Reports

Comet Encke: Meteor Metallic Ion Identification by Mass Spectrometer

Abstract. *Metal ions including 23+ (Na+), 24+ (Mg+), 28+ (Si+), 39+ (K+), 40+ (Ca+), 45+ (Sc+), 52+ (Cr+), 56+ (Fe+), and 58+ (Ni+) have been detected in the upper atmosphere during the period of the Beta Taurids meteor shower. The abundances of these ions relative to Si+ show agreement in most instances with abundances in chondrites. A notable exception is 45+, which, if it is Sc+, is 100 times more abundant than neutral scandium found in chondrites.*

Positive metallic ions have been measured in the earth's atmosphere between 85 and 120 km, during the period of the β Taurids meteor shower, which is associated with Comet Encke. These ions originate during and following ablation of extraterrestrial debris by the earth's atmosphere.

The existence of metallic ions in the upper atmosphere has been known for some time. Many elements have been discovered with the aid of rocket-borne ion mass spectrometers. In most cases the major components are Mg^+ and Fe^+, with lesser quantities of Na^+, Al^+, K^+, Ca^+, Cr^+, Si^+, and other metals (*1–4*). Normally, a layer of these constituents is observed near 95 km with a half-width of 3 to 5 km. Since metallic ions are atomic, they have long lifetimes and can be acted on by external forces such as those generated by wind shears in the presence of the terrestrial magnetic field (*5*). At mid-latitudes this can result in additional layers of enhanced metal ions having extremely narrow half-widths (½ to 2 km) and located between 105 and 130 km at the wind shear levels. When these layers are observed by ground-based ionosondes, they are termed sporadic E-layers (E_s-layers).

The enhancement of the metal ion density during meteor showers is primary evidence for the extraterrestrial origin of the ions (*1, 3*). In addition, Junge *et al.* (*6*) have argued that constituents such as sodium could not diffuse from the earth's lower atmosphere to 100 km in a reasonable time. Comparisons of the relative abundances of metallic ions in the earth's upper atmosphere with those of neutral species in samples of the earth's crust and in chondrites have shown closer agreement with the chondritic relative abundances, even though such comparisons disregarded transport processes for ions and neutral species and ion-neutral chemistry in the atmosphere (*7*).

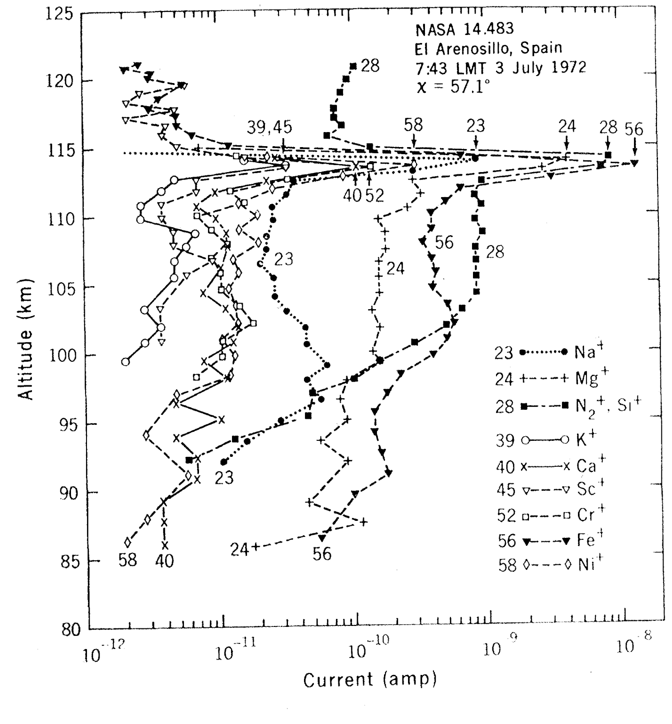

Fig. 1. Vertical height profile of the positive metallic ion composition observed during the upleg flight of NASA 14.483. Arrows mark the observed peak value for each metallic constituent within the E_s-layer.

The results reported here were obtained from a rocket-borne ion mass spectrometer, similar to that discussed previously (*4, 8*). The instrument was flown aboard NASA 14.483 on 3 July 1972 at 7:43 local mean time (LMT) (solar zenith angle, 57.1°) from El Arenosillo, Spain (37.1°N, 6.7°W), and reached an apogee of 122.8 km. The launch occurred during a growing enhancement of the E_s-layer, which was observed just before the rocket flight and during it by a ground-based ionosonde.

Figure 1 illustrates the measured currents for the observed metallic ion distribution (major isotope for each constituent) from 85 to 120 km. Metallic ions [24+ (Mg^+), 40+ (Ca^+), 56+ (Fe^+), and 58+ (Ni^+)] were first detected at 85 km. Near 90 km the ions 23+ (Na^+) and 28+ (Si^+) also appeared. The density of ions continued to increase to 100 km, where other constituents emerged. Above 100 km the distribution remained nearly constant to 112 km. At this height, the density increased approximately 30 times to form a well-defined metallic ion peak, which terminated abruptly at 115 km. The vertical arrows indicate the maximum observed value for each constituent within the peak.

The total metal ion density comprises 15 percent of the total ion density within the layer at 114 km, and is less at other altitudes. Narcisi (*3*) has shown that during the Leonid meteor shower, metal ions may comprise as much as 40 percent of the total ion density. The β Taurids shower normally extends over a few weeks (*9*) with typical flux increases of only a few percent, which may account for the reduced enhancement of metal ions observed during the β Taurids shower.

A comparison of local ionograms for the time period of the rocket flight on days before it and during the day of the flight shows an abnormal enhancement of the critical frequency f_oE_s to 10 Mhz from the more nominal 5 Mhz values observed on the preceding days. This enhancement occurred within the 10-minute period before launch and disappeared 45 minutes after launch. It is possible that enhanced meteoric activity before launch could have contributed to this phenomenon.

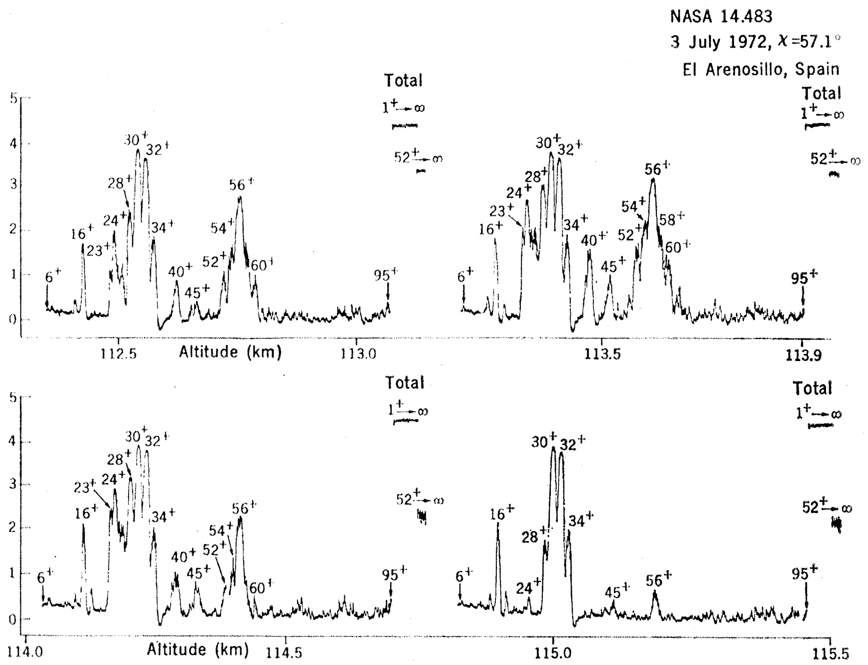

Fig. 2. Raw spectra depicting ion composition during transit through the E_s-layer on the upleg of NASA 14.483. The voltage display is approximately logarithmic in current and therefore in relative composition among species.

Figure 2 illustrates four upleg spectra obtained during transit through the E_s-layer. The ordinate of the spectra in volts is approximately logarithmic in current. The region between each spectrum reflects the period during which the spectrometer operated in a high-pass filter mode, obtaining data that are not pertinent to this discussion.

If we assume that the ions are singly ionized, the metallic constituents with their principal isotopes in the E_s-layer are identified as 23+ (Na+); 24+, 25+, 26+ (Mg+); 28+ (Si+); 39+ (K+); 40+ (Ca+); 45+ (Sc+); 52+ (Cr+); 54+, 56+ (Fe+); and 58+, 60+ (Ni+). Other isotopes and constitutents, such as 27+ (Al+) and 55+ (Mn+), may have been present, but the resolution of the instrument did not permit accurate identification of such constituents during the flight. The ions 16+ (O+), 30+ (NO+), and 32+, 34+ (O_2+), as well as a certain fraction of 28+ (N_2+), are gaseous ions normally present at these altitudes. They result from ionization of the different neutral constituents in the earth's atmosphere, together with ion-neutral chemistry.

Table 1 shows the observed relative abundance of each metallic ion species normalized to that of Si+, near 101 km and 114 km. Values for the major constituents are believed to be accurate to ±20 percent, and those for the minor constituents to ±100 percent. Each result contains contributions from all isotopes; the measured value for the principal isotope and the known isotopic abundance ratios were used to more accurately evaluate the minor isotopic concentrations. Since the height resolution near 114 km is 0.8 km, the narrowness of the ledge required comparison of the observed rather than the exact maximum value for each constituent within the ledge. Between 101 and 114 km, most constituents maintained a constant relative abundance, with the exception of 28+, which became dominant between 102 and 112 km. This effect was caused in part by a contribution from N_2+, estimated to be not greater than 10 percent at 114 km and unknown at 101 km. The ratios are therefore lower limits and subject to a uniform increase due to N_2+. However, the similarity of the abundances at both heights would tend to suggest a negligible or equivalent contribution of N_2+ to 28+ at either height. For comparison, the abundances of the neutral metals in chondrites and in the earth's crust (*10*) are also included. Because Si+ concentrations are low below 100 km, ratios based on Si+ are usually not possible except within the E_s structure. This may reflect a low proportion of Si in the normal daily meteor influx, a higher altitude for Si+ ablation, or a unique atmospheric behavior of Si+ for sufficient periods of time to permit ion-neutral reactions to oxidize Si+ and enhance recombination, at least below 100 km.

Table 1 demonstrates the similarity of the relative abundances of metallic ions in the atmosphere to those of neutral metals in chondrites. In particular, the species Mg, Cr, Fe, and Ni most clearly illustrate the extraterrestrial origin of the ion composition. We also note the apparent overabundance of Na+, an enhancement that has also been observed during other metal ion samplings (*7*). The origin of the large sodium ion densities is not understood.

One intriguing aspect of these data is the relatively high abundance of 45+, identified as Sc+. This is the first reported observation of the mass-to-charge ratio $m/e = 45$ at metallic ion heights. The identification as Sc+ is not a comfortable one because of the apparent difficulty of producing a source so rich in this constituent. The suggestion that the source might be the molecule NH_2HCO, which is believed to be a stable precursor in cometary material, appears unlikely, as ablation processes would probably dissociate this molecule before ionization. Doubly

Table 1. Relative abundances of ions (NASA 14.483 rocket data) and neutral elements (chondritic and crustal data) (*10*) normalized to Si+, Si = 100.

Element	Ions		Neutral elements	
	101 km	114 km	Chondrites	Crust
Na	12	9.1	3.8	8.5
Mg	49	57	80.9	6.9
Si	100	100	100	100
K	0.81	0.38	0.51	7.4
Ca	3.6	1.2	7.9	14.9
Sc	1.0	0.35	0.005	0.008
Cr	3.4	1.77	1.7	0.0035
Fe	149	158	141	19.9
Ni	4.2	4.7	7.6	0.027

ionized constituents seem to be ruled out because of the rapid recombination rates required for such ions and because there are no observed ions at $m/e = 90$. This constituent also exhibits its peak concentration in the E_s-layer (Fig. 1), which implies a high probability that it is atomic in structure. Instrumental contaminants and irregularities do not appear likely since 45^+ reappears at the same altitude in the downleg data. The above indicate an ion enhancement of the order of 100 times the normal relative abundance of Sc seen either in chondrites or in the earth's crust. This may be a property of the cometary debris.

The measurement of metallic ions in the upper atmosphere during the period of the β Taurids meteor shower suggests that extraterrestrial debris can contain enriched abundances of trace constituents not predictable from the cosmic abundance of these constituents. The enhanced densities of such constituents are still quite small and probably below the threshold of detection by other techniques, such as ground-based optical sensing. Hence, in situ measurements of the ion composition of the atmosphere during and after the entry of significant amounts of extraterrestrial debris offer a unique opportunity to analyze and study such material.

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11. This research occurred through a cooperative scientific program between members of the Spanish Comisión Nacional de Investigación del Espacio and the National Aeronautics and Space Administration. We thank them as well as members of our own scientific and technical team for making this program successful.

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Lignification in Trees: Indication of Exclusive Peroxidase Participation

Abstract. *Syringaldazine did not turn purple on cross sections of tree branches or saplings or on cambial tissue cultures unless hydrogen peroxide was added; this indicated the absence of laccase but presence of peroxidase in lignifying cells. Peroxidase, therefore, apparently is the only enzyme that polymerizes* p-*coumaryl alcohols to lignin in trees.*

The occurrence of coniferin in the sap of many gymnosperms helped to establish a theory that lignin is formed from its aglycon, coniferyl alcohol. Testing this theory, Freudenberg *et al.* (*1*) used indican to detect a β-glucosidase in the region of lignification in xylem cells near the cambium of *Araucaria excelsa*. The glucosidase released indoxyl that autoxidized to indigo, indicating the amount and distribution of β-glucosidase in the wood: a weak color in cells near the cambium intensified inward through thickening lignifying cells to a breakoff point in mature xylem tissue.

However, the enzyme involved in the next stage of lignification, the polymerization of *p*-hydroxycinnamyl alcohol precursors to lignin, remained unknown.

The Freudenberg group used a fungal phenol oxidase, later shown to be laccase (*p*-diphenol : O_2 oxidoreductase, E.C. 1.10.3.2), to make biosynthetic lignins (dehydrogenation polymer) in vitro from coniferyl alcohol alone or its mixtures with sinapyl and *p*-coumaryl alcohols (*2, 3*). It was thought that laccase catalyzed an analogous polymerization to produce lignin in wood (*2, 4*).

The incidence of laccase in fungi is widespread. However, lack of information on its distribution in higher plants, well-documented data on peroxidases in many lignified species, and the ability of peroxidase and H_2O_2 to transform *p*-coumaryl alcohols into lignin-like

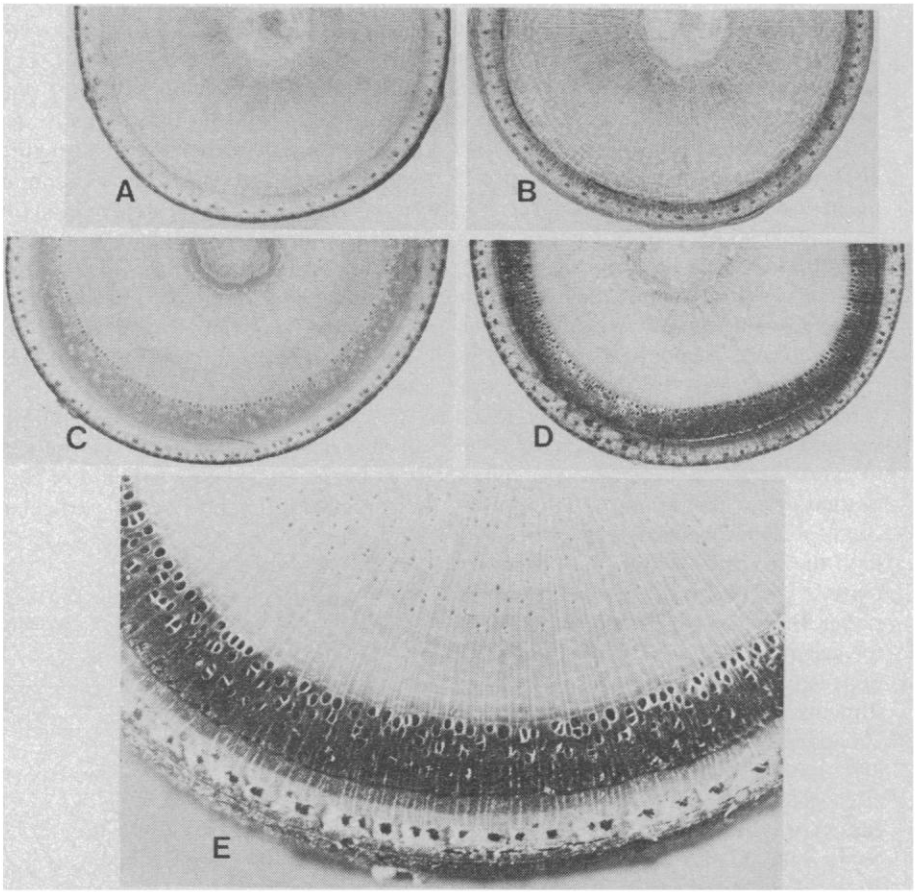

Fig. 1. Freshly cut surfaces of green ash sapling stems swabbed with dilute aqueous alcoholic furoguaiacin: (A and C) before adding H_2O_2; (B, D, and E) after adding dilute H_2O_2 in ether.