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A CASE FOR SiO_2^+

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ABSTRACT

Silicon ions are normally detected at altitudes above 100 km and within sporadic E layers. Traces have rarely been observed within the more permanent metallic layer near 93 km. This is surprising since silicon is an important constituent of chondritic meteorites, which ablate material in this region to provide a primary source of the metallic species observed there. In this work, we present evidence that Si^+ ions form SiO_2^+ at the lower altitudes, and exist in this ionic state prior to recombination. A rocket launched from El Arenosillo, Spain on 3 July 1972, at 0743 LMT ($X = 57.1°$), during the predicted period of the β Taurids meteor shower, passed through a continuous belt of metallic ions that began near 85 km, ended near 115 km, and exhibited an order of magnitude increase in the form of a layer near 114 km. Si^+ was measured in and below the ledge down to 103 km. It showed a rapid decrease below this height. A comparison of the isotopic ratio for nickel, $[^{60}Ni]/[^{58}Ni]$, with the measured ions shows too large a ratio for the ions below 100 km, suggesting contribution to 60^+ from other sources. A prime candidate is SiO_2^+, since Si^+ is observed to decrease in the region where the ratio becomes too large. No evidence for SiO^+ (44^+) is present in the data, indicating that Si^+ forms SiO_2^+ either directly or through SiO^+ in a short lived state. Radiative association is offered as a primary mechanism for SiO_2^+ production and yields a calculated reaction rate of 2×10^{-16} cm^3 sec^{-1}.

ILLUSTRATIONS

SILICON IONS BELOW 100 KM: A CASE FOR SiO_2^+

by Richard A. Goldberg

Numerous rocket-borne mass spectrometric measurements of ion composition
in the upper atmosphere have defined a metallic ion belt between 90 and 95 kilo-
meters as a reasonably permanent feature independent of location and time
(e. g. Young et al, 1967; Narcisi 1967; Johannessen and Krankowsky, 1972;
Aikin and Goldberg, 1973).   Figure 1 illustrates this layer as observed at the
daytime equator by Aikin and Goldberg (1973).   The data have shown the domi-
nant species within the layer to be Fe^+ and Mg^+ with reduced quantities of Na^+,
Al^+, K^+, Ca^+, Ni^+, and other metal ions.   These constituents are believed to be
principally of extraterrestrial origin, deposited at these altitudes by meteoric
ablation.   The remainder must be terrestrial, precipitated by natural and arti-
ficial processes.   A thorough knowledge of the species' abundances can thereby
provide information concerning structure and evolution of certain extraterrestrial
bodies such as comets, and simultaneously assist study of the transport processes
responsible for bringing trace constituents of terrestrial origin into the upper
atmosphere.

Ion-neutral chemistry plays a critical role in analyzing this problem, especially
since most of the rocket measurements to date have only provided ion informa-
tion.   Silicon is a semi-metallic constituent that must be important because of
its high abundance in meteoric materials (e. g. Mason, 1971) yet as an ion it is
distributed in a manner unexplainable in terms of its known chemistry.   Above
100 km and primarily within the confines of mid and high latitude sporadic E(Es)
layers, metal ions are observed to dominate the ion structure (Istomin, 1963;
Young et al, 1967; Narcisi, 1967; Goldberg & Aikin, 1973) and here Si^+ is usually
observed to be an important, if not dominant atomic ion.   However, within the
permanent metallic ion layer below 95 km, Si^+ has rarely been observed.   The
ion-neutral chemistry of silicon must therefore be unique, to permit its exis-
tence in a free ionic state above but not below 100 km.   This work is concerned
with an investigation of this problem, made possible by the study of an unusual
metal ion structure recently observed during a meteor shower event.

The region between the permanent metallic ion layer near 95 km and the Es
layers above 100 km does not normally exhibit significant metallic ion structure
except during specific events such as a meteor shower.   An example is that of
Goldberg and Aikin (1973), illustrated in Figure 2.   These results were obtained
during the β Taurids meteor shower on July 3, 1972 at 0743 LMT ($\chi = 57.1°$)
with a rocket-borne quadrupole ion mass spectrometer launched from El
Arenosillo, Spain.   Absolute ion magnitudes were obtained by normalization
procedures, using the measured total electron and ion densities determined by

Faraday rotation radio wave propagation and Gerdien probe experiments aboard the same flight.

These data exhibit an Es peak near 114 km. The metal ions dominating this peak are Fe^+ (56^+), Si^+ (28^+), and Mg^+(24^+). Identification of 28^+ as N_2^+ is not feasible because of the difficulty in explaining the presence of a short lived molecular constituent within the peaked distribution. Here, the only constituents present should be metal atomic ions, since only these possess sufficiently long lifetimes to permit transport mechanisms to redistribute them into the narrow ledge observed. Above the ledge, 28^+ takes on the chemical equilibrium distribution predicted for N_2^+.

Under the metal ion ledge, metallic ions are observed in abundance to altitudes below 93 km, the region where meteoric ablation is maximum. Si^+ is observed to rapidly decay below 102 km, and at 93 km is a very minor atomic ion. The high abundance of metallic ions between 95 and 105 km has also been observed by Narcisi et al (1972) during a polar cap absorption (PCA) event and by Zbinden et al (1973) during the Geminid meteor shower. Both results display a similar profile for 28^+.

Figure 3 represents the relative number abundances of the metal ion species when normalized to 28^+ as silicon. The results within the layer are compared to those obtained near 101 km. These results are further compared with the neutral relative number abundances measured for the same constituents in chondritic and crustal materials (converted from the weight abundances given in Ahrens, 1965). The agreements obtained demonstrate the validity for identifying 28^+ as Si^+ within and below the metallic ledge, and suggest most species observed to be of extraterrestrial origin.

The rapid depletion of Si^+ below 100 km and its minor contribution within the primary metallic layer shows the Si^+ chemistry to be more complicated than that of the more common metallic constituents, e.g. Fe^+ and Mg^+. As noted by Brown (1973) in his recent review on metallic ion chemistry in the upper atmosphere, production processes for Si^+ are not significantly different than for other metal ions, unless silicon ablates from meteorites in a unique form currently unspecified. If we turn to loss processes for an explanation of the unique Si^+ distribution, we must consider oxides (e.g. SiO^+, SiO_2^+) since dissociative recombination of these constituents is far more rapid than radiative recombination of Si^+.

Information concerning SiO_2^+ is available in the data of 14.483. SiO_2^+ (60^+) has the same mass as the nickel isotope $^{60}Ni^+$. By comparing the known isotopic ratio of $[^{60}Ni]/[^{58}Ni]$ to the measured ratio of $[60^+]/[58^+]$, as shown in

Figure 4, we find a trend leading to values well in excess of the nickel ratio below 105 km, thereby suggesting a second contribution to 60^+ (e. g. SiO_2^+). This is of interest because the 60^+ enhancement occurs at the very location where Si^+ begins to deplete.

The reader is cautioned to note that this result has been extracted from data obtained near the sensitivity limit of the instrument. This also accounts for the absence of data points below 100 km, where 60^+ was not clearly discernable. Figure 5 offers a comparative plot for the measured ratios of $([25^+] + [26^+])/[24^+]$ as referenced to the known relative abundance of the magnesium isotopes. In this case the scatter of measured data is tightly bound to the theoretical line throughout the entire altitude range where measurement was possible. This result is offered to demonstrate the scatter expected, and lend credence to the $[60^+]/[58^+]$ curve.

If, in fact, the data does provide a measurement of SiO_2^+, then we arrive at a magnitude of 2 cm^{-3} near 100 km. Swider (1969) has suggested SiO_2^+ formation by the process $Si^+ + O_2 + N_2 \rightarrow SiO_2^+ + N_2$ with a rate coefficient $k_1 = 10^{-30}$ cm^6 sec^{-1}. This would then be followed by dissociative recombination $SiO_2^+ + e \rightarrow Si + O_2$ with a rate $k_2 = 3 \times 10^{-7}$ cm^3 sec^{-1}. An equilibrium value for SiO_2^+ of 0.1 cm^{-3} is calculated for 100 km, suggesting need of a larger value for k_1/k_2 than that used. On the other hand, assuming Swider's numbers to be correct, this low value for SiO_2^+ implies that either 60^+ contains an additional unknown component, or that another SiO_2^+ source is present. If we postulate this source to be the product of radiative association, i.e. $Si^+ + O_2 \rightarrow SiO_2^+ + h\nu$, then we calculate a rate k_3 of 2×10^{-16} cm^3 sec^{-1} for this process.

The above equilibrium system seems feasible since Fehsenfeld (1969) has found $SiO^+ + O \rightarrow Si^+ + O_2$ to be exothermic, implying that SiO^+ production through the reverse process is not likely. The absence of SiO^+ (44^+) within the metallic ion region observed on this rocket flight, or for that matter, in any other metallic ion data obtained by this observer, appears to concur with the laboratory result.

In conclusion, we have interpreted an excess abundance of 60^+ ions measured near 100 km to be caused by the presence of SiO_2^+. The results, although somewhat marginal due to the sensitivity restrictions of the detector, appear valid. Furthermore, the unusual metallic ion distribution present on the day of the measurement provided a unique opportunity for the silicon problem to be studied. The results suggest that below 100 km Si^+ is rapidly depleted by two and three body reactions with O_2, forming SiO_2^+ which then recombines. Further measurements under similar conditions should be conducted to determine the validity of the results suggested here, especially to establish the importance of radiative association, which has a reaction rate too small for laboratory verification.

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REFERENCES

Ahrens, L. H. (1965) Distribution of the Elements in Our Planets, p. 97, McGraw-Hill, New York.

Aikin, A. C. and R. A. Goldberg (1973) Metallic Ions in the Equatorial Ionosphere, J. Geophys. Res., 78, 734-745.

Brown, T. L. (1973) The Chemistry of Metallic Elements in the Ionosphere and Mesosphere, Chem. Rev., 73, 645-667.

Fehsenfeld, F. C. (1969) Si^+ and SiO^+ Reactions of Atmospheric Importance, Canadian J. Chem., 47, 1808-1809.

Goldberg, R. A. and A. C. Aikin (1973) Comet Encke: Meteor Metallic Ion Identification by Mass Spectrometer, Science, 180, 294-296.

Istomin, V. G. (1963) Ions of Extraterrestrial Origin in the Earth's Ionosphere, Space Research, 3, 209-220.

Johannessen, A. and D. Krankowsky (1972) Positive-ion Composition Measurement in the Upper Mesosphere and Lower Thermosphere at a High Latitude During Summer, J. Geophys. Res., 77, 2888-2901.

Mason, B. (1971) Introduction in Handbook of Elemental Abundances in Meteorites ed. by B. Mason, Gordon and Breach Science Publishers, New York.

Narcisi, R. S. (1967) Processes Associated with Metal-ion Layers in the E Region of the Ionosphere, Space Research, 8, 360-369.

Narcisi, R. S., C. R. Philbrick, D. M. Thomas, A. D. Bailey, L. E. Wlodyka, D. Baker, G. Frederico, R. Wlodyka, and M. E. Gardner (1972) Positive Ion Composition of the D and E Regions During a PCA in Proceedings of COSPAR Symposium on Solar Particle Event of November 1969 ed. by J. C. Ulwick, REP. AFCRL-72-0474, Air Force Cambridge Research Laboratories, Bedford, Massachusetts.

Swider, W., Jr. (1969) Processes for Meteoric Elements in the E Region Planet. Space Sci., 17, 1233-1246.

Young, J. M., C. Y. Johnson and J. C. Holmes (1967), Positive Ion Composition of a Temperature Latitude Sporadic E Layer as Observed During a Rocket Flight, J. Geophys. Res., 72, 1473-1479.

Zbinden, P. A., M. A. Hidalgo, P. Eberhardt, and J. Geiss (1973), Positive Ion Composition in the Lower Ionosphere During the Geminid Meteor Shower and the Occurrence of a Winter Anomaly, paper presented at the 16th Plenary Meeting of COSPAR, Konstanz, May, 1973.
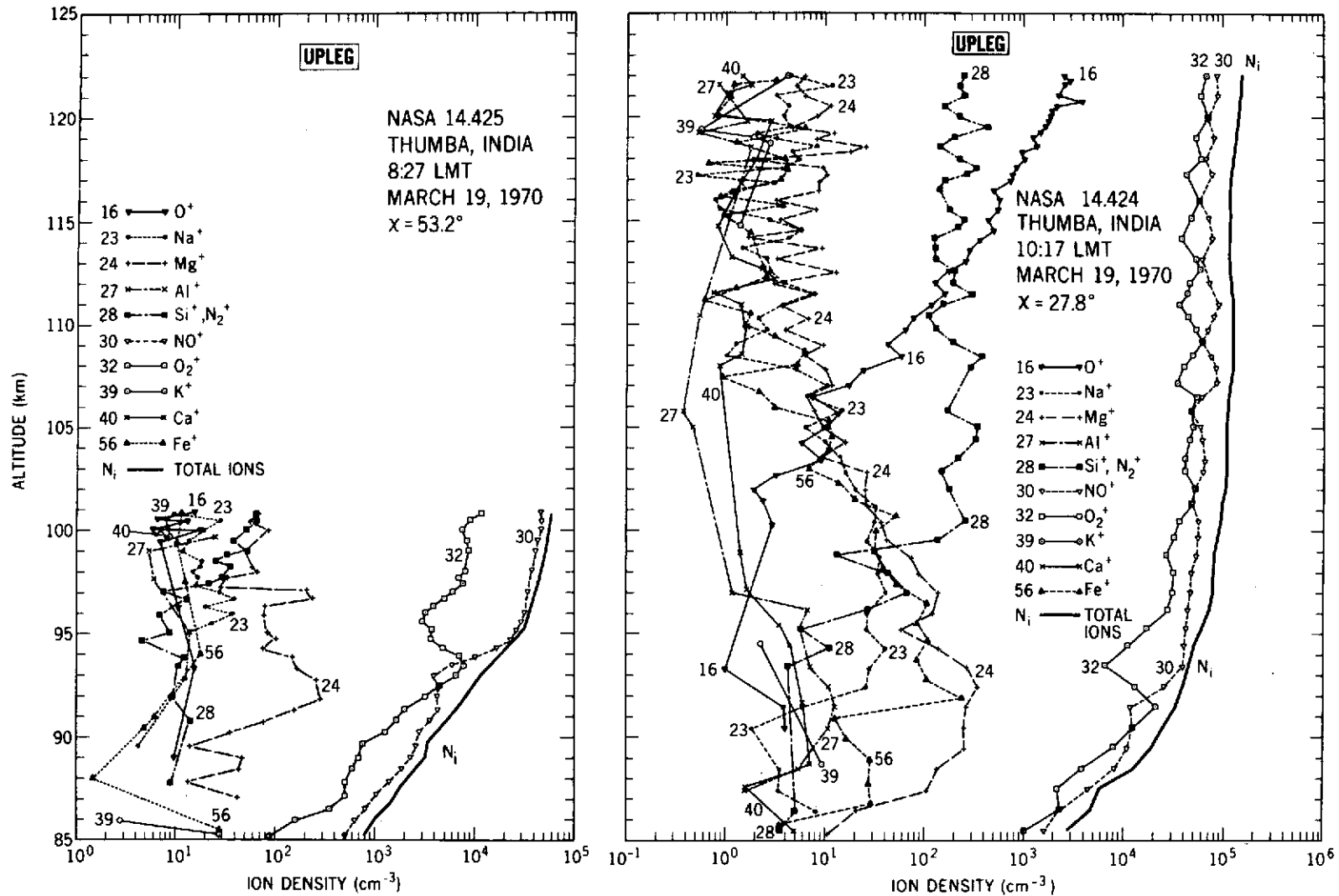
Figure 1. Two observed distributions of positive ion species in the daytime lower thermosphere over Thumba, India on 19 March 1970, illustrating the metallic layer near 93 km.
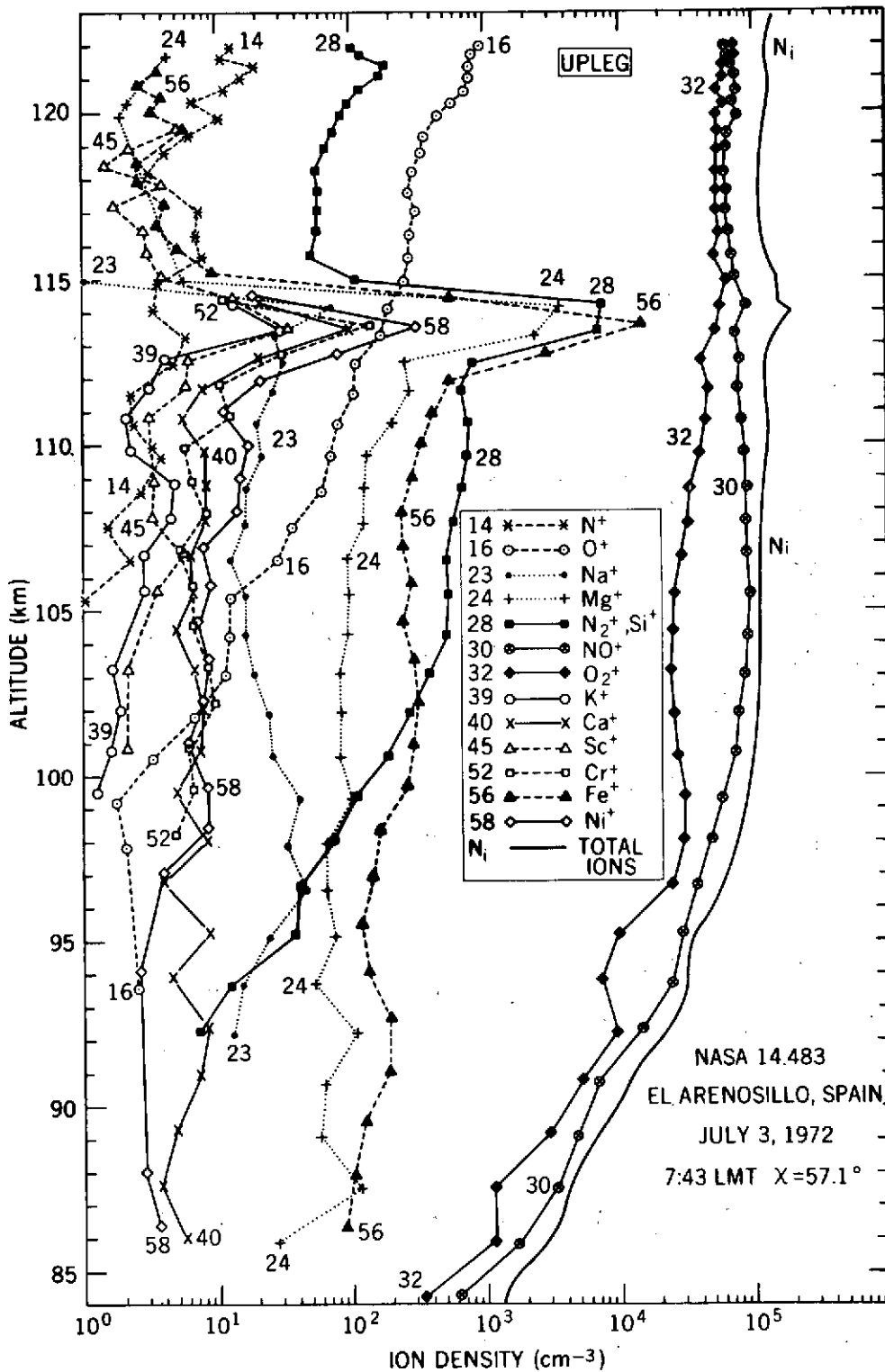
Figure 2. Observed distribution of positive ion species in the lower thermosphere over El Arenosillo, Spain during the β Taurids meteor shower on 3 July 1972.

ELEMENT	ION ABUNDANCES NASA 14.483		NEUTRAL ABUNDANCES (AHRENS, 1965)	
	101 km	114 km	CHONDRITES	CRUST
Na	12	9.1	4.6	10.4
Mg	49	57	93.5	8.0
Si	100	100	100	100
K	0.81	0.38	0.37	5.3
Ca	3.6	1.2	5.5	10.4
Sc	1.0	0.35	0.003	0.005
Cr	3.4	1.77	0.92	0.02
Fe	149	158	70.9	10.0
Ni	4.2	4.7	3.6	0.13

Figure 3. Relative number abundances of ions (NASA 14.483 rocket data) and neutral elements (chrondritic and crustal data) normalized to Si^+ , Si = 100.
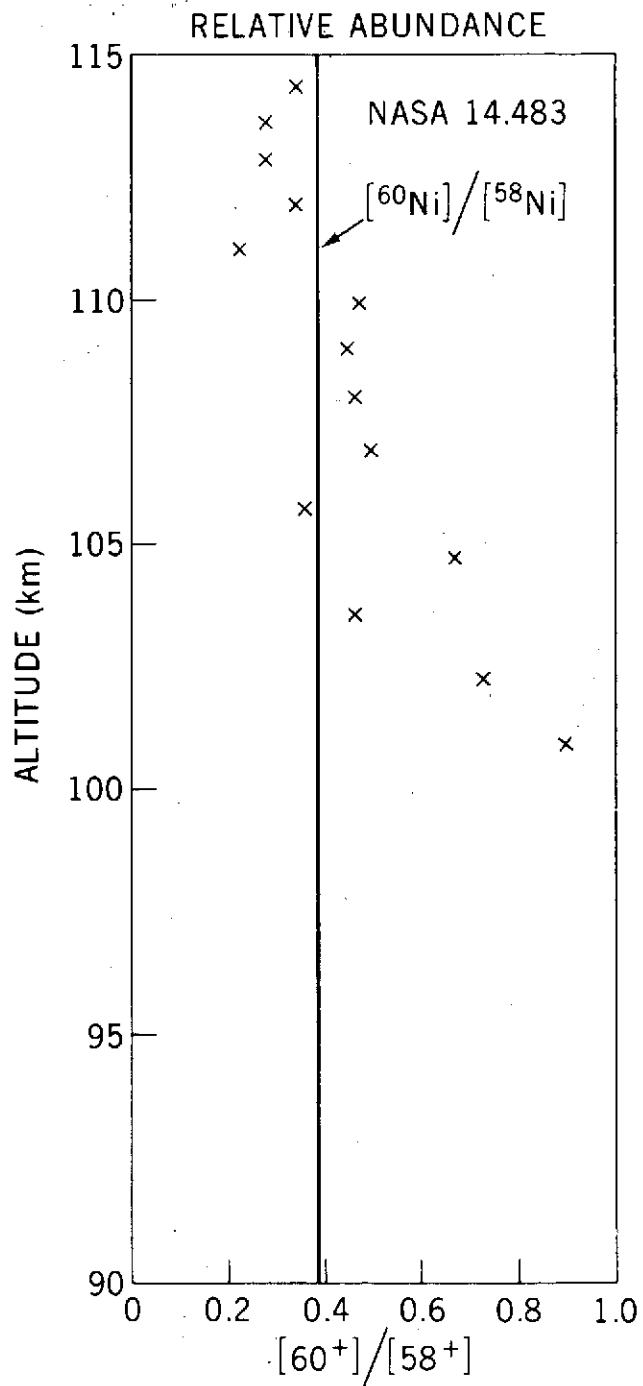
Figure 4. Comparison of measured ratio $[60^+]/$ $[58^+]$ to the known ratio $[^{60}Ni]/[^{58}Ni]$ for nickel isotopes.
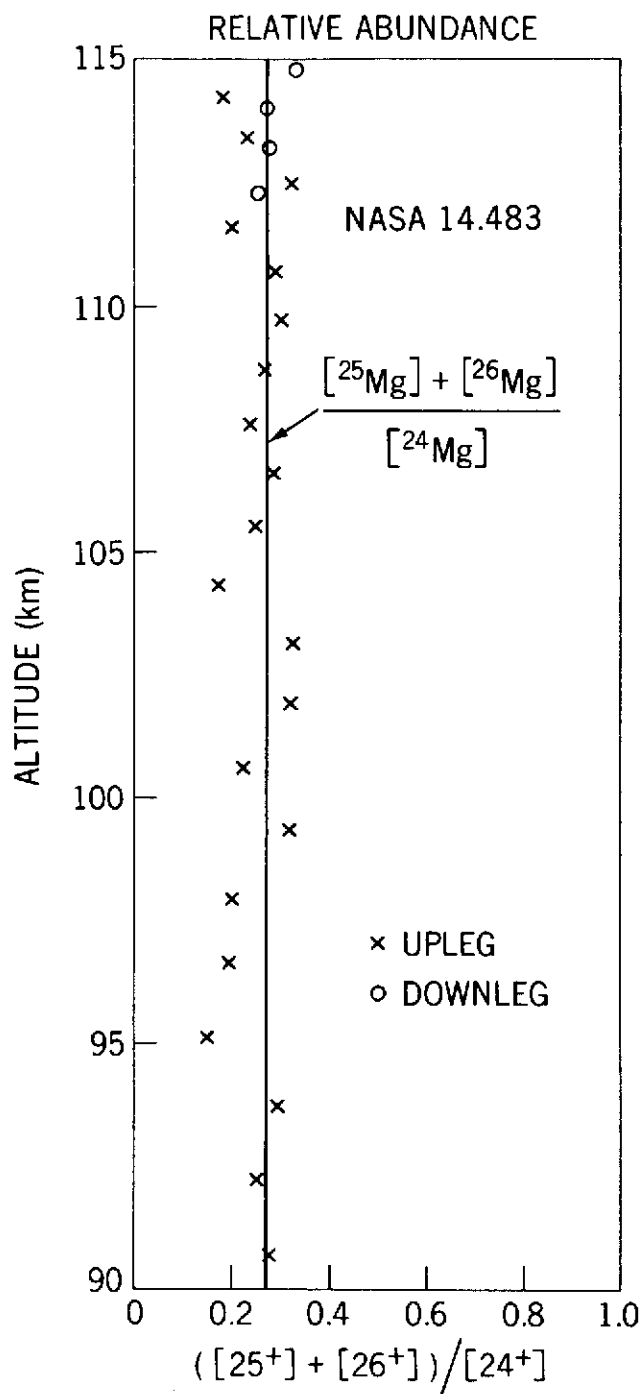
Figure 5. Comparison of the measured ratio $([25^{+}] + [26^{+}])/[24^{+}]$ to the known ratio $([^{25}Mg] + [^{25}Mg])/[^{24}Mg]$ for magnesium isotopes.