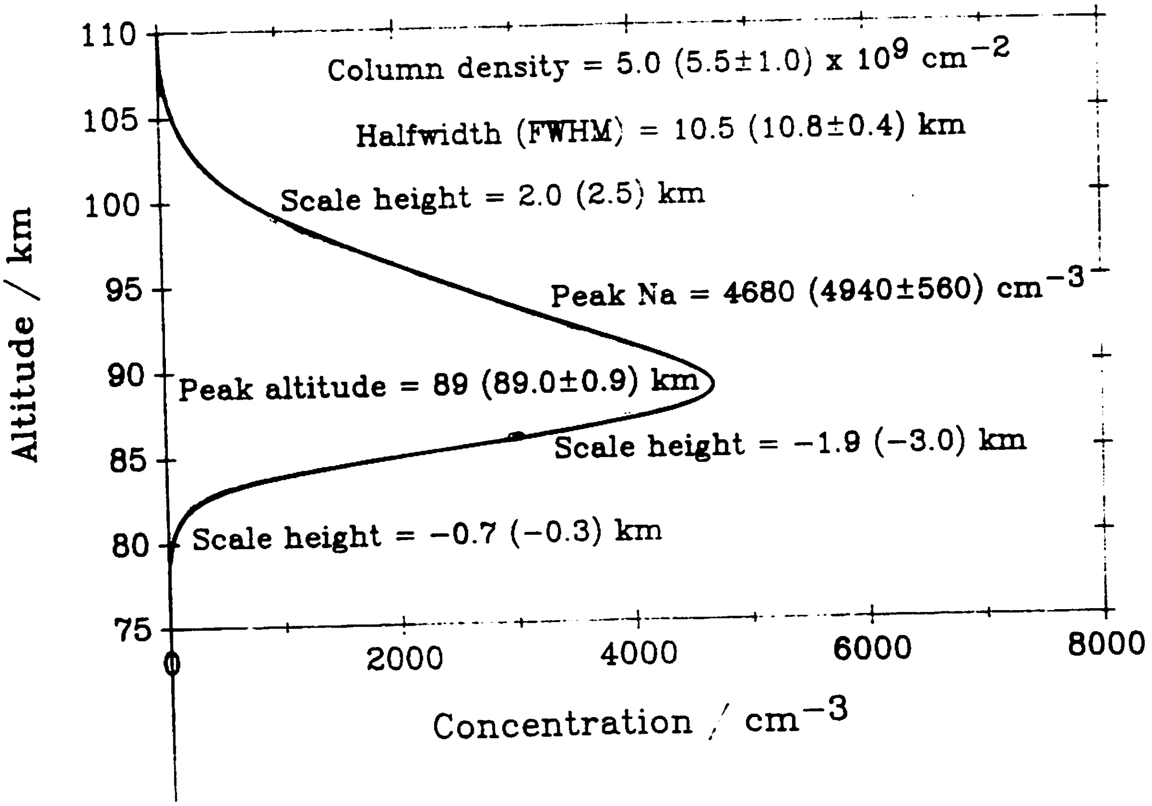
40°N, Summer, Midnight

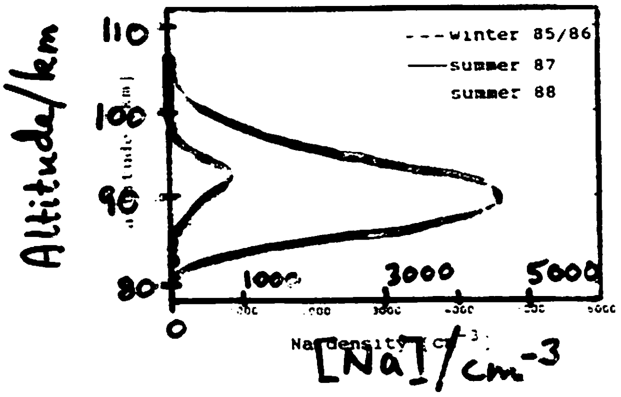



40°N, Summer
Altitude / km
110
105
100
95
90
85
80
75
70
65
1
10
100
1000
1E4
Concentration / cm^{-3}
Noon
Midnight

Comparison between Model and Tilgner and von Zahn (1988)

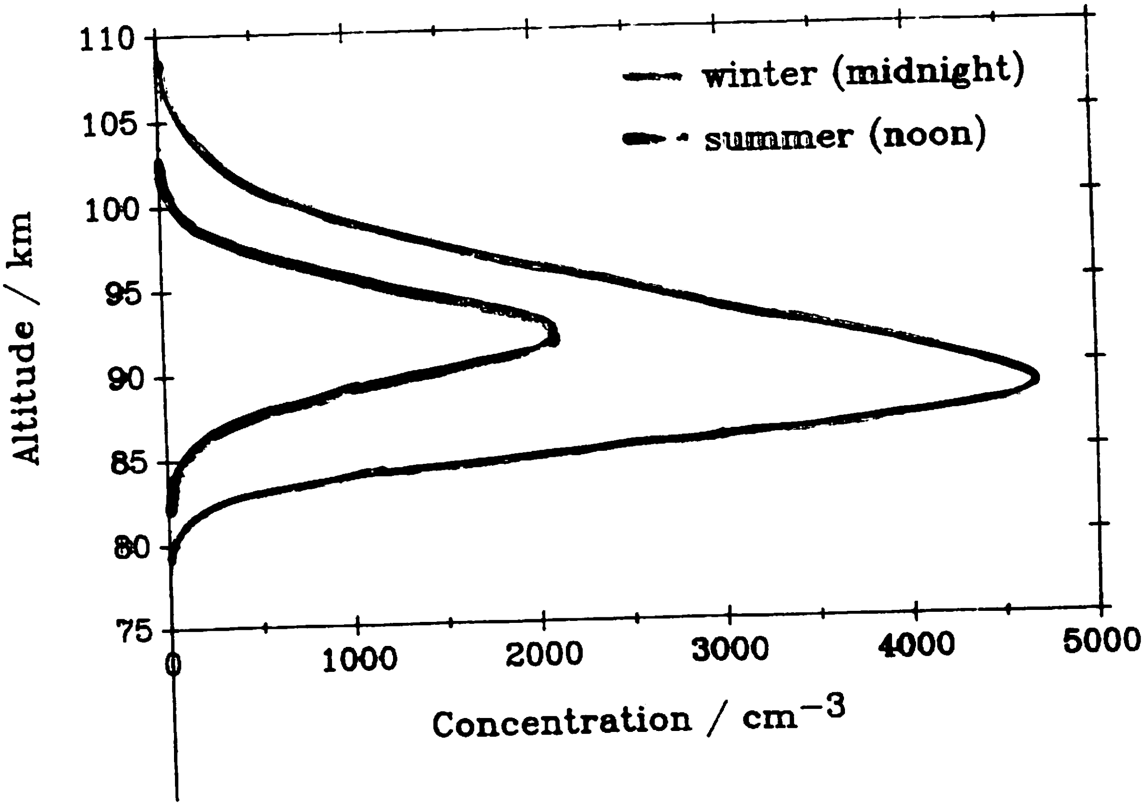
70°N, Winter, Midnight

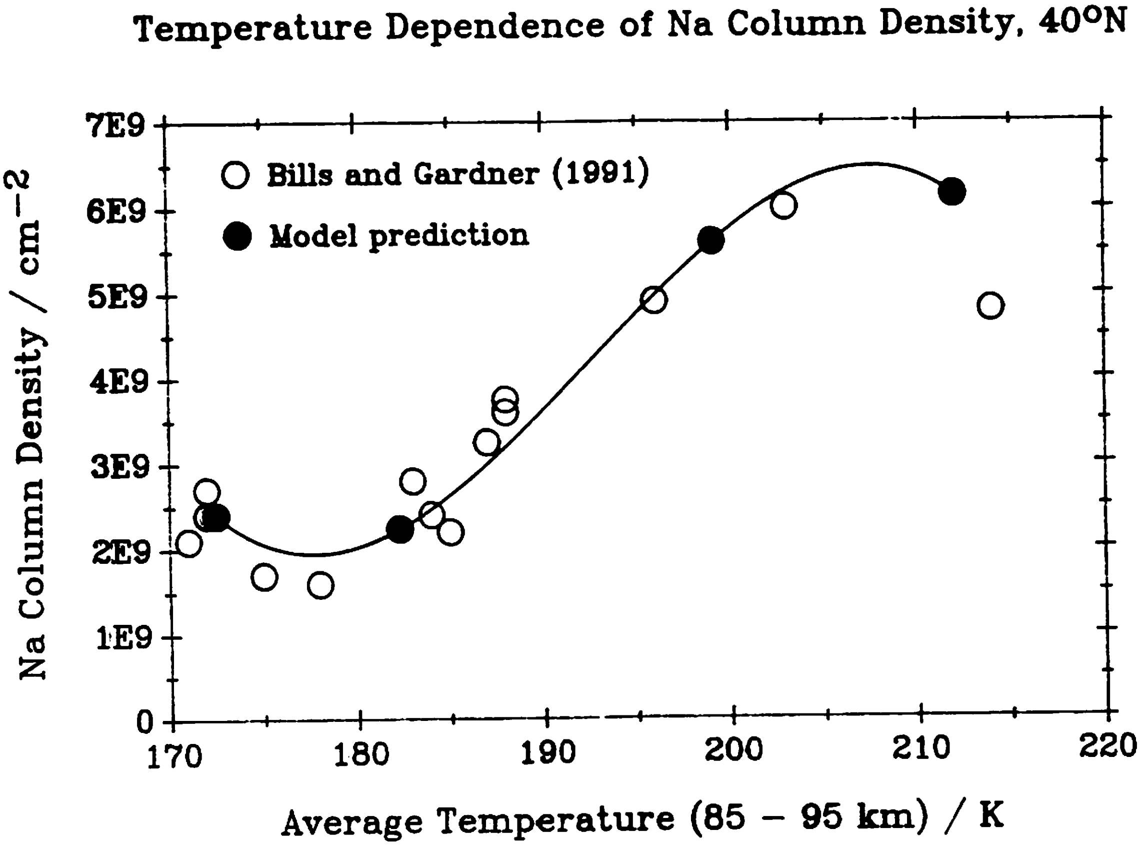




Kurzawa & von Zahn

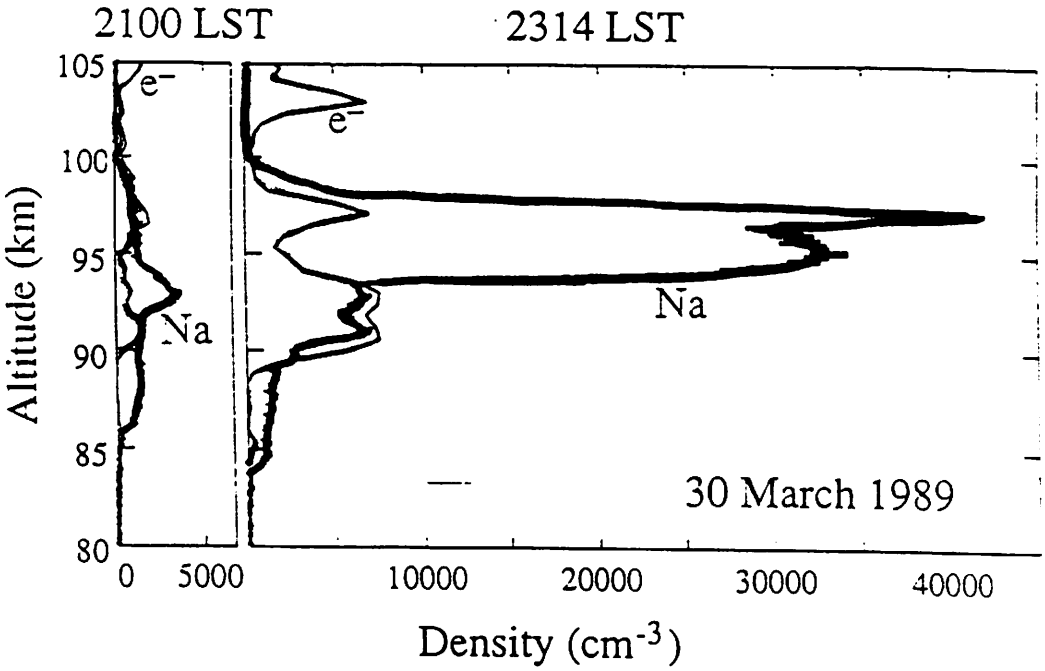
Sodium Density Profiles at 70°N




Temperature Dependence of Na Column Density, 40°N
○ Bills and Gardner (1991)
● Model prediction
Na Column Density / cm⁻²
7E9
6E9
5E9
4E9
3E9
2E9
1E9
0
170
180
190
200
210
220
Average Temperature (85 – 95 km) / K

Characteristics of Sudden Sodium Layers (SSLs)

- form explosively at altitudes between 93 and 102 km, i.e. several kilometres above the permanent global Na layer
- have lifetimes of tens of minutes to a few hours, and then disappear rapidly
- the Na atom density in SSLs can be up to 40 times greater than in the background Na layer: **SSLs appear to come from a fresh source of Na**
- can extend over several hundred kilometres horizontally
- appear most commonly between 1500 and 0000 hrs local time
- occur quite frequently at low and high latitudes, but very rarely at mid-latitudes *cf.* sudden Fe layers
- strong correlation between sporadic-*E* and SSLs
- also appear when there is strong local heating (e.g. from 170 to 220 K in under an hour) e.g. due to the passage of a tidal wave



Kane, Gardner, Zhou, Mathews and Tepley

AIDA-89

2. Chemical mechanisms

The striking correlation between SSLs and sporadic-*E* suggests that SSLs could be formed by the action of electrons or ions on a reservoir. These charged particles could have large kinetic energies if they were caused by auroral precipitation, although this would only explain SSLs at high latitudes. Possible reservoirs include:

- **neutral sodium compounds** involved in dissociative electron attachment reactions (von Zahn and Murad, 1990)

  e.g. $NaHCO_3 + e^- \text{-->} Na + HCO_3^-$

  Our recent *ab initio* calculations (Rajasekhar and Plane, 1992) indicate that this reaction is about 50 $kJmol^{-1}$ *endothermic*, so that $NaHCO_3$ is stable with respect to thermal electrons. Reaction with atomic O may also be important: we have recently shown that the reaction
  $NaO_2 + O \text{-->} NaO + O_2$, $k(300\ K) = 1.6 \times 10^{-11}\ cm^3 molecule^{-1} s^{-1}$
  is fast (Helmer and Plane, 1992), so that a sudden increase in [O] will produce Na from NaO_2.

- **Na^+ ions**; these recombine with electrons extremely slowly, so the rate of formation of molecular Na ions is important

  e.g. $Na^+ + X + N_2 \text{-->} Na.X^+ + N_2$
  $Na^+ + O_3 \text{-->} NaO^+ + O_2$

  The formation of the molecular Na ions would then be followed by dissociative recombination with electrons:

  e.g. $Na.X^+ + e^- \text{-->} Na + X$

The rates for the clustering reactions are not known. However, this mechanism may work if the rate of re-ionisation of Na by the reactions

e.g. $Na + NO^+, O_2^+ \rightarrow Na^+ + NO, O_2$

was slowed down by the removal of NO^+ and O_2^+ by the high electron density in a sporadic-*E* layer.

Also, if a large concentration of *negative* ions could be produced (Swider, 1992):

e.g. e^- (fast, 6eV) $+ O_2 \rightarrow O^- + O$
then $O^- + Na^+ \rightarrow O + Na$

Unfortunately, O^- also reacts very rapidly with O:

$O^- + O \rightarrow O_2 + e^-$

so that the concentration of negative ions will be limited.

- **Na cluster ions on the surface of dust particles**. These are formed from the recondensation of meteoric silicates, and are thought to be about 10 nm in diameter:

$(Na_xY_y)^+_{(ads)}$ + charged particle $\rightarrow (Na_xY_y)^+_{(g)}$
$(Na_xY_y)^+_{(g)} + e^- \rightarrow x.Na + y.Y$

Thus, several Na atoms are formed for every electron that is consumed, in accord with very recent observations (Gardner and coworkers, 1992).

Mesospheric Chemistries of Other Meteoric Metals

Potassium

- seasonal column abundance appears to be constant *cf.* sodium
- difficult to explain since the alkalis should all have very similar chemistries
- only the reaction $K + O_2 + N_2$ has been measured - twice as fast as Na reaction

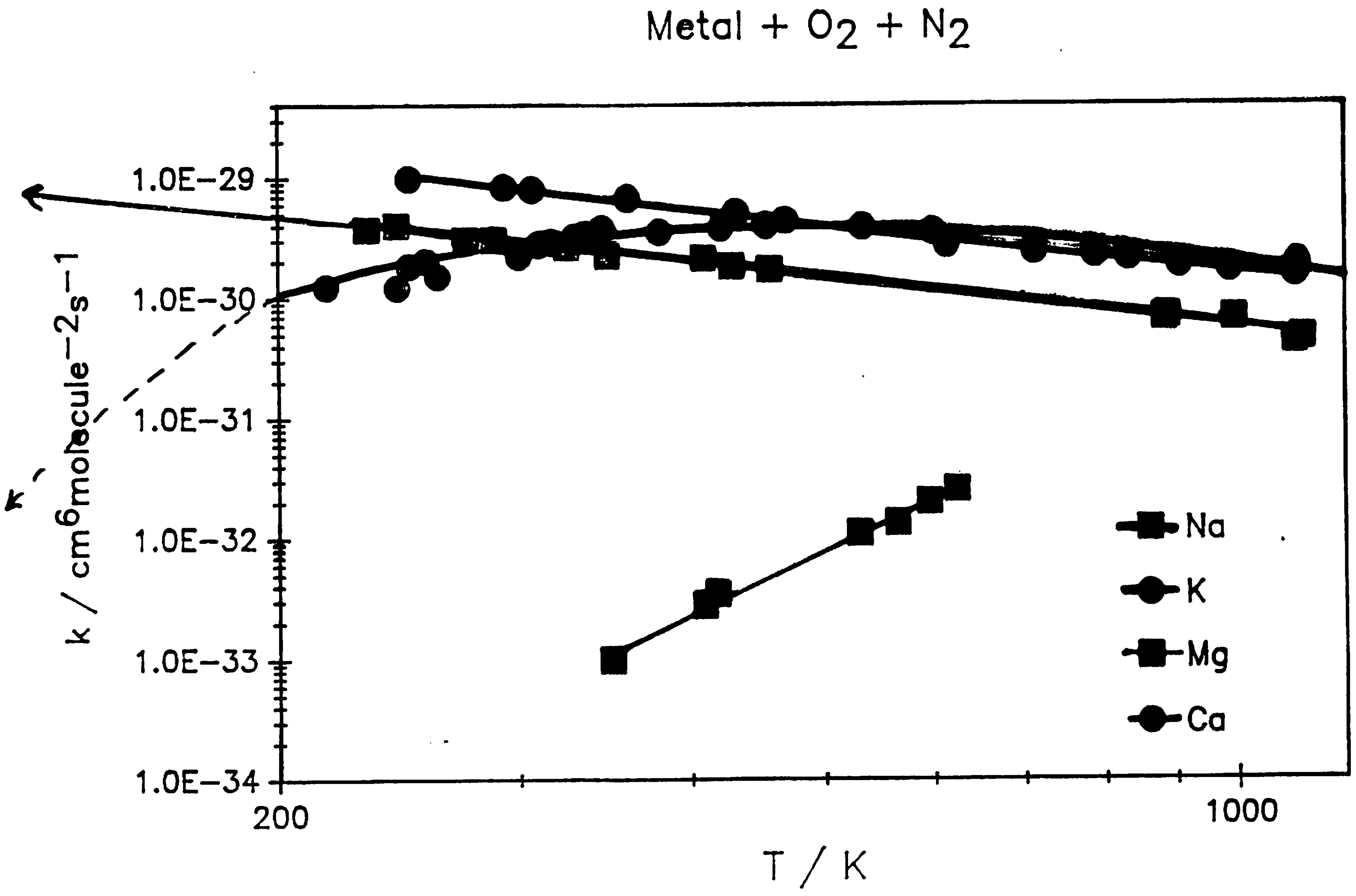
Calcium

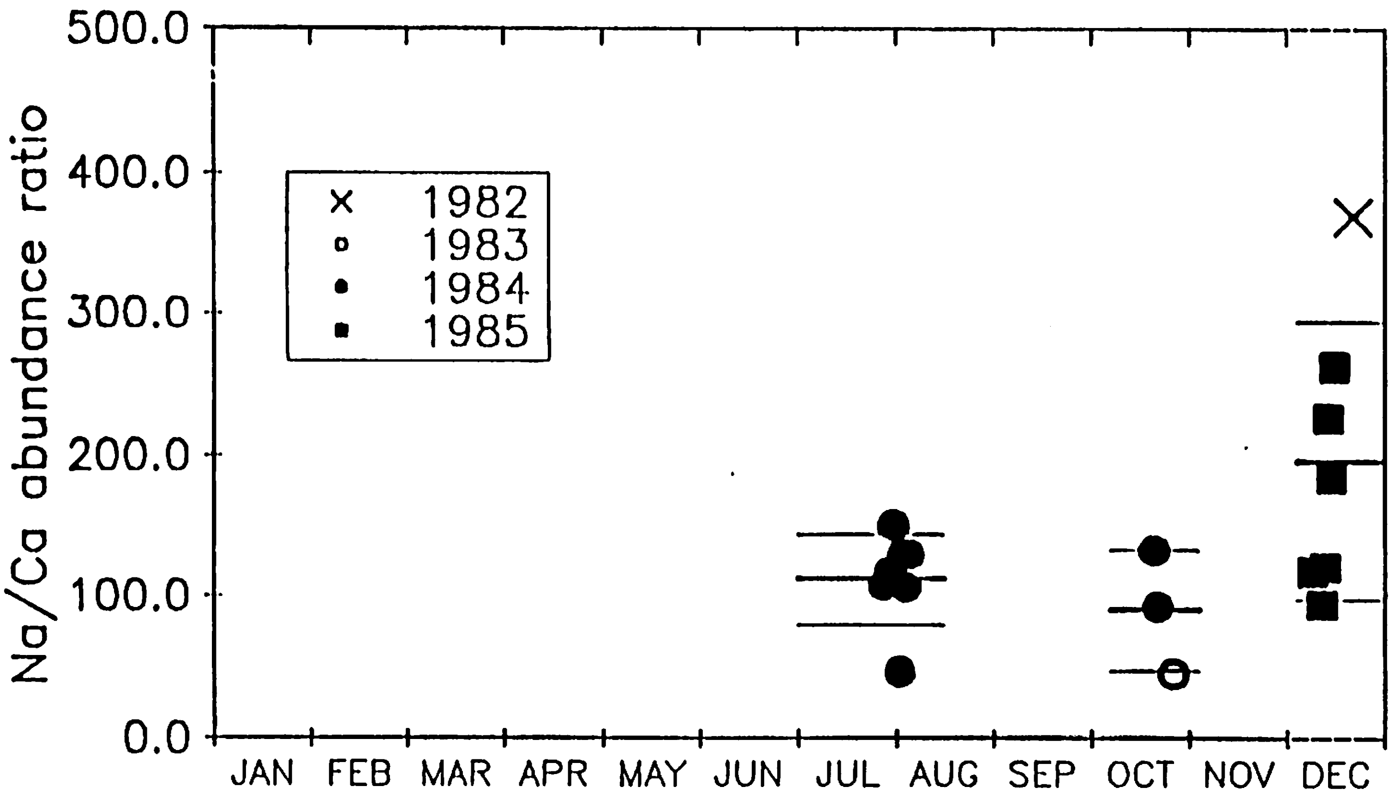
- depleted relative to sodium by about 120, although the Ca/Na ratio in meteorites is about unity
- the reaction $Ca + O_2 + N_2$ has a *positive* temperature dependence at low temperatures - this could explain the summertime enhancement of Ca to Na
- the reaction $Ca + O_3 \rightarrow CaO + O_3$ is very fast - perhaps further reactions such as

$$CaO + CO_2 + N_2 \rightarrow CaCO_3 + N_2$$

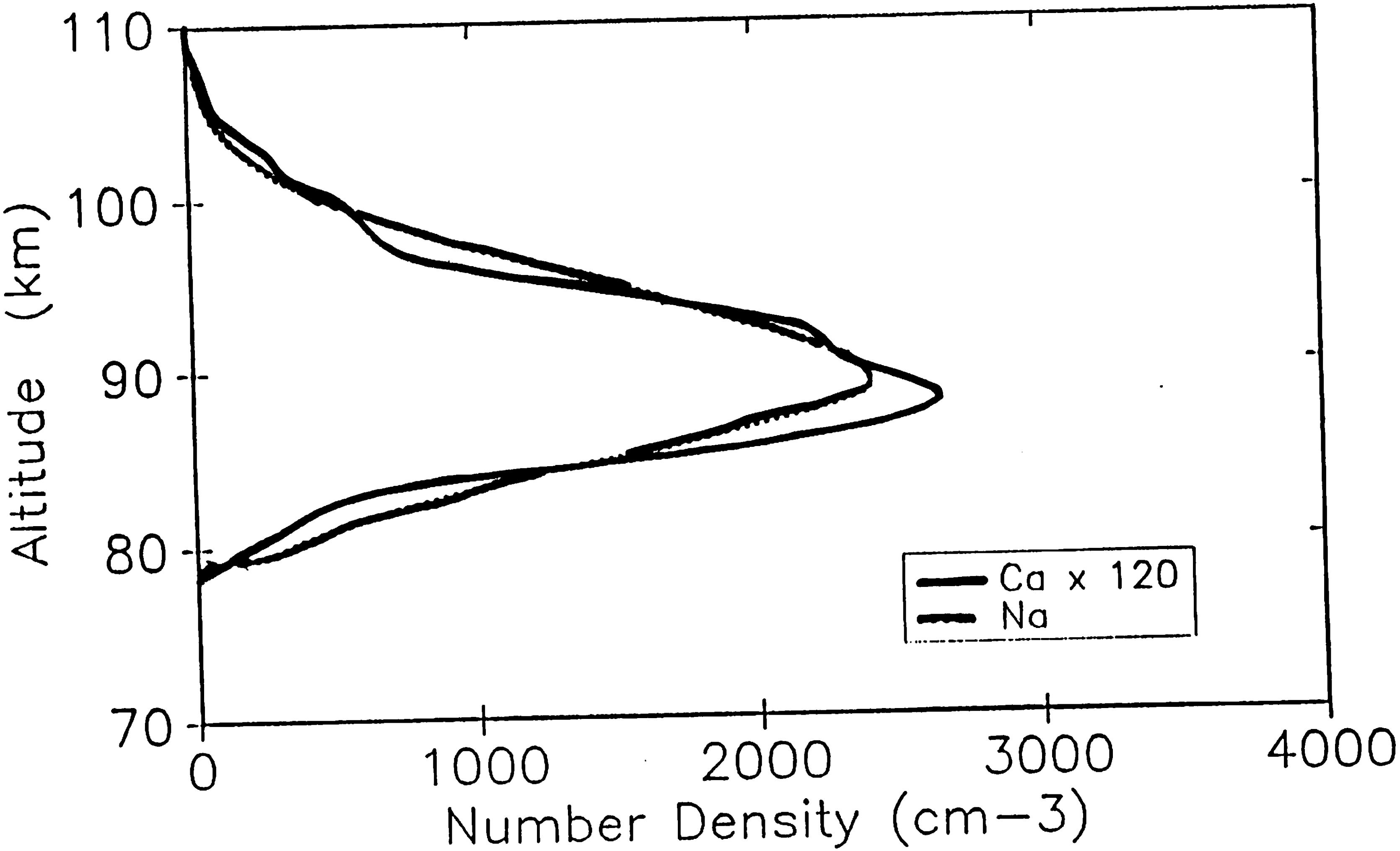
$$CaO + H_2O + N_2 \rightarrow Ca(OH)_2 + N_2$$

remove Ca permanently


Metal + O_2 + N_2
1.0E-29
1.0E-30
1.0E-31
1.0E-32
1.0E-33
1.0E-34
200
1000
T / K
k / $cm^6 molecule^{-2} s^{-1}$
Na
K
Mg
Ca



Na/Ca abundance ratio
500.0
400.0
300.0
200.0
100.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
× 1982
○ 1983
● 1984
■ 1985


110
100
90
80
70
Altitude (km)
0
1000
2000
3000
4000
Number Density (cm−3)
Ca x 120
Na

Magnesium

- cannot be seen spectroscopically from the ground because of the Hartley band of ozone
- the reaction $Mg + O_2 + N_2 \rightarrow MgO_2 + N_2$ is extremely slow
- the reaction $Mg + O_3$ remains to be measured; if MgO formation is rapid, then formation of $MgCO_3$ and $Mg(OH)_2$ may remove Mg
- the ionic chemistry of Ca and Mg is more complex than Na, because the Group 2 metals can form stable oxide cations:

$$Mg^+ + O_2 + N_2 \rightarrow MgO_2^+$$

$$Mg^+ + O_3 \rightarrow MgO^+ + O_2$$

However,

$$MgO_2^+ + O \rightarrow MgO^+ + O_2$$

$$MgO^+ + O \rightarrow Mg^+ + O_2$$

compete very effectively with dissociative recombination with electrons.

Iron

- Fe is depleted relative to Na by factors ranging from 3 to 20; the Fe layer is more variable and is a few kilometres lower
- recent lidar observations (Gardner and coworkers) indicates large enhancements at the equinoxes (comprehensive winter observations yet to be reported?)
- Fe, like Mg and Ca, has a closed electronic *s* shell. Thus, it reacts very slowly with O_2. The O_3 reaction is unknown at present.