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OBSERVING CHEMICAL ABUNDANCES IN COMETS

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Abstract

The atomic resonance lines of the major elements have been observed in the atmospheres of a few comets, by using vacuum ultraviolet spectrographs on board rockets or orbiting observatories. Dust-to-gas ratios have also been deduced for two comets through a Finson-Probstein's analysis of their dust-tail isophotes. The geometric albedo of the dust for the phase angle α of the observations is not accurately known ($A\phi(\alpha) = 0.20 + 0.05$) but, fortunately enough, the dust-to-gas ratio is not overly sensitive to the actual value of this albedo. Next, infrared observations of the dust head of some comets have shown that the bulk of cometary dust must be silicates, although a minor component (5-10 percent) of carbon compounds is rather likely, because of poor dielectric properties of the grains. This interpretation is confirmed by the fact that interplanetary dust probably of cometary origin, that has been collected in the stratosphere by NASA-U2 Spacecraft, is chondritic in nature. Finally, metal abundances in the head of a sungrazing comet support the chondritic hypothesis. Combining the previous data together, and assuming chondritic composition for the cometary dust, it is possible, at least in principle, to deduce the elementary abundances of the bulk of these volatile compounds of H,C,N,O,S, normalized to (chondritic) silicon and metals. These data give some clues on the origin of comets, in particular on their chemistry before accretion from pristine volatile grains. Unfortunately, present data come from different comets at different times, and their significance for a "mean" comet is rather uncertain. It is urged that a coordination between V.U.V. observations and ground-based photographs of dust tails be established for the same comets, in particular for the incoming passage of Comet Halley. Optimum times for improving the accuracy of the dust-to-gas ratio usually are after passage to perihelion.

1. The Physical Study of Comets

By necessity, the physical study of comets has traditionally been more concentrated on the qualitative understanding of the transient phenomena (coma, dust tail and plasma tail) than on a more quantitative understanding of the underlying permanent features (structure and chemistry of the nucleus).

However, the last decade has brought a harvest of quantitative data that can be used as clues for a more fundamental approach about the chemical nature of the nucleus, yielding new insights on its origin and history.

If all the recent observations had been properly coordinated to observe the same comets at the proper dates, we would already be several more steps ahead in this direction.

This paper is therefore an effort to promote a better understanding of the fundamental problems, in order to encourage a better coordination, so that the proper quantitative data be collected at the proper times.

2. The Two Fractions of the Cometary Nucleus

Fundamental chemical data that are clearly connected to the origin of comets, can be derived from the fact that the cometary stuff is a mixture of two constituents with very different properties: a volatile fraction, apparently a mixture of molecules from H,C,N,O,S atoms, and a refractory fraction apparently made up from fine grains of dust.

The refractory fraction must not be very different from chondritic material, if we believe three circumstantial lines of evidence:

a) the reflexion spectrum of the dust in the infrared shows the signature of silicates; this implies that silicates are a major component of the dust grains, although some impurities (probably carbon or carbynes) seem to diminish their dielectric properties (Ney 1974)

b) the vaporization of this dust in a sun-grazing comet (Ikeya-Seki) produced emission lines due to neutral atoms of metals, namely Ti, V, Cr, Nm, Fe, Co, Ni, Cu. Their abundances were essentially solar (= chondritic); the few exceptions all come from atoms that are known to make very refractory condensates. This is consistent with a fractional vaporization of the refractory grains by solar radiation. (Arpigny 1978).

c) interplanetary dust, presumably of cometary origin, has properties closely similar to C1 and C2 carbonaceous chondrites (Brownlee *et al*. 1977).

The volatile fraction's major constituent is apparently water snow, with minor constituents probably like HCN, CH_3CN, CO and CO_2 (Delsemme 1977, Delsemme and Rud 1977); but many other minor constituents are still missing.

All of the atomic, ionic and molecular fragments that have been observed in the cometary heads and in the ion tails (Table 1) clearly come from the vaporization of the volatile fraction; but because of the chain of several unobserved processes, including ion-molecular reactions in a small collision zone near the nucleus, their "parent" molecules cannot be reconstructed unambiguously.

The atoms, ions and molecules observed in the cometary head are not a permanent atmosphere surrounding the nucleus, but are rather a continuously renewed exosphere that is steadily escaping, simultaneously with the dust that it drags away towards the interplanetary space.

Table 1

Observed in Cometary Spectra

Organic:	C	C_2	C_3	CH	CN	CO	CS	HCN	CH_3CN	
Inorganic:	H	NH	NH_2	O	OH	H_2O	S			
Metals:	Na	K	Ca	V	Mn	Fe	Co	Ni	Cu	
Ions:	C^+	CO^+	CO_2^+	CH^+	H_2O^+		OH^+	Ca^+	N_2^+	CN^+
Dust:	Silicates (infrared reflection bands)									

In order to know what is escaping from the nucleus, it is therefore essential to measure simultaneously the production rates of dust and of all the molecules present in the coma. Several measurements of this type, during several days or weeks, can tell whether a steady state has been reached. If it has, the results can be deemed to be represenative of the outer layers of the nucleus.

This is of course an almost impossible task, in particular because of the major difficulties of establishing consistent molecular production rates for the significant constituents. Let us list just a few of the difficulties.

First, a direct comparison of the contents of a cometary atmosphere may be misleading. For instance, for comet Bennett, when the average lifetime of H in the Lyman alpha halo was 13 days, that of OH was 2 days only. The analysis of the two-component velocity of the H atoms leaves little doubt that the bulk of H and OH comes from water vapor; however, if we want to compare the stoechiometry of the two production rates at a certain date (for instance to establish if there is an extra amount of OH, coming from a minor constituent), we must look at the atmosphere of OH two days later, but at that of H thirteen days later -- and pray for a steady state covering at least thirteen days.

Second, from ground-based observatories, the production rate of a given molecule can be reached only through the observation of the monochromatic flux of light reaching the earth (often emitted by one of its fragments only); this requires the use of two different parameters, namely:

1. the number of photons scattered per second per molecule (the so-called "emission rate factor" g).

2. the exponential lifetime of the molecule τ against all decay processes.

The product $g\tau$ establishes the number of fluorescence cycles, that is the number of photons scattered per molecule produced.

Now, the emission rate g depends on the oscillator strength f of the transition involved, and on the flux of solar light reaching the molecule; both parameters are moderately well known for some molecules. But the effective lifetime τ is the result of several competitive processes of photoionization and of photodissociation that are often poorly known not only because of the uncertainties of the cross-section involved, but also because of the poor data from the extreme ultra-violet of the sun.

Actual molecular lifetimes can and should certainly be established more often thanks to the exponential scale lengths deduced from the brightness profiles of the cometary head in the light of a given molecule. As expansion velocities are moderately well known in some important cases, the scale length can then be translated into an effective lifetime against all decay processes.

3. Measuring Elementary Abundances

From what has been said so far, it is clear that we cannot yet write a complete balance sheet including all the observed radicals and molecules, and explaining their origin in quantitative terms.

A less ambitious task seems however to have become possible, because the resonance lines of the elements H,C,N,O,S have become accessible at least in principle in the vacuum ultraviolet through rockets and orbiting telescopes. Only the resonance line of N has not yet been observed, assumedly for mere technical reasons (it is weak and near Lyman α). Since most if not all the volatile molecules seem to be different combinations of the H,C,N,O,S atoms and of these atoms only, a measure of their relative abundances would already produce such a balance sheet at the elemental level.

The rationale comes from the fact that all molecules are photo-dissociated into their constituent atoms sooner or later, but much sooner than the atoms themselves become ionized. The proper handling of the photometric profiles of these resonance lines yields therefore the total atomic production rates after all molecules have been dissociated.

Now, to measure the actual elemental abundances in respect to the cometary dust, the dust-to-gas ratio must be established, through a Finson-Probstein analysis of the dust tail isophotes. This implies either the existence of a steady state during all usable observations, or the knowledge of the variations when production rates are unsteady.

4. Steady State and Outbursts

The question of the steady state brings the question of the vaporization mechanism of the nucleus, and the well-known occurrence of outbursts. Recent models (Mendis and Brin 1977, Brin and Mendis 1979) have addressed rather convincingly the problem of the possible existence, in the cometary evolution and decay by the solar radiation, of a more or less outgassed "mantle" of dust rather depleted of volatiles, covering more pristine layers of volatile material.

The models show the existence of three possibilities: either the mantle grows thick enough to inhibit the vaporization of the nucleus, yielding an apparently "dead" comet suggestive of the Apollo -or Amor-type asteroids, or the mantle does not appear ever, leaving a "bald" pristine nucleus with a steady-state sublimation in which the dust is dragged away exactly in proportion to the vaporizing gases; the third possibility shows a dust cover that grows first but is blown away from the nucleus by a violent outburst of activity. This happens before perihelion, at the time when production rates grow very much so that larger grains can be blown away.

Outbursts have often been observed; for comet Arend Roland, one of them that happened six days before perihelion coincided with a rapid change of the dust-to-gas mass ratio, from about 6.2 three days before outburst (when more outgassed dust was dragged away) down to 1.4 three days after outburst. This suggests that more volatile material had been reached and therefore, that the dust mantle was being blown away almost completely.

During the following days, the dust-to-gas ratio stabilized asymptotically to lower and lower values, near 1.0 to 0.8 nine days after perihelion (Delsemme 1977, deduced from Finson and Probstein's data, 1968).

Since this spectacular decrease in the dust-to-gas ratio is predicted by the model, at least in a semi-quantitative fashion, we conclude that the phenomenon is correctly interpreted and that the observations can effectively be used to settle the matter of the dust-to-gas ratio in the pristine layers of a "new" comet like Comet Arend-Roland.

The only other Finson-Probstein's analysis that we used to establish another dust-to-gas ratio, is that of Comet Bennett (Sekanina and Miller 1973). It is discussed in the next section.

The third and last Finson-Probstein's analysis ever attempted, was on sungrazing comet Seki-Lines (Jambor 1973); assumedly because of the extreme conditions and very large grain sizes involved, it could not be used for establishing a dust-to-gas ratio.

A discussion of the accuracy and the significance of the Finson-Probstein's analysis is now deemed necessary.

5. Discussion of the Finson-Probstein's Analysis

Let us first consider the idealized case in which the dust leaves the cometary nucleus with no initial velocity. Then (Fig. 1) the isophotes of the dust tail represent a two-dimensional resolution of two parameters, that are therefore completely separated without ambiguity:

a) the particle size distribution varies along each of the synchones (traced by all particles emitted the same day by the nucleus)

b) the production rate of dust (of a given state) varies along one of the syndynes (traced by all particles of a given size) as a function of its emission time. This is a beautifully simple problem of kinematics that yields a unique and accurate solution.

In practice however, a third parameter must be introduced: the initial (isotropic) velocity of the grain substitutes a sphere with radius growing with time to each of the points we have previously described. The deconvolution remains straightforward, because the third parameter produces a very large widening of the tail's trailing edge only, that clearly separates the initial velocity (specially of the smaller grains) from the other two parameters. This initial velocity is due to the hydrodynamics of the gas dragging the dust out from the nucleus, and specifies therefore the dust-to-gas mass ratio $\mathcal{M}$.

Now, the dust-to-gas mass ratio is derived by adjusting the curve of the grains' initial velocity (function of their size) derived observationally from the growing fuzziness of the tail's trailing edge, to the family of curves (Fig. 2) predicted from the drag hydrodynamics. It looks more difficult to do from the description than it really is. However, it is clear from Fig. 2 that the inaccuracy grows considerably when the grains' velocity v_1 is smaller.

The accuracy on comet Arend-Roland was helped by the fact that it was observed three weeks after perihelion, and that the perihelion distance was as short as 0.316 AU. The grains ejected with the largest velocities near perihelion were still visible in the critical part of the tail, therefore the accuracy was remarkable. My estimate is that the fitting gives $\mathcal{M}$ = 1.7 ± 20 percent (from 1.4 to 2.0) assuming that the other parameters are accurately known.

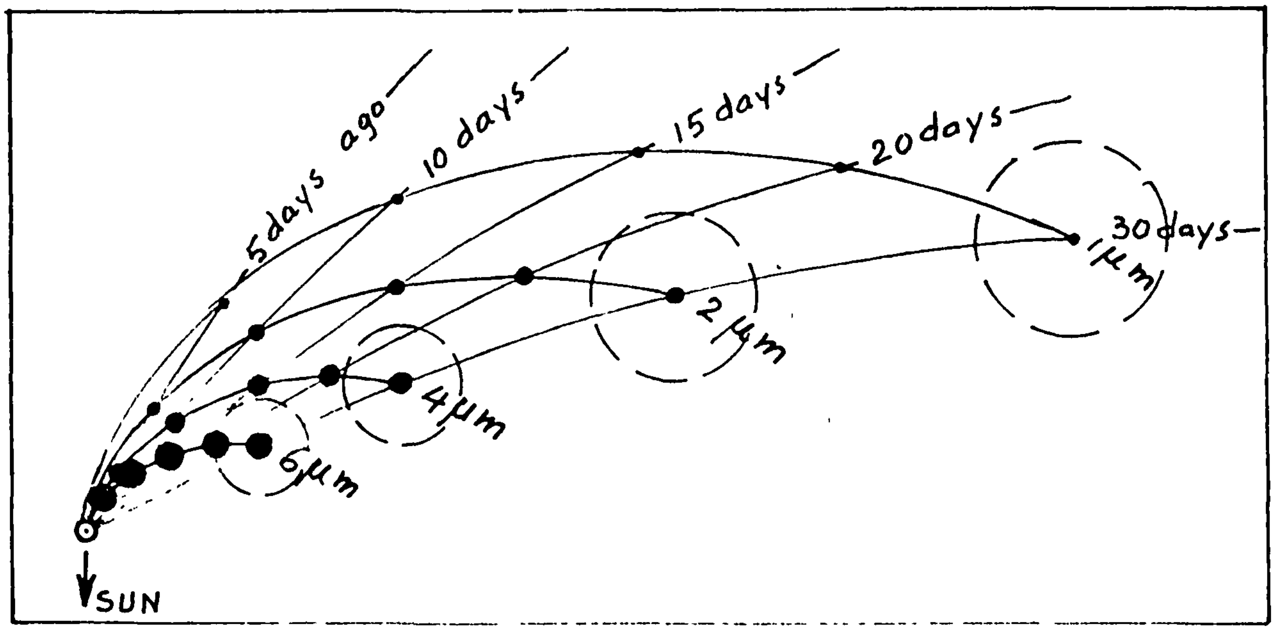

Figure 1. Dust distribution in cometary tail. Grain trajectories for different sizes are indicated by black dots of different diameters. Emission dates from the nucleus are indicated in days. Dashed circles represent the fuzziness of the trailing edge of the tail, coming from the isotropic initial velocity v_i of the grains.

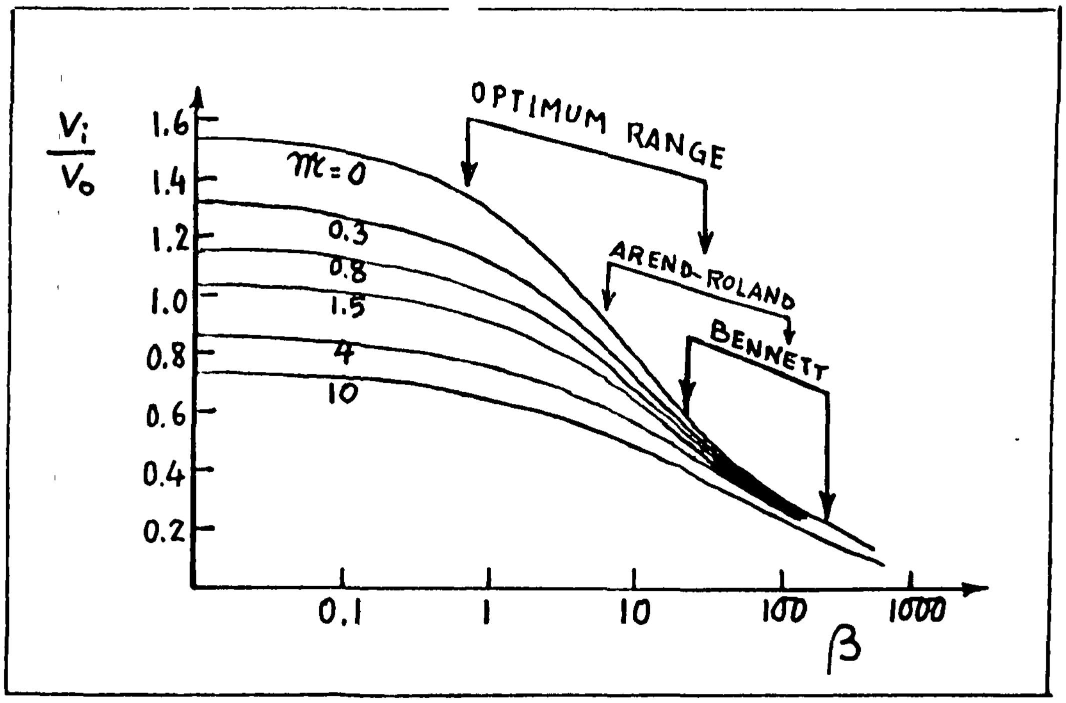

Figure 2. This diagram is used to compute the dust-to-gas ratio by adjusting the curve of the observed initial velocities of the dust grains v_i as a function of their sizes. Parameter β is a similarity parameter proportional to the dust size.

As far as comet Bennett is concerned, it was observed slightly *before* perihelion; the grains that were critical for the assessment of the initial velocities were ejected at much smaller velocities because the comet was then at a much larger heliocentric distance (0.7 AU to 1.0 AU) and therefore the family of curves of Fig. 3 does not discriminate easily the dust-to-gas ratio. My estimate is that $\mathcal{M} = 0.5\ (+1.0, -0.5)$. Another consequence: even if we assume that the major constituent's molecular weight is known ($m = 18$ for water), the radius of the nucleus cannot be assessed better than within a factor of 2 at most. The major conclusion is that due to unfortunate observational circumstances, this dust-to-gas ratio cannot be used for the purpose of deducing elemental abundances in the nucleus of comet Bennett. We should not be too sorry for it, because after all, comet Bennett was *not* a new comet; therefore even significant results might have been difficult to assess in terms of cometary origin and evolution.

5. The Choice of the Proper Geometric Albedo $A\phi(\alpha)$

The Bond Albedo A is proportional to the observed radiation scattered in the visible, whereas (1-A) represents its absorbed fraction, which at steady state is proportional to the radiation reradiated back to space in the infrared. Infrared measurements (O'Dell 1971) for three different comets show a weighted average of $A = 0.30 \pm 0.15$, much larger than early expectations. Ney (1974) also finds for four comets that most observations show a geometric albedo of 0.18, with variations from 0.10 to 0.4 partially due, assumedly, to the variation of the phase angle. Ney and Merrill (1976) have derived the scattering function of comet West from 34° to 150° phase angle by the same infrared method. They confirm that the Bond albedo is very large, 0.40 ± 0.10; but reflectivity is strongly anisotropic. The wrong assumption that scattering was isotropic has led to the smaller values published earlier in the literature. The present discussion concludes that, for a geometric albedo in the general range of a phase angle $\alpha = 90^\circ$, the value $A\phi(\alpha) = 0.20 \pm 0.05$ should be adopted. The production rate of dust grows linearly with the reciprocal of the geometric albedo; however, the production rate of gas is also affected in the same direction but more slowly. The dust-to-gas ratio, computed for what is believed to be an asymptotic value for the "pristine" ratio of Arend-Roland, is given as a function of the geometric albedo in Table 2.

Table 2

Comet Arend-Roland

"Pristine" dust-to-gas ratio after outburst, as a function of the albedo.

Geometric Albedo $A\phi(\alpha)$	"Pristine" dust-to-gas mass ratio
0.15	0.78
0.20	0.64
0.25	0.53

6. A Heuristic Model of the Elemental Abundances of Comet Arend-Roland

The variation of the efficiency factor for radiation pressure, which falls off very rapidly for particle radii of 0.2 μm or smaller, has not been taken into account by the Finson-Probstein's analysis, but it concerns only the extreme end of the particle distribution (Hanner 1980). Most of the particle distributions introduce a cutoff for small particles, which may be a partial artifact of their smaller scattering power for visible light when they are much smaller than the wavelength of the scattered light. To take this small missing mass into account I would arbitrarily add 10 percent to the average dust-to-gas ratio and will therefore use 0.70 for the dust-to-gas ratio. Finally, I will assume that the amount of carbon and sulfur compounds not volatile enough to vaporize from the silicate matrix are the same as in C I chondrites (Mason 1971, 1979). For the volatile fraction, I will use the revised production rates of the major constituents (Delsemme 1971 Table IV) based on the average ratios $H/O = 1.8$, $C/O = 0.31$ and $N/O = 0.08$ from atomic lines and molecular bands in comets Bennett, Kohoutek and West. A cosmic ratio has been assumed for S/O from a guesstimate based on the ultraviolet data of comets West and Seargent (Feldman and Brune 1976, Jackson et al. 1979). Table 3 shows the results of this exercise, compared with Cameron's (1980) recently revised cosmic abundances, which now incorporate Ross and Aller's (1976) data for solar CNO, that we had already used previously.

7. Discussion of Heuristic Model

It is remarkable that, based on a dust-to-gas ratio of 0.70, cometary oxygen reaches exactly a cosmic abundance. The sulfur value is not very significant, but there is no doubt that sulfur abundance is also very high, whereas Hydrogen is depleted by almost exactly a factor of 1000.

The most interesting result seems however to be the depletion of Carbon to 42 percent cosmic. A permissible decrease of the dust-to-gas ratio could easily bring enough gas to accommodate more carbon compounds, but then it would drastically change the total amount of either H, or O or both. For instance, an undetected methane fraction could indeed explain the missing carbon, but it would exactly double the total hydrogen content; this is completely ruled out by the observational results, mainly from the Lyman α halo, but also from the resonance line of carbon. In the same way, a large enough CO_2 excess would not only drastically change the amount of oxygen detected in the ^1D state (forbidden red line) but would produce an amount of oxygen much larger than cosmic abundances, that could only be justified by a large cosmic depletion of metals in the dust, contradicting Arpigny's (1978) results, as well as all arguments developed previously for a chondritic dust. The only other possible place where the missing carbon could be hidden is in the dust, but this would imply that dust would contain 30 percent carbon (as opposed to 6 percent in C I chondrites). Perhaps this extremely large amount cannot be totally ruled out, but it seems difficult to reconcile it with Ney's (1974) infrared observations of a strong silicate signature. A better alternate possibility would be that a very volatile fraction containing carbon is already missing from the present model. Since oxygen reaches its cosmic abundance, it would not be CO, whereas it could easily be CH_4. This would imply that a very volatile fraction of the solar nebula, namely methane, has never condensed or has already been lost earlier from our model of a "new" comet. It would be of a great interest to verify whether this methane could still be present in comets that show a great activity at large heliocentric distances. In spite of the apparent strength of the previous arguments, this discussion must be accepted with a grain of salt because this heuristic model is a composite model based on fragmentary information coming from five different comets. Arend-Roland is rightly used for the gas-to-dust ratio of a "new" comet, but the mean elemental abundance ratios for H,C,N,O,S have been assumed to be the same for the five comets, - and this is hardly an acceptable assumption in the present state of our ignorance. The large carbon depletion remains however a puzzling feature that no fiddling of the uncertain data can make easily disappear.

Table 3

Heuristic Model for a "New" Comet (1)

Elemental abundances in numbers of atoms, Silicon= 1,000

Number of Elements	Cosmic abund. (Cameron 1980)	Cometary Abundances Dust	Gas	Total	(Delsemme 1980) Percent Cosmic
H	26,600,000	2,000	24,000	26,100	0.1
C	11,700	700	4,200	4,900	42
N	2,310	50	1,100	1,150	50
O	18,400	5,000	13,400	18,400	100
S	500	350	150	500	100
Mg	1,060	1,060	-	1,060	100
Si	1,000	1,000	-	1,000	100
Fe	900	900	-	900	100
Ni+Cr	60	60	-	60	100
Nominal Dust-to-gas ratio:					

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(1) Dust-to-gas ratio from "new" comet Arend-Roland; average ratios of H/O, N/O, C/O and S/O from atomic lines and molecular bands in comets Bennett, Kohoutek, West and Seargent; C I chondrite assumption for dust.

8. Recommendations for Future Observations

The present data completely confirms Delsemme's (1977) earlier findings that comets are much more "primitive" (that is, less differentiated) than the most primitive CI carbonaceous chondrites. So far, their only unquestionable depletion is that of their hydrogen, because it is depressed by a factor of 1000. The other observed depletions, namely those of C and N, must be reconfirmed by better observations. The cometary abundances of C,N,O,S are telltales of those processes that have shaped the chemistry of the cometary nucleus and have therefore a great significance in understanding its origin and evolution.

Measuring quantitative production rates, from the vacuum ultraviolet resonance lines of the elements H,C,N,O,S, supplemented by the balance sheet of the major radicals, ions and molecules, is the basic process that is now available. However, their abundance ratios do not tell the whole story; to be significant, they must be connected to the abundance of the refractory elements. These elements, mainly, silicon, magnesium and iron cannot be elsewhere than in those silicates found in the cometary dust. As I have proposed earlier, the only route available from ground-based observations to establish elemental abunances normalized to silicon is the dust-to-gas ratio of comets, available through a Finson-Probstein's analysis of the dust isophotes. The best conditions to use such a technique are found in dust-tail photographs four to ten weeks *after* perihelion, (if the geometry is right). Comets with a perihelion distance between 0.3 and 0.1 AU are the best candidates, because their gas drag accelerates their dust grains to velocities larger than 0.5 km/sec, making the reduction of the observations more accurate. It is essential to synchronize tail photographs with observations in the vacuum ultraviolet.

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