# THE CHEMICAL COMPOSITION OF COMETARY METEOROIDS

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Evidence for the chemical composition of cometary meteoroids is available from the spectra of shower meteors, from the analysis of extra-terrestrial dust particles, from a study of residues in the bottom of microcraters on plates exposed to the interplanetary environment, and from measures of the relative abundances of non-atmospheric ions in the E-region of the earth's upper atmosphere. Quantitative measures of chemical abundances in meteoroids, based on the four techniques listed, show that in general the cometary meteoroids encountered by the earth conform to the carbonaceous chondrites type 1 in the case of the commonest metallic elements. There is also qualitative evidence of the presence of significant quantities of some of the light volatiles.

There is good evidence that the small particulate material encountered by the earth, in the size ranges below kilogram weights, has a cometary origin (Jacchia and Whipple 1961; Jacchia *et al.* 1967). Particles of mass  $10^{-4}$  to  $10^{-6}$  g contribute the largest fraction of the total mass swept up by the earth each day (Whipple 1967; Millman 1975). Hence, in discussing the chemical composition of this complex, we should not extrapolate from the large amount of laboratory data on the composition of meteorites. It is significant that no meteorite has shown clear evidence of any association with the cometary meteor streams.

There are a number of areas of observational data which give independent evidence concerning the chemistry of small meteoroids. Impact microcraters on surfaces exposed directly to the interplanetary space environment sometimes exhibit residues that are foreign to the target chemistry. These residues presumably originate from the impacting particle. The techniques for the collection and analysis of small particles in the earth's upper atmosphere have recently been perfected to the extent that we can identify with some certainty material of extraterrestrial origin. Rocket-borne mass spectrometers have recorded unusual quantities of metallic ions at heights from 90 to 120 km above the earth, and under circumstances which strongly indicate a meteoritic origin. Meteor spectroscopy has made possible a qualitative chemical analysis of all the major meteor streams, and in some cases quantitative abundances have been calculated. It is the purpose of this review to summarize briefly the information on meteoroid chemical composition that has resulted from the types of research noted above.

Brownlee et al. (1974) have published quantitative abundances for nine elements found in a residue at the bottom of a 110  $\mu$ m crater on an aluminum sur-

face exposed for 67 days during Skylab-IV. They used the scanning electron microscope and energy-dispersing X-ray analysis. These relative abundances for seven elements, by weight, have been plotted in Figure 1, normalized to Si at a log weight of 6.00. In this plot, Cameron's values for the solar system are almost identical to the relative abundances for Cl chondrites taken from Mason (1971) and Schmitt *et al.* (1972). In a smaller crater with a diameter 35  $\mu$ m Brownlee *et al.* also found a different type of residue, consisting mainly of Fe and S in proportions that suggested the mineral troilite. C. L. Hemenway and D. S. Hallgren (unpublished) have found Fe, Si, Mg residues in four craters out of 20 produced on rocket-borne copper plates by submicron particles. These residues give qualitative confirmation of the relative abundances of the three elements, as found by Brownlee's team.

Brownlee et al. (1976a) have more recently published a detailed analysis of a small spherical micrometeoroid,  $12 \mu m$  diameter, that is considered to be an ablation product from a larger meteoritic particle. These data for six elements are plotted in Figure 1.



Figure 1. The relative abundances, by weight, of seven elements commonly found in cometary meteoroids. Values are plotted as log weight and normalized to Si at 6.00. Since Si values for meteor spectra are not available, normalization in this case was to the mean of Fe and Mg.

\_\_\_\_\_\_\_solar system, Cameron, 1973, also true for carbonaceous chondrites, type Cl.

.....earth's crust, Ahrens 1965.

- micrometeoroid, Brownlee et al. 1976a.
- ▲ microcrater residue, Brownlee et al. 1974.
- E-region ions, Goldberg and Aikin 1973.
- + 12 meteor spectra, Millman 1972a, 1972b.
- X 4 meteor spectra, Harvey 1973.

Some 150 particles with good evidence of extraterrestrial origin have been collected on balloon and U-2 flights (Brownlee *et al.* 1976b; Brownlee and Rajan

#### MILLMAN

1977). These are in the size range 2 to 30  $\mu$ m with three main types, divided according to chemical composition as follows:

60% - aggregates with grain size 0.1  $\mu m$  and Mg, Fe, Si, S, Ca, Ni in about solar system relative abundances.

30% - mainly Fe and S with a few % Ni, suggestion of troilite.

10% - Mg Fe silicates, and iron poor olivines and pyroxenes.

Additional proof of extraterrestrial origin comes from the detection of large amounts of  ${}^{4}$ He (10<sup>-2</sup> to 10<sup>-1</sup> ccSTP g<sup>-1</sup>) in six particles. This is most likely due to solar wind implantation. Six particles, analyzed for C, gave a mean carbon content of over 5% (Brownlee *et al.*, unpublished).

Mass spectrometers have been used with upper-air rockets by several groups (Goldberg and Aikin 1973; Krankowsky et al. 1972; Narcisi 1968) and a consistent pattern of ions in the upper atmosphere results from all these programs. In addition to the characteristic atmospheric ions, which are always present, occasional marked enhancements of metallic ions are found. These peak at heights which correspond to levels where small meteoritic particles disintegrate and vaporize. There has been a correlation in some cases between the time when the earth passes through a known meteor stream and the enhancement of the metallic ions in the upper atmosphere. Goldberg and Aikin (1973) have published quantitative abundances for an enhancement that took place on July 3 in 1972, after the earth had passed through the  $\beta$  Taurid meteor stream, associated with Comet Encke. These data have also been plotted in Figure 1.

Meteor spectroscopy has supplied a large amount of qualitative data on the elements present in the cometary meteoroids, and H, N, O, Na, Mg, Al, Si, Ca, Ti, Cr, Mn, Fe, Co, Ni, Sr, N2, CN, and possibly Li, K, Ba, FeO, CH have been identified in meteor spectra (Halliday 1961; Millman 1963; Ceplecha 1971). The difficulty has been to reduce this material to quantitative values. An empirical approach to this problem was provided by Savage and Boitnott (1973), who made laboratory measures of atomic collision cross-sections under conditions that attempted to simulate these corresponding to the production of visible meteor radiation. Harvey (1973) has favoured a more theoretical approach, using a concept of thermodynamical equilibrium and effective temperatures. The first technique is limited by the fact that luminous efficiencies are available for only four atoms and apply directly only to the higher collision speeds in the regime of molecular free-flow, that is in the high-level, early portions of meteor trajectories. The second technique is suspect on theoretical grounds, as evidenced by the widely varying effective temperatures found for different atoms and molecules in the same meteor spectrum, and the necessity of using various correction factors that have to be assumed without adequate theoretical or observational background. Personally, I favour the first approach, as far as it goes, and emphasize here the need for more laboratory work on collision cross-sections. Average results from the analysis of 10 Giacobinid and 2 Perseid spectra by Millman (1972a, 1972b) and of 4 meteors, a Taurid, Geminid, Perseid and Leonid, by Harvey (1973) mainly based on the Savage and Boitnott luminous efficiencies, are plotted in Figure 1.

When we examine the overall picture, as presented in the Figure, it is quite clear that all four independent types of research combine to show that, on the average, the small meteoritic particles, which are predominately cometary, agree much more closely with the chemical abundances of the solar system average mix than with the composition of the earth's crust. As Brownlee and his group have shown, a more detailed study of individual particles reveals examples, like the iron-sulphur-nickel particles, which depart from the general average for elemental abundances. This is also true for the small submicron grains that make up the larger particle aggregates.

Little can be said concerning the amount of light elements, such as H, C, N and O, present in the cometary meteoroids. Unfortunately, although there is considerable qualitative evidence for some of the light volatiles, as I have

#### MILLMAN

pointed out previously (Millman 1976), we have little in the way of quantitative data. It is hoped that further advances in the techniques of the collection and analysis of micrometeoroids, and in the reduction of meteor spectra, will soon result in filling this gap in our knowledge of the interplanetary environment.

## REFERENCES

- Ahrens, L. H. 1965, Distribution of the Elements in our Planet, McGraw-Hill Book Co., New York, N.Y., p. 96.
- Brownlee, D. E., Tomandl, D. A., Hodge, P. W., and Hörz, F. 1974, Nature, 252, 667.

Brownlee, D. E., Horz, F., Tomandl, D. A., and Hodge, P. W. 1976a, The Study of Comets (eds. B. Donn, M. Mumma, W. Jackson, M. A'Hearn, R. Harrington) NASA SP-393, Washington, D.C., p. 962.

Brownlee, D. E., Tomandl, D. A., and Hodge, P. W. 1976b, Interplanetary Dust and Zodiacal Light (eds. H. Elsässer and H. Fechtig), Springer-Verlag, New York, N.Y., p. 279. Brownlee, D. E., and Rajan, R. S. 1977, this volume.

Cameron, A.G.W. 1973, Space Sci. Rev., 15, 121.

Ceplecha, Z. 1971, Bull. Astron. Inst. Czecho., 22, 219.

Goldberg, R. A., and Aikin, A. C. 1973, Science, 180, 294.

Halliday, I. 1961, Publ. Dominion Obs., 25, 1.

Harvey, G. A. 1973, J. Geophys. Res., 78, 3913.

Jacchia, L. G., and Whipple, F. L. 1961, Smithsonian Contrib. Astrophys., 4, 97.

Jacchia, L. G., Verniani, F., and Briggs, R. E. 1967, Smithsonian Contrib. Astrophys., 11, 1.

Krankowsky, D., Arnold, F., Wieder, H., and Kissel, J. 1972, Intern. J. Mass Spectr. Ion Phys., 8, 379.

Mason, B. 1971, Meteoritics, 6, 59.

Millman, P. M. 1963, Smithsonian Contrib. Astrophys., 7, 119.

Millman, P. M. 1972a, From Plasma to Planet (ed. A. Elvius) Almqvist and Wiksell, Stockholm, p. 157.

Millman, P. M. 1972b, J. Roy. Astron. Soc. Canada, 66, 201.

Millman, P. M. 1975, The Dusty Universe (eds. G. B. Field and A.G.W. Cameron) Neale Watson Academic Pubs., New York, N.Y., p. 185.

Millman, P. M. 1976, Interplanetary Dust and Zodiacal Light (eds. H. Elsässer and H. Fechtig) Springer-Verlag, New York, N.Y., p. 359.

Narcisi, R. S. 1968, Space Research VIII (eds. A. P. Mitra, L. G. Jacchia and W. F. Newman) North-Holland Publ. Co., Amsterdam, p. 360.

Savage, H. F., and Boitnott, C. A. 1973, Evolutionary and Physical Properties of Meteoroids (eds. C. L. Hemenway, P. M. Millman, A. F. Cook) NASA SP-319, Washington, D.C., p. 83.

Schmitt, R. A., Goles, G. G., Smith, R. H., and Osborn, T. W. 1972, Meteoritics, 7, 131.

Whipple, F. L. 1967, The Zodiacal Light and the Interplanetary Medium, (ed. J. L. Weinberg) NASA SP-150, Washington, D.C., p. 157.

#### DISCUSSION

HUGHES: I'm worried about the 114 km high enhancement in the metallic ion density reported by Goldberg and Aitken. Wouldn't you expect the main mass ablation of a  $\beta$ -Taurid to occur much lower down, around 75 to 85 km?

MILLMAN: Metallic ion enhancements have been observed over a wide variation in height within the range 80 - 120 km above the earth. It just happens that the most marked enhancement for the case quoted (where quantitative values were

## COMPOSITION OF COMETARY METEOROIDS

published) was at 114 km, but the relative values of the elements were very similar at 101 km and the results I have plotted are the mean of measures for the two heights, 101 and 114 km. As a matter of fact very small meteorite particles vaporize at heights above 90 - 100 km and these represent the greater part of the total mass contributed to the atmosphere, apart from the micrometeoroids which do not vaporize.

EBERHARDT: The altitude at which the metal ions in the upper atmosphere are observed is not necessarily the altitude at which they were formed. Vertical transport processes due to horizontal winds occur and in some cases more than one layer has been observed with indication of vertical movement. Generally a strong metal layer at approximately 100 km altitude is present.

WASSON: The smaller the sample, the greater the potential for sampling inhomogeneities. As a result, I was surprised at the very good agreement beteween the analyses of individual dust particles and the composition of CI chondrites. Contamination is still a serious problem in the atmospheric collection of dust particles. I wonder if it is possible that some extraterrestrial particles having compositions deviant from chondritic compositions are misinterpreted as terrestrial contaminants, and whether this could result in a biasing of the results toward CI-like compositions.

MILLMAN: It is quite possible that some extraterrestrial particles impacting on the upper atmosphere, may be rejected if they masquerade as terrestrial particles in their physics and chemistry. From what we now know, the possibility of this happening in a significant number of cases is of small probability.

ANDERS: The sampling error mentioned by John Wasson is mainly a function of grain size. For carbonaceous chondrite matrices we can get an idea of the magnitude of this effect from electron microprobe measurements. If I am not mistaken, (and perhaps Dr. Kurat or Grossman will correct me), the variation for major elements is no more than 10-20% over distances of a new microns.

WETHERILL: In discussing comparisons of meteor and microparticle compositions with those of Cl, C2, and C3 chondrites, sampling problems, etc., it should be remembered that this general type of unfractionated primordial non-volatile composition is found in many parts of the solar system - the sun and probably Jupiter, comets, and some asteroids. Therefore this composition is much less useful in diagnosing a source than is the case when dealing with a particular pattern of chemical fractionation.

LIPSCHUTZ: What are the standard deviations (based upon the dispersion of the individual measurements) of the means for the elements reported in meteors-like the Giacobinids - where statistics are best?

MILLMAN: They range from ±5% for Fe and Mg to ±10% for Na and Ca.

ANDERS: To determine whether cometary meteors are of Cl or C2 chondrite composition, you may want to take advantage of the fact that the latter, but not the former, contain  $Mg_2SiO_4$  chondrules low in Fe. Thus, when a C2 chondrite breaks up, at least a few of the fragments of ~10<sup>-3</sup> g or smaller will be high in Mg, Si, but low in Fe.

MILLMAN: So far, on a qualitative basis, few meteor spectra show a significant depletion of Fe. It is certainly a good point to consider in future statistical studies of meteor spectra.

# MILLMAN

GROSSMAN: Have some of these same collection techniques not been used immediately after the fall of a known type of carbonaceous chondrite? If so, how do the results compare?

MILLMAN: I am not aware of quantitative values published for the complete chemical composition of individual dust particles. There are cases where the study of the particle was used to define the hature of the meteorite which fell.