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Hypersonic Meteoroid Entry Physics

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Chapter 4

The flux of meteoroids over time: meteor emission spectroscopy and the delivery of volatiles and chondritic materials to Earth

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Every night the apparently immutable night sky can be observed, but suddenly a shooting star can cross our field of view. Perhaps, in that moment, Mother Nature reminds us that our existence is linked to the continuous influx of extraterrestrial materials. The truth is that even when it is not noticeable, except for the appearance of meteors, the current flux of interplanetary matter to Earth is about 100 000 Tm yr^{-1} [1]. Obviously the flux at the top of the atmosphere must be several orders of magnitude higher, providing a continuous rain of elements to the upper atmosphere and, in the process, generating interesting chemistry between highly reactive phases (see for example the review of Plane *et al* [2] and references therein). It causes the formation of layers of metal atoms and ions in the mesosphere and lower thermosphere leading to the formation noctilucent clouds and other chemical interactions with stratospheric aerosols [3]. As well as the ablated materials, meteoroid fragments and ablation condensates reach the ground as micrometeorites and remain in the substrate allowing its flux to be quantified [1]. The mass influx was quantified and compiled in a histogram that reveals the bimodal contribution in the flux distribution (see figure 4.1): one peak corresponds to particles of about 100 μm and larger, producing visual meteors, while the other is associated with asteroids and comets with sizes of tens to one hundred meters that produce meteorite falls or even excavate craters [4].

Most of this interplanetary material coming to the Earth originates from undifferentiated bodies, small asteroids and comets that produce porous aggregates containing primordial minerals. These materials are formed by minerals condensing from the gas surrounding the proto-Sun about 4.6 Ga ago and accreted into fragile aggregates that were thermally processed to form planetesimals [5]. Small amounts were incorporated into the protoplanetary disk from nearby stars as we know by

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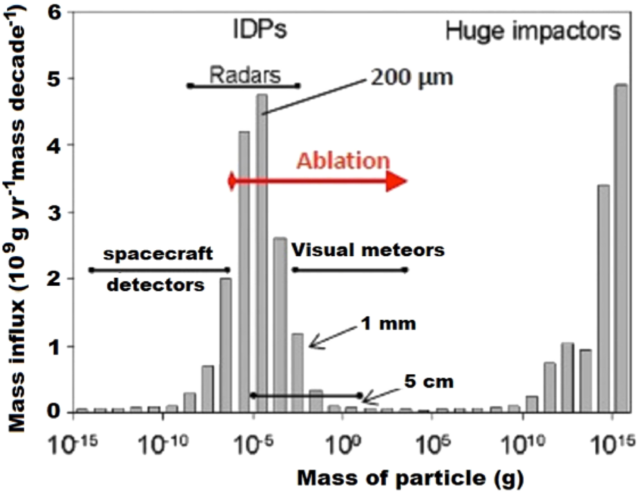

Figure 4.1. Mass influx of interplanetary materials [4].

peculiar isotopic signatures [6–8]. The unusual chemical signatures of tiny presolar grains provide clues on the peculiar formation environment of our star, and it is clear evidence that our Sun formed in a stellar association [9]. A significant fraction of these asteroidal bodies survived the heavy accretion of planetary bodies and remained undifferentiated thus producing meteorites called chondrites, and more fragile tiny aggregates that have been collected by dedicated planes in the stratosphere, called interplanetary dust particles (IDPs) [1]. The components of chondrites and IDPs represent the primordial starting materials from which the undifferentiated bodies formed. To complete the flux of extraterrestrial materials to Earth there is a much smaller contribution of meteoroids that are associated with differentiated bodies. When they survive atmospheric passage, they produce different types of differentiated meteorites that are called achondrites. Some common sources of achondritic meteorites are the Moon, Mars or Vesta (see e.g. [10]), but some small asteroids might be just fragments of large planetary bodies [11] and also be a possible source.

Undifferentiated bodies are composed of unequilibrated components that formed part of a primordial planetary disk from which the small bodies were accreted. Consequently, any view of solar system formation, as well as considering the Sun and planets, should include the many small bodies that populate different regions and have a key relevance in the chemical evolution of planetary bodies [12]. The minor bodies are smaller than the planets and are subjected to continuous erosion and decay by cosmic irradiation and impacts with other objects (a process known as gardening). As a consequence of these processes the space between the planets becomes populated by billions of particles that follow heliocentric orbits, and are usually associated with asteroids and comets. This system is known as the Zodiacal cloud and is in constant replenishment because millimeter-sized meteoroids tend to fall into the Sun in time-scales of tens of millions of years (Ma) as a consequence of the loss of kinetic energy caused by mutual collisions and non-gravitational effects [13, 14]. Obviously, the mere existence of the Zodiacal cloud requires a continuous replenishment of the interplanetary space by small fragments of other solar system bodies [15, 16]. These particles orbiting the Sun are called meteoroids and were defined by the International Astronomical Union (IAU) as a particle larger than a micron and smaller than one meter in diameter that follows a heliocentric orbit in our solar system.

Some meteoroids originated through the natural collisions of asteroids, while outgassing dominates the release of cometary meteoroids onto heliocentric orbits. In repeated approaches to the Sun a comet sublimates abruptly and releases tons of meteoroids due to the weak gravitational field and the gas outgassing. In fact, the gas pressure from the cometary surface makes the process of injection of micrometric to millimetric particles into heliocentric orbits very efficient [15]. So, it is not surprising that comets are important in producing meteoroids. These will be fragile undifferentiated objects formed in the outer solar system and composed of a weak mixture of ices, organic materials and micrometric mineral grains with solar composition [17]. These volatile-rich objects suffer significant ice sublimation when approaching the Sun. Then, volatile-rich regions produce jets of gas that drive out tons of meteoroids with diameters from decimeters to tens of microns [17]. These released particles are gravitationally distributed around the Sun, forming meteoroid streams that produce meteor showers when the Earth crosses them. Studying meteor showers using different instrumentation gives insight into the physico-chemical properties of their parent bodies. These particles are often aggregates whose constitutive mineral grains exhibit typical diameters of a few microns that are considered to be dust, so when they dynamically and collisionally evolve they become part of the Zodiacal dust [18]. An additional process releasing chondritic meteoroids is the catastrophic disruption of rubble-piles by tidal forces in close approaches to planets [19].

Although interplanetary space is populated by meteoroids originating in the decay of asteroids and comets, planetary bodies also contribute. Achondrites are meteorites coming from differentiated bodies, usually larger than about 1000 km in diameter. Lunar or Martian achondrites are also reaching the Earth, but they are not so abundant because they can only escape the gravitational field through a grazing impact [20].

To summarize, most meteoroids coming from asteroids were released by impacts, while outgassing is the main force driving cometary meteoroids to heliocentric orbits [15]. The volatile nature and small gravitational field of comets makes them dominant contributors to the so-called Zodiacal cloud. These bodies are fragile objects composed of a mixture of ices, organic materials and mineral grains with an average tensile strength close to 10 Pa [21]. The nature of weakly bounded aggregates, being a mixture of crystalline silicates, organics and dirty ices, was also revealed by the Stardust (NASA) and Rosetta (ESA) space missions [17, 22]. These objects suffer significant ice sublimation when approaching the Sun, so volatile-rich regions produce jets of gas that drive out tons of meteoroids with diameters in the typical range of centimeters to tens of microns [16]. These meteoroids form meteoroid streams that remain stable in their orbits for thousands of years [15]. Despite their large numbers, most of these particles do not undergo atmospheric entry and indirect systems are needed to understand their origin and composition.

Meteoroids can have very diverse origins, as meteor studies reveal. By obtaining their heliocentric orbits from multiple-station meteor monitoring plus meteor spectra chemical information, it is possible to better understand the delivery mechanisms and nature of exogenous material to Earth. This paper will summarize the role of emission spectroscopy of meteors and fireballs in gaining insight into the bulk elemental chemistry of meteoroids. The progress made during the last decades in reference to the role of chondritic flux in chemical evolution of the biosphere and origin of life will be reviewed. Meteor spectroscopy can be regarded as an added-value technique in order to understand the astrobiological significance and relevance of the delivery of volatiles to terrestrial planets from the continuous meteoroid flux.

4.1 The meteor phenomenon and the origin of Earth's volatiles

It follows from the formation processes described above that meteoroids are particles that moved around the Sun with typical velocities of a few tens of km s^{-1}. When they collide with a planetary atmosphere they are decelerated and ablate producing a luminous phenomenon called a meteor. The relative geocentric velocity to the Earth (hereafter V_g), the velocity with which the meteoroid enters the top of the atmosphere (before suffering significant deceleration), lies in the range $11 < V_g < 72$ km s^{-1}. When these particles penetrate into the atmosphere at these supersonic velocities the meteoroids suffer increasing collisions with atmospheric atoms or molecules and their surfaces are quickly heated to become incandescent. Then, a physical process called ablation takes place which produces the vaporization, fragmentation and sputtering of the meteoroid, forming minerals. From the ground the observed meteor phenomenon consists of three differentiated parts: the *head* or the region around the meteoroid in which the interaction is taking place, the *wake* left just behind and the *train* or meteor column. The meteor head is the part where the more energetic collisions take place and mostly contributes to light production. It is also the main source of emission lines as the meteoroid-forming minerals are progressively vaporized and the elements are released, suffering excitation and/or ionization as a consequence of the exposure of the released particles to the collisions, producing a cloud of ions and free electrons which form a significant part of the ablated material. The electrons are transmitting energy, and the ions emit light through well-defined emission lines, while the surviving dust contributes to a continuum emission. In general, emission lines can be reproduced assuming chemical equilibrium, while the emission lines coming from the *meteor train* are out of equilibrium. This is explained in further detail in the next section.

Meteoroids penetrating the Earth's atmosphere are experiencing collisions with air components, and are heated progressively. As the meteoroid minerals are heterogeneous and exhibit different vaporization temperatures, a step-by-step ablation process takes place. First, the hydrous (if any) and organic phases are ablated, second, the silicates and metals, and finally the refractory minerals. As a consequence, the moderately volatile elements, such as Na and K, are released at greater heights than the refractory ones. As a consequence the so-called differential ablation process takes place (figure 4.2).

A comparison between terrestrial rocks and chondrites suggests that enstatite and ordinary chondrites were the dominant building blocks of the early Earth. Most of these chondrites were formed in reduced conditions, so the origin of terrestrial volatiles is debated. The existence of a N-rich terrestrial atmosphere from direct outgassing seems likely, and it has been hypothesized that some of this N arrived as nitrides. Despite this, during the late accretion period large impacts eroded significant amounts of the Earth's volatile inventory. In this sense, a depletion in N and Xe has been noted with respect to other volatiles that are in chondritic proportions. Such depletion could be explained as a consequence of large impacts producing a thermal escape and affecting the atmospheric components. In fact, a giant impact was probably responsible for the origin of the Moon and eroded the early atmosphere of the Earth [23–24]. In consequence, the early atmosphere of our planet could have evolved as consequence of high-energetic impacts [25]. The last of those impacts probably had a special role in the final evolution of the entire Earth–Moon system. In fact, it has been recently demonstrated that the similarity in composition between the Earth and Moon could be a natural consequence of a projectile exhibiting similar composition to Earth in a late giant impact [26]. Recent

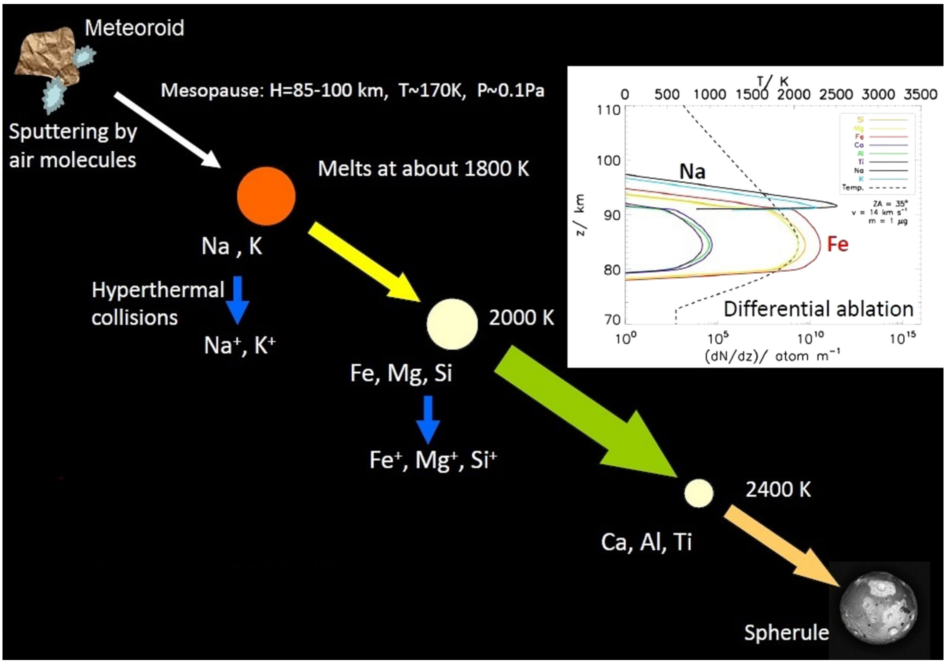

Figure 4.2. This schematic represents meteoroid ablation in a planetary atmosphere. Differential ablation is a direct consequence of the selective ablation at different heights of meteoroid minerals having different vaporization temperatures [3].

evidence is also constraining the composition of the projectile, called Theia, that could be preserved in the Moon [27].

4.2 Meteor spectroscopy: an added value to Meteoritica

Meteor spectroscopy is a technique to delve into the physical processes taking place during meteoroid ablation, but it is also a pathway to study the delivery processes of exogenous materials to Earth. From the very beginning of this field early in the 20th century, photographic plates were used to capture emission spectra that allowed the identification of emission lines from rock-forming elements (see e.g. [28, 29]). Emission spectroscopy was developed to understand the components of cometary meteoroids that did not survive atmospheric interaction. These fragile materials represent a significant fraction of the delivery of primordial materials coming from undifferentiated bodies [1]. Meteoroids of cometary origin are typically centimeter- or millimeter-sized aggregates that are fragile in nature, and are weakly bonded aggregates formed by fine micron-sized dust, organics and volatiles [30]. In consequence, they fragment and do not survive atmospheric interaction (see e.g. [31, 32]).

Obviously, there is a significant degree of difficulty in capturing and reducing the recorded meteor and fireball spectra. The light emitted during the unpredictable entry of a meteoroid must be decomposed with the right observational geometry by a prism or diffraction grating set up in front of imaging systems. In such a way the luminous column is separated in emission lines for each elemental transition. Photographic systems were the only way to obtain reliable spectral information during most of the 20th century, but new CCD and video imaging techniques now provide additional clues on the meteor phenomenon. The emission lines of the main rock-forming elements were identified by pioneers [33], but they did not obtain a clear model of the light generation process (see e.g. [29]). A tentative model was proposed by Ceplecha [34] who developed a complex cylindrical model for the radiating column, assuming local thermal equilibrium. In that approach, the theoretical curve of growth was built up, also describing the self-absorption of the lines and obtaining some physical parameters (see e.g. [35]). Unfortunately, the resulting computed number of Fe atoms in the radiating volume and the involved mass determined from the meteor luminous efficiency were not always accurate. A simpler model was proposed by Borovicka [36] and tested on the excellent Cechtice fireball photographic spectrum. With such an extraordinary emission spectrum, also obtained during routine sky monitoring from the Ondrejov Observatory, Borovicka [36] obtained for the first time a computed meteor synthetic spectrum. It adjusted exceptionally well to the observed spectrum, even though the physical approach was very simple: thermal equilibrium and constant temperature and density in the whole volume. Meteor spectra consist of two different components: the main spectrum characterized by a temperature of about 4500 K and a second spectrum that usually reaches 10 000 K [37, 38]. The second component originates in the front wave where high-energy collisions can produce the excitation of atoms increasing the ionization of the meteoroid components. It is important to remark that the high-temperature component produced in the shock wave is not detected for meteoroids penetrating into the atmosphere at velocities below $V < 35$ km s^{-1} [35].

Table 4.1. The main atoms and ions found in meteor spectra. The wavelength, multiplet number and binding energy is given for each line. Adapted from [40]. Spectral components: *p*—principal, *s*—secondary, *a*—atmospheric line.

Atom or ion	λ (Å)	Multiplet	E_2 (eV)	Relative intensity		Reference
H I	6563	1	12.09	3	*s*	[33, 41, 42]
Li I	6708	1	1.85	2	*p*	[43, 44]
N I	8680	1	11.76	4	*s, a*	[33, 41]
	6465	21	13.66	1	*s, a*	[33, 42, 45]
	4110	10	13.70	1	*s, a*	[33, 42, 45]
N II	5680	3	20.66	1	*a*	[33, 44]
O I	7772	1	10.74	5	*s, a*	[33, 41]
	6158	10	12.75	3	*s, a*	[33, 42, 45]
Na I	5890	1	2.11	5	*p*	[33, 37, 42]
Mg I	5184	2	5.11	5	*p*	[33, 37, 42]
	3838	3	5.94	5	*p*	[33, 37, 42]
Mg II	4481	4	11.63	4	*s*	[33, 42, 46]
Al I	3962	1	3.14	3	*p*	[37, 42, 44]
Si I	3906	3	5.08	3	*p*	[33, 37]
Si II	6347	2	10.07	3	*s*	[33, 37, 42]
	4131	3	12.83	2	*s*	[33]
Ca I	4227	2	2.93	4	*p*	[33, 37, 42]
	6162	3	3.91	3	*p*	[33, 37, 42]
Ca II	3934	1	3.15	5	*s, p*	[33, 37, 42]
	8542	2	3.15	4	*s, p*	[33, 41]
Ti I	4982	38	3.33	2	*p*	[37, 42, 44]
Ti II	3349	1	3.74	3	*s, p*	[46, 47]
Cr I	4254	1	2.91	4	*p*	[33, 37, 42]
	5208	7	3.32	3	*p*	[33, 37, 42]
	3593	4	3.44	3	*p*	[33, 47]
Cr II	3125	5	6.42	2	*s*	[47]
Mn I	4031	2	3.08	3	*p*	[33, 37, 42]
Fe I	3860	4	3.21	5	*p*	[33, 37, 42]
	4384	41	4.31	4	*p*	[33, 37, 42]
	5270	15	3.21	4	*p*	[33, 37, 42]
Fe II	5018	42	5.36	2	*s*	[33, 42]
	3228	6	5.51	2	*s*	[47]
Co I	4813	158	5.79	1	*p*	[42]
	4121	28	3.93	1	*p*	[37]
	3506	21	4.05	1	*p*	[48]
Ni I	5477	59	4.09	2	*p*	[37, 42]
	3462	17	3.60	2	*p*	[47]
Si II	4078	1	3.04	2	*s, p*	[33]

Consequently, the most important contribution of meteor spectroscopy is its ability to extract very relevant chemical information from the relative intensity of the emission lines contributing to each meteor spectrum (see table 4.1) [39]. Depending on the disperser system the spectral resolution will be variable, but a synthetic spectrum can always be obtained and compared with the recorded spectrum. This is made by adding the contribution of the involved chemical element lines. The main emission lines contributing to meteor spectra are compiled in table 4.1 [39, 40].

The spectral profile can be fitted to a physical model that allows the temperature and elemental abundances of their rock-forming to be computed, having taken into account the intensity of the lines [36]. The model assumes thermal equilibrium in the meteor head, and considers as a simplification that the radiating volume is a prism where the physical parameters and the chemical abundances can be determined. Then, the chemical abundances of incoming meteoroids can be inferred from the sequential recording of the variable line intensity along the luminous trajectory of a meteor or fireball [35]. That paper for the first time applied a systematic study to obtain averaged chemical abundances along the meteor columns that provided chemical clues on the chondritic composition of asteroidal and cometary meteoroids [18]. While most elements have chondritic ratios that were later proved to be consistent with particular mineral mixtures that could form chondritic aggregates [49], it was also discovered that meteoroids of cometary origin were exhibiting a peculiar feature: being overabundant in Na [21]. Consequently, emission meteor spectroscopy first pointed towards the overabundance of Na recently confirmed from Rosetta studies of comet 67P/Churyumov–Gerasimenko dust [50].

Many photographic spectra became available from the Ondrejov Observatory at the end of the 20th century, but most of them remained unstudied. Trigo-Rodríguez [39] selected some and these are shown in table 4.2. He also presented an innovative idea to infer the average elementary abundances of the incoming particles from the sequential study of the meteor spectrum. The basic idea is simple, most relative abundances of the elements present in the meteor column are many orders of magnitude over that expected in the atmosphere at the meteor ablation height (see e.g. [18]). Consequently, it is possible to estimate the chemical abundances relative to one reference element (such as Fe, which has many omnipresent emission lines) at different heights, as shown in figure 4.3 [18, 39]. Then, it is statistically possible to infer an averaged composition for the particles as inferred from the independent study of sequential ablation patterns made by Rietmeijer [49].

The intensity of emission lines recorded on the Ondrejov photographic plates was accurately measured by using a microdensitometer, an obsolete instrument to quantify the density of signal in photographic plates that is no longer needed because current detectors are digital. Trigo-Rodríguez [39] computed a synthetic spectrum for each fireball and compared it directly to the observed one until he found the best match. Then, Trigo-Rodríguez [39] obtained the relative chemical abundances of incoming meteoroids from the sequential spectroscopy of the luminous trajectories of photographic fireballs during their entry into the terrestrial atmosphere. In that work, the averaged chemical abundances for the main rock-forming elements of

Table 4.2. The photographic emission spectra analyzed by Trigo-Rodríguez [39] indicating the meteoroid source, geocentric velocity, semi-major axis, inclination and type of spectrum.

Assigned code	Recording date	Stream	V_g (km s^{-1})	a (UA)	i (°)	Spectrum type
GEM	14/12/1961	Geminid	37.8	1.7	39	Grating
PER1	2-3/8/1962	Perseid	59.9	23.0	112	Prism
PER2	12-13/8/1967	Perseid	60	11	113	Prism
PER3	11-12/8/1969	Perseid	60.9	250	114	Prism
PER4	11-12/8/1969	Perseid	60.7	19.0	114	Prism
SPO2	6-7/6/1970	Sporadic	26.4	3.0	39	Prism
PER5	12-13/8/1970	Perseid	60.6	115	113	Prism
KCIG1-1r	18-19/8/1971	κ Cignid	25.6	4	36	Prism and grating
SPO1	17-18/9/1974	Sporadic	68	∞	148	Prism
AND	8-9/10/1977	Andromedid	24.3	2.9	4	Prism
LEO	17-18/11/1980	Leonid	72.4	13	162	Prism
SPO3-3r	30-01/11-12/1989	Sporadic	25.6	2.4	5	Prism and grating
SPO4	19-20/5/1974	Sporadic	57.1	12.9	103.9	Prism

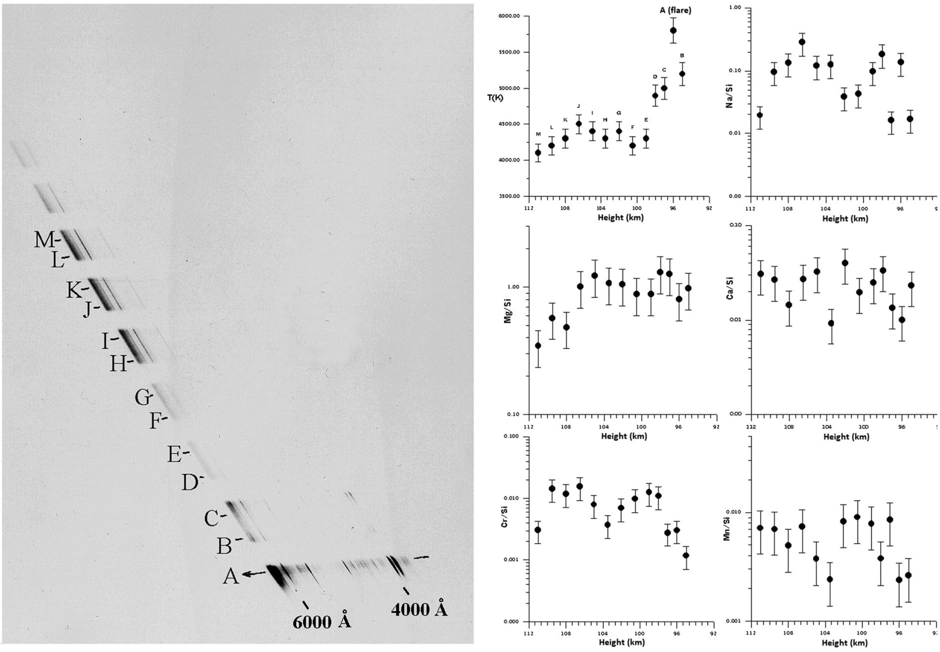

Figure 4.3. The temperature (in kelvins) and the elemental abundances relative to Fe and as a function of height for the sporadic fireball spectrum shown on the left; SPO1 in table 4.2 [39].

meteoroids were obtained, and were later discussed in [18, 21, 35]. In the next section the observational methodology and data reduction are explained.

4.3 Relative elemental abundances and cosmochemical ratios from photographic, video and CCD spectroscopy

Several research groups have been exploring the use of video and CCD spectroscopy during the last decade [9, 51]. The new techniques represent a significant improvement because the sensitivity and temporal resolution can be much higher than in photographic techniques. CCD video spectrometers are achieving a temporal resolution capable of observing physical processes during meteoroid ablation (figure 4.4) [19, 31, 52] .

As described in previous sections, there are many difficulties in recording and reducing meteor and fireball spectra. To obtain chemical information, the light emitted during the unpredictable entry of a meteoroid must be decomposed by a prism or diffraction grating set up in front of imaging systems. The system records the light emitted by the meteor as separated emission lines, but significantly reduces the limiting magnitude of the imaging system. The usual systems are only able to record fireball spectra that are bright enough to be efficiently recorded, at least during a significant part of the meteor column. Fireball spectra are currently recorded using CCD or digital video cameras, but in the past the pioneers did so using photographic plates [28, 33].

The Spanish Meteor and Fireball Network (http://www.spmn.uji.es), that has been operating with an increasing degree of completeness since 1999, has been exploring CCD and video techniques. Video emission spectroscopy has allowed the detection of moderately bright fireballs, but also extremely bright events, such as the superbolide produced by a damocloid observed in Spain on 13 July 2012 [51]. The rock-forming materials of solar system bodies reflect significant differences as a consequence of different formation times and diverse building blocks. This fact

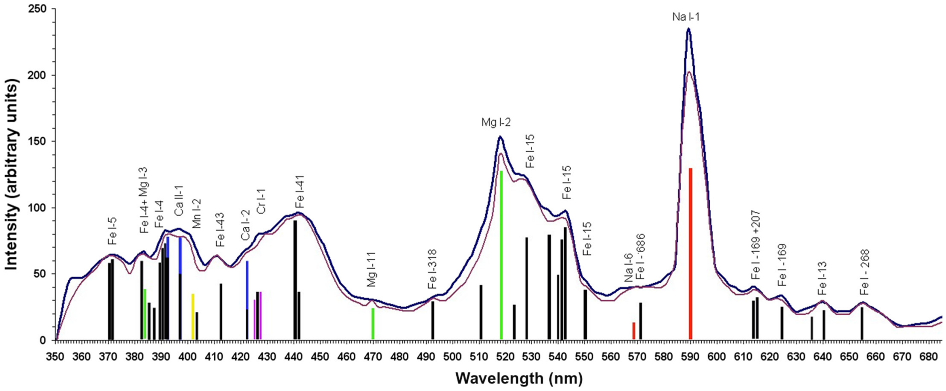

Figure 4.4. Example of the fit of a video spectrum (averaged on top) with a synthetic one produced by adding the spectral lines indicated in the 350–680 nm spectral window.

produces chemical signatures that are distinctive of achondritic materials, such as Martian rocks or the HED clan of achondrites associated with asteroid 4 Vesta (see e.g. [53]). Consequently, a comparative analysis of the inferred meteoroid elemental ratios relative to Si (such as Mg/Si, Na/Si, Ca/Si, Mn/Si) with different meteorites can exemplify that not all meteoroids reaching the top of the atmosphere are chondritic. That was the case for the bright fireball associated with PHA 2012XJ112 that was inferred to exhibit an achondritic nature [54]. The Mg/Fe or Mg/Si ratios are particularly informative to identify achondritic meteoroids. For example, two sporadic meteors studied in [35] exhibited a non-chondritic chemical composition with rock-forming phases particularly poor in Mg.

4.3.1 Obtaining meteoroid chemical abundances

As previously explained, photographic or digital spectroscopy allows the comparison of the recorded lines with synthetic spectra. As these procedures can be repeated for bright meteors along several points all along the atmospheric trajectory, it is possible to infer the abundance ratio relative to Fe for several elements [18, 35, 39].

In emission spectra produced by meteoroids with a high geocentric velocity, usually with $V_g > 40$ km s^{-1}, the second (high-temperature) component appears and the Si abundance can be inferred by fitting the intensity of the Si II lines. Unfortunately, for slow meteors it is not possible to determine the Si abundance from the spectra because that second component is very faint or non-existent [32]. This can be solved to a certain extent if high-resolution spectra, capable of separating the contribution of the Si I line (multiplet 3 at $\lambda = 3905.5$ Å) are taken. It is certainly not easy because the spectra can be noisy and this Si I line is placed in a spectral region where Fe I and Ca II lines are very prominent. As a compromise solution, when the Si abundance cannot be measured, a typical chondritic ratio of Si/Fe = 1.16 can be assumed [35].

4.3.2 Some examples of elemental abundance ratios

As previously stated, interesting conclusions about the elemental abundances can be reached by studying fireball spectra. Here we discuss the averaged abundance along the trajectories of the fireballs described in Trigo-Rodríguez *et al* [35]. The composition of most fireballs was measured in more than ten segments but the exact number of selected segments depended on the characteristics of each fireball. The exact number of segments and the values averaged in each fireball are given in Trigo-Rodríguez’ PhD thesis [39].

In figure 4.5 the relative chemical abundances for selected rock-forming elements are plotted against the geocentric velocity.

Na/Si: In general the sodium ratio (Na/Si) was found to be larger than that of typical chondritic meteorites and IDPs [55], but also than the sodium content in the dust of 1P/Halley [56]. These results support that this volatile element is probably trapped in the meteoroid components, in the matrix. Trigo-Rodríguez *et al* [18] proved that the observed Na is not due to the terrestrial atmosphere and neither has it been overestimated due to our assumptions in the model to determine abundances.

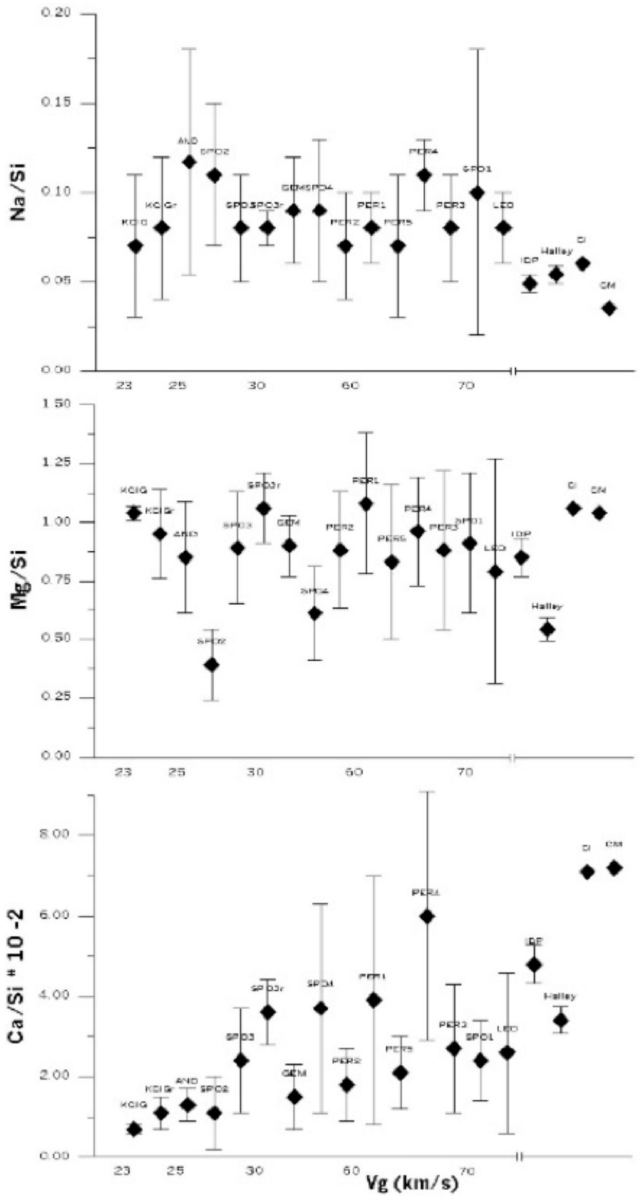

Figure 4.5. Elemental abundances relative to Si for Na, Mg and Ca for the fireball spectra studied in [39]. The average values for IDPs, Halley dust, and CI and CM are shown out of scale for comparison. Note the Na overabundance for most cometary meteors and the lack of Ca producing light in the vapor phase, an example of incomplete evaporation for its presence in refractory minerals [18, 35].

Mg/Si: This is a key cosmochemical ratio because primordial silicates were mafic in origin, but incorporated Fe as consequence of thermal processing in the protoplanetary disk or the parent bodies. The values found by Trigo-Rodríguez *et al* [35] and Madiedo *et al* [31] were within the expected range for IDPs and chondrites, but were far off the 1P/ Halley fine dust composition studied using the Giotto spectrometer [56].

Ca/Si: It is well known that calcium forms refractory mineral phases exhibiting special resistance to volatilization. In most meteor spectra the Ca lines are present without any ambiguity. In the main component the line of Ca I belonging to multiplet 2 is always evident at 4227 Å. Moreover, the lines of Ca II doublet originating by multiplet 1 appear at 3934 and 3968 Å, which are also clearly visible, particularly in high-velocity meteors. In figure 4.5 we can see the clear dependence between the observed Ca abundance and the geocentric velocity of the meteoroids. The explanation of this fact is the effect of incomplete evaporation first proposed by Boročicka [36, 37]. When the geocentric velocity increases, the main temperature reached in the meteoric column also increases. Due to the location of Ca in refractory phases, when the temperature is higher the volatilization is more efficient, contributing more to the luminous spectra. In general we note that for meteoroids with geocentric velocity between 20 and 40 km s^{-1} the effect of incomplete evaporation is that only ~30% or 50% of the calcium contributes to the luminous spectra. For fast meteors the relative abundance observed for Ca reaches larger values, but rarely the expected values for IDPs or chondritic meteorites. This is a clear trend of incomplete evaporation that produces ablation products: cosmic spherules or refractory fragments [57].

Ti/Si: Titanium is a minor element that in meteor spectra has several lines along the main spectrum and also in the high-temperature component. Usually the brightest line of Ti I is at 4982 Å and at 4550 Å for Ti II, both quite close to Fe lines and quite faint in comparison. This makes it difficult to extract conclusions in noisy segments, but it can be separated quite well for bright spectra. The derived Ti abundances are between the expected values for IDPs and chondritic meteorites.

Cr/Si: This transition element is easy to identify in meteor spectra since Cr exhibits three intense lines at 4254, 4275 and 4290 Å. In addition the multiplet 7 generates another bright emission line at 5206 Å. As many lines can be identified the fit of the synthetic spectra is easy, and permits good accuracy in the determination of Cr elemental abundances. Trigo-Rodríguez found that the Cr abundance for the photographic spectra analyzed was between the values of IDPs, chondritic meteorites and 1P/Halley dust. Some differences in the amount of Cr in cometary meteoroids were also found. Perseid meteoroids from comet 109P/Swift-Tuttle meteoroids are richer in Cr than sporadic meteoroids.

Mn/Si: Manganese can be easily identified in meteor spectra. Multiplet 1 has an important line at 4033 Å and other secondary lines at 4750 and 4850 Å. The estimated abundances of Mn are clearly below the expected values for IDPs. The incoming meteoroids had Mn/Si ratios very similar to chondritic meteorites, although three meteoroids (KCIG, PER1 and PER2) had abundances similar to those estimated by the Giotto spacecraft for 1P/Halley dust.

Fe/Si: The abundance of iron can be extracted from the second component by comparing the lines of Si II and Fe II. Using the second component, the accuracy is slightly less than for the other elements and the process is not applicable to low-velocity meteors where the Si II lines are missing. In any case, the results show that the Fe/Si ratio is clearly between the expected values for IDPs and chondritic meteorites, all very far from 1P/Halley dust values.

Co/Si: The abundance of this transition metal is low and only appears clearly in the bright segments of some detailed spectra (AND, LEO and SPO3), where the estimated Co/Si ratio is around 3×10^{-3}.

Ni/Si: Nickel lines are difficult to observe in meteor spectra. A line of Ni I lies at 5477 Å. Its intensity could be measured in only seven spectra and yielded values of Ni/Si around 2.5×10^{-2}. This is around half of the solar abundance, 5×10^{-2}. It is interesting to note that some meteoroids such as AND and PER4 showed low Ni/Si, very close to that observed for 1P/Halley dust by the Giotto spacecraft.

4.3.3 Other ratios of cosmochemical interest

In addition to the chemical abundances with reference to silicon cited above, other ratios are of particular interest in cosmochemistry: Mg/Na, Fe/Na and Mg/Fe, in particular.

Mg/Na: The observed values for this ratio are of great interest. Most of them are around the typical values for 1P/Halley dust although some cometary meteoroids (KCIG, PER1, PER2, PER3 and SPO3) have Mg/Na ratios closer to IDPs or CI typical values. Considering the possibility that we overestimated the abundance of Na, all ratios could be closer to IDP values.

Fe/Na: This ratio shows again the similarity of the incoming meteoroids to IDPs and CI and CM chondrites. We also note that the largest meteoroids (AND, KCIG and SPO3) have nearly identical averaged values. The remaining values are very close to those expected for IDPs or carbonaceous chondrites.

Mg/Fe: Again this ratio confirms the general differences with the 1P/Halley dust chemical composition. All meteoroids are within the expected value for IDPs or CI and CM chondrites, showing a typical Mg/Fe value of 1.2. Again two sporadic meteors show an anomalous composition due to their low content of magnesium.

Among the elements that were present in the primeval inner solar nebula, Si, Mg and Fe were more abundant. Their individual responses to high temperatures were probably responsible for their different abundances in the bodies condensed there [58]. These three chemical elements are the major components of inner solar system bodies because is accepted that they all formed from the condensation of a vapor rich in Mg–Fe–SiO–H_2–O_2 and small particles of silicates that were forming the protoplanetary nebula 4.5 Mya [55]. Consequently, the relative proportions of these three elements is usually a good tool to find possible relationships between different objects. Figure 4.6 shows the ternary diagram Mg–Fe–Si where the chemical similitude between the meteoroids producing the spectra analyzed in this work and the IDPs and chondritic meteorites is again implicit. All spectra are clustered between the typical IDPs and chondritic values, except for two sporadic meteoroids (SPO2 and SPO4), characterized by being poor in Mg. It is important to note that both meteoroids are unique, in that they are close to the Mg abundance of 1P/Halley dust although their content of Fe and Si is different. But are the particles of this comet really anomalous or could this be an artefact of the measurements? To answer

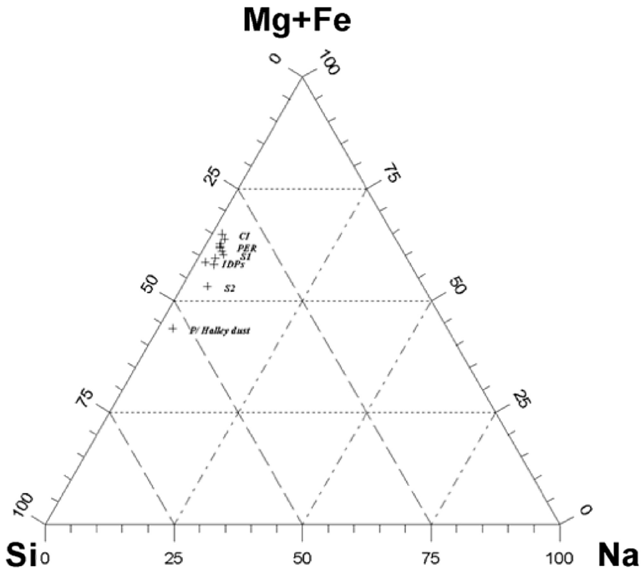

Figure 4.6. This ternary diagram compares the Mg + Fe, Si and Na abundances in the selected sample of cometary particles compared to the CI chondritic, aggregate IDPs and 1P/Halley dust abundances. The Na abundance of most cometary meteoroids is larger than in chondritic meteors. Additional labels are: S2 (SPO2) and PER (Perseids).

this we must note that Fomenkova *et al* [59], combining the mass and the composition of each particle detected by the Giotto mass spectrometers, concluded that the dust of this comet is formed by three kinds of particles: (i) the so-called CHON particles; (ii) particles rich in carbonaceous compounds and silicates; and (iii) mineral particles with Fe, Mg and Si as the main components. It is important to note that the CHON particles have not yet been recovered in the terrestrial atmosphere, probably due to their fragility to solar radiation during their sojourn in the interplanetary medium or, as was suggested by Rietmeijer [60], due to being melted during their fast entry into the terrestrial atmosphere. The Halley mass spectrometers detected only very small particles that have a mass equivalent to the so-called principal components (PCs) that are inside the matrix of IDPs. Neither PCs nor any other constituent (e.g. mineral grains) have chondritic element proportions. In consequence, the Giotto measurements were biased towards small cometary particles and from our results we conclude that they not are representative of other cometary particles arriving at Earth.

From meteor spectroscopy we usually infer that most meteoroids ablate, producing a luminous phase with characteristic chondritic bulk elemental chemistry [18, 35]. This is a direct consequence of the fact that the chondritic bodies are dominant in the current flux on Earth [1]. Laboratory experiments are also needed, and the ablation of chondrites can provide clues about the pathways for the delivery of volatile and moderately volatile elements to Earth (see e.g. [3]).

4.4 The Na overabundance: clues on the delivery of volatiles from fragile meteoroids and IDPs

From the analysis of ablation columns of cometary meteoroids using meteor spectroscopy, it appears that Na is mainly contributing to the meteor light during the first stages of ablation [35]. The inferred Na overabundance in reference to the chondritic ratios was evident in Trigo-Rodríguez *et al* [35]. The study of the specific abundance of Na in meteor columns and its comparison to Na abundance in the upper atmosphere pointed to the fact that cometary meteoroids must have significant enrichment of this moderately volatile element [18, 21]. This was explained by Na not only forming part of the rocky minerals, but also being trapped in organics and/or ices in the outer disk regions where comets formed. It was envisaged that during the early stages of the protoplanetary disk the materials fell continuously onto the protostar, causing vaporization of rocky components. At that stage the intense solar wind from the young Sun depleted the content in some lithofile elements such as Na, K or Mn in chondritic meteorites [61, 62]. Today the process of sodium depletion of the inner solar system continues due to the solar wind removing this element from young comets and tenuous atmospheres where it is accumulating by vaporization of meteoroids. For these reasons, Na abundances are probably higher in comets formed in the outer region of the disk [62]. It is likely that the Na became incorporated into the volatile-rich interstitial fine-grained matrix, consistent with recent Rosetta observations [50]. Such a model is consistent with our meteoroid bulk chemical data for the main rock-forming elements in which Na was shown to be overabundant ([18] figure 4.6).

Sodium has also been widely observed in cometary comae, but there is an intrinsic difficulty in establishing the origin of Na and its relative abundance from those data [63]. The measured Na/Si atomic ratio of 3×10^{-5} in the coma of comet Hale–Bopp was explained as being produced from sputtering of the particles' surfaces only. The sodium present in the tail of some comets forms a well-defined Na-tail [64]. These authors suggested that this sodium could be being produced in a near-nucleus region, probably by cometary degassing or through an extended source such as the break-up of Na-bearing molecules, ions or dust particles. Detailed studies are required in order to infer the exact mechanism of neutral sodium release from dust particles. If sodium was embedded into organic material or ices associated with low-temperature melting phases, as suggested by our meteor spectrum results, the amount of sodium released from some comets could be easily explained. This overabundance has also been explained as a consequence of aqueous alteration processes in comets [65].

4.5 Astrobiological implications of the continuous arrival of chondritic components to Earth's surface

As previously mentioned, the carbonaceous chondrites (CCs) contain highly reactive minerals and have been continuously reaching the terrestrial surface, although the flux has significantly changed over time. The study of CCs reveals that they formed part of the undifferentiated parent bodies that formed in the outer protoplanetary disk, and their composition reinforces the idea of a continuum between asteroids and comets (figure 4.2). Some CCs have experienced little thermal homogenization so they are considered highly unequilibrated meteorites that contain the primordial components of the protoplanetary disk, just weakly compacted [8]. The parent bodies of these accretion aggregates were highly porous [66] and retained significant amounts of water, organics and volatile compounds that were widely available in the outer disk formation regions. Small asteroids and comets are formed from primordial materials, and at the very beginning were subjected to planetary perturbations and fragmentations during close approaches to planets, so were probably easily disrupted [8]. Such processes later extended during the late heavy bombardment [67]. Consequently, it seems plausible that at early times and subsequent later periods of time the Earth was subjected to a meteoritic flux at least 5–6 orders of magnitude greater than the current one [68]. Consequently, a large amount of chondritic materials reached the Earth's surface at an annual rate of thousands of billions of metric tons. Hence the amount of volatiles delivered under such meteoroid high-flux circumstances was also very significant, probably playing a key role in fertilizing the Earth's surface [69]. To support the previously outlined hypothesis, significant progress has recently been made in understanding the role of chondrites in prebiotic evolution [69]. The catalytic effect of six CCs (table 4.1) was analyzed in the presence of water and formamide, namely Allan Hills 84 028 (group and petrologic type: CV3), Elephant Moraine 92 042 (CR2), Miller Range 05 024 (CO3), Larkman Nunatak 04 318 (CK4), Grosvenor Mountains 95 551 (C-ung) and Grosvenor Mountains 95 566 (C2-ung). The carbonaceous chondrites (CCs) were requested from the Johnson Space Center facility in the framework of two Spanish research projects (AYA2011-26522 and AYA2015-67175-P) to identify pristine meteorites in the NASA Antarctic collection and study their properties [69]. We found that, once the intrinsic organics hosted by the matrix of the carbonaceous chondrites are removed, the minerals forming these meteorites are able to catalyze complex organics under warm (100 °C) interaction with water and formamide. Thus, in view of the unique reactive properties of carbonaceous chondrites, it can be deduced that the reactive minerals forming CCs reached the surface of Earth and other planetary bodies, and when exposed to a warm and water-rich environment could have started catalytic reactions to promote organic complexity (figure 4.7). These reactions, independent of the ability of complex organics to survive atmospheric deceleration, probably initiated the first steps in increasing the organic complexity necessary to promote the origin of life [69, 70].

4.6 Conclusions and future work

The study of undifferentiated bodies is able to provide clues on the role of these primordial materials in the formation of planets, the delivery of volatiles and the origin of life. The main conclusions of this work are:

- Not all meteoroids have enough strength to survive long periods of time in the interplanetary medium, or the loading pressure experienced during their fast

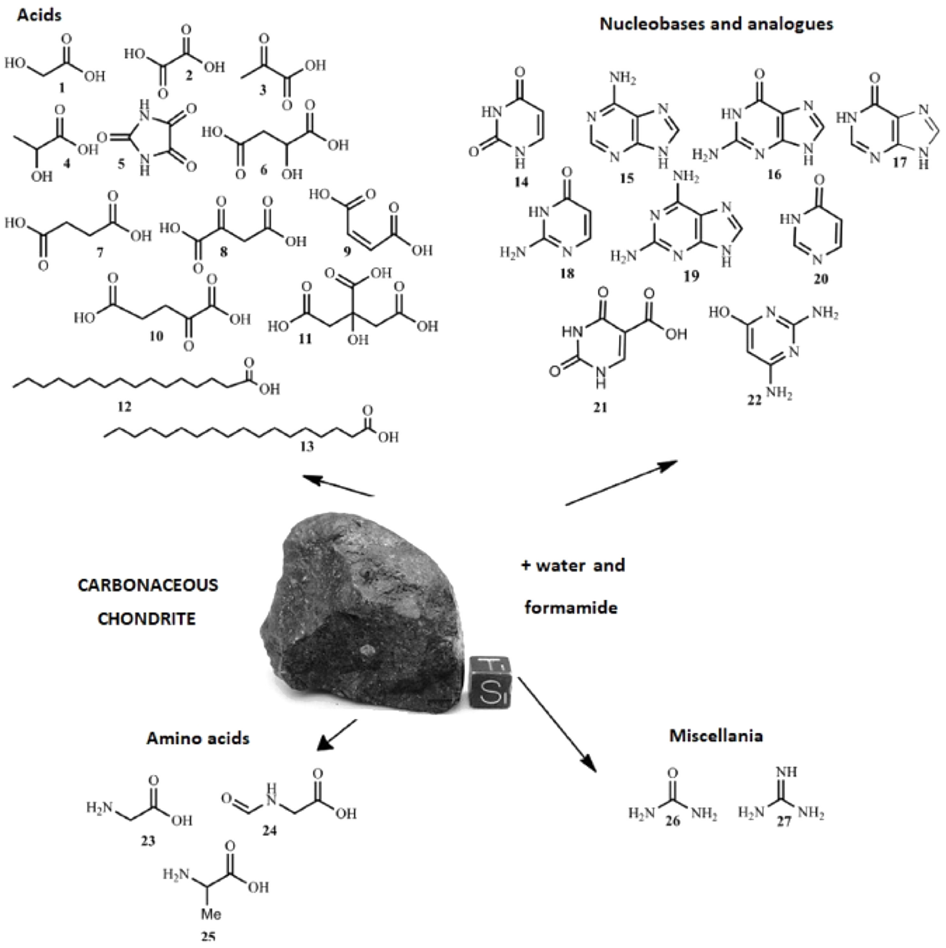

Figure 4.7. Catalysis of organic compounds from chemical reactions promoted by carbonaceous chondrite minerals in the presence of water and formamide [69].

deceleration in the atmosphere. These materials are probably associated with transitional C-rich asteroids or comets that cannot produce meteorites, but some of them that reach our planet with velocities lower than 12 km s^{-1} are able to survive as micrometeorites or IDPs. This produces a continuous flux of micrometric materials reaching the Earth's surface that, at the present time, is estimated to be about 40 000 Tm, but which was probably much higher in the past, particularly at the time of the late heavy bombardment.

- For all these materials that reach the top of the atmosphere, but leave no surviving meteor, spectroscopy can be a promising way to understand the processes taking place during ablation. The study of meteor ablation columns provides a pathway to a better understanding of the decay of these materials in the atmosphere and the pathways of volatile delivery to our planet.

- Future fireball spectra with new instrumentation will provide additional insight into some key spectral windows (UV and NIR, for example) where we can find spectral lines of interest to learn about the formation of the vapor cloud, and the decay of organic compounds.

From the very beginning of this field early in the 20th century, emission spectra allowed the identification of emission lines from rock-forming components. A systematic and statistical approach allows meteor emission spectroscopy to provide direct evidence on the chondritic materials and volatiles participating in the continuous delivery of primitive materials from undifferentiated bodies. In fact, most meteoroids are fragile and are severely fragmented in the atmosphere. These materials that are unable to survive atmospheric interaction are of key importance. We know now that this is a direct consequence of the fragile nature of these bodies that are weakly bonded aggregates formed of fine micron-sized dust, organics and volatiles. IDPs represent a fascinating and enriched continuous bathing of our planet in the Cosmic Ocean.

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