Six Phases of Cosmic Chemistry

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1. Introduction

The steady development of astrophysical and cosmological sciences has led to a growing appreciation of the continuity of cosmic history throughout which all known phenomena come to being. This also includes chemical phenomena and there are numerous theoretical attempts to rewrite chemistry as a "historical" science (Haken 1978; Earley 2004). It seems therefore vital to organize the immense volume of chemical data – from astrophysical nuclear chemistry to biochemistry of living cells – in a consistent and quantitative fashion, one that would help to appreciate the unfolding of chemical phenomena throughout cosmic time.

Although numerous specialist reviews exist (e.g. Shaw 2006; Herbst 2001; Hazen et al. 2008) that illustrate the growing appreciation for cosmic chemical history, several issues still need to be solved. First of all, such works discuss only a given subset of cosmic chemistry (astrochemistry, chemistry of life etc.) using the usual tools and languages of these particular disciplines which does not facilitate drawing large-scale conclusions. Second, they discuss the history of chemical structures and not chemical processes – which implicitly leaves out half of the totality chemical phenomena as non-historical. While it may now seem obvious that certain chemical *structures* such as aromatic hydrocarbons or pyrazines have a certain cosmic "history", it might cause more controversy to argue that chemical *processes* such as catalysis or polymerization also have their "histories". The purpose of this article is to:

a) outline the global cosmic history of chemical phenomena (where the word *phenomenon* will include both structures and processes);

b) derive certain general properties of that history, including its "punctual" character: most chemical innovations arise in spectacular "revolutions" similar to phase changes;

c) discuss the perspectives of extending this method to areas beyond chemistry.

The problems standing before such a venture are obvious and numerous.

First of all, there are still considerable gaps in our understanding of cosmochemical history, the most dramatic of which is probably the transition from non-living to living systems – abiogenesis. However, the general "story of the universe" seems to be secured and there is ample observational data to support it. This concordant cosmic history, backed up by preliminary quantitative estimates, forms the background for the analysis presented below and is introduced in Section 3.

Second, there is no generally agreed-on language that would serve to express the growth of chemical complexity through time. In other words, if one were to present the vast universe of chemical

phenomena in an evolutionary fashion, the assembly of a list of such phenomena would be the first obstacle. In order to actually produce a systematic review of cosmic chemical evolution, we may not limit ourselves to mentioning whatever comes to our mind. Here, I wish to present a solution, admittedly tentative, to this second problem, by borrowing a list of chemical phenomena from the Universal Decimal Classification (UDC 2005): a library cataloguing system. UDC is a detailed hierarchical system for classifying library resources and contains a list of ca. 2700 topics in chemistry which can be read at any level of detail. Although it may seem an odd and risky choice to employ library catalogues for the purposes of quantifying natural phenomena, I believe that this is in fact a rational decision and works exceedingly well as a first approximation. The UDC system, its basic properties and the rationale for its use are discussed below in Section 2.

2. Why use library classification systems?

In order to appreciate the growth of natural complexity throughout the cosmic evolution, it does not simply suffice to tell the cosmic story. A quantitative element, if only tentative or even semi-quantitative, seems necessary. A good illustration of that principle is paleontology, where evolution of life is often quantified by the number of extant taxa of given rank (genera, families, orders, classes, phyla) throughout geological time (see e.g. Valentine 2004, Rohde and Muller 2005). At first sight, the method may seem fully quantitative, yet it isn't, because it is not based on an robust method of attributing ranks to taxa. For instance, there are no good reasons why there are, say, 3 orders of leeches (class Hirudinea), 13 orders of monocot plants (class Liliopsida) and 45 orders of bony fish (class Osteichthyes) and, in fact, why these three groups have been assigned the rank of class. The number of orders (or any other high ranks) does not easily correlate with species richness or any other obvious measure, and is rather a function of tradition, convenience and, increasingly, phylogenetics – which leads, in the opinion of at least some biologists, to even less balanced classification systems (Cavalier-Smith 1998). Yet, any discussion of the history of biological complexity based on order counts would attribute to the emergence of bony fish exactly 15 times more "power" than to the emergence of leeches. Have bony fish as a group really been *measured* to be 15 times more complex/important than leeches?

This example is intended to demonstrate two things. First, there is no real hope of developing a "natural" or, even more so, "objective" list of phenomena of given type at a defined level of detail that would enable us to "measure" the growth complexity of different groups of natural objects. Second, even an intuitive measure that is created simply for convenience may lead to valuable insights, as demonstrated by the ubiquitous and creative use of the above-cited biological diversity measure in paleontology (for a broad sample of such diagrams, see: Valentine 2004). The "list of chemical phenomena" used throughout this article is very much similar to the "list of living organisms" that one would get by choosing a particular taxonomical rank (e.g. order) and listing all currently recognized biological groups of that rank. Here, out of numerous other possibilities, UDC's class names are used.

Universal Decimal Classification was first published in 1905 and has been steadily modified and extended since then to now include ca. 69000 hierarchically ordered classes. To get a feel of the system and its structure, let's note the class names of successive levels of hierarchy leading to the most detailed class that would be used to tag library resources concerning anthracene:

- 5 Mathematics. Natural sciences
- 54 Chemistry. Crystallography. Mineralogy
- 547 Organic chemistry

- 547.6 Polynuclear benzene derivatives and their hydrogenated derivatives
- 547.67 Trinuclear systems
- 547.672 Anthracene and its derivatives

Here and below, the name "level-*n* class" will denote the class whose class number contains *n* digits.

The similarity to the biological classification system is striking and, in fact, a taxonomical treatment of life forms a subset of UDC. Also, one encounters here the seemingly insoluble problem of rank assignment and handling the complexity across disciplines. Above, we have shown how three distantly related groups of organisms were assigned the rank of classes and subdivided into a seemingly arbitrary number of lower rank subgroups (orders). In UDC one witnesses the exact same issue. The level-V class "552.55 Siliceous rocks" contains 3 level-VI subclasses, the class "547.67 Trinuclear systems" contains 6 such subclasses and there are 9 subdivisions of the class "591.43 Organs of animal nutrition". Is there even a slightest hope of determining the *appropriate* ranking system? I leave this issue open as an interesting question on its own.

Although I realize that this short exposition may not suffice to convincingly present the case for using the number of library catalogue entries as a proxy for natural complexity, I hope that the example of paleontology shows at least that analogous procedures have been successfully used in other disciplines. Also, the (intended) exhaustive nature of the system should be noted – just as *any* living creature should in theory have a place in the taxonomical system of biology, *any* book or article concerning any aspect of chemistry should have its place somewhere within the UDC system. Even if this noble vision is forever out of reach, the use of a library catalogue is intended as a simple measure against the possibility of writing a natural history of chemical evolution based simply on those chemical phenomena that a particular author had in mind at a particular day. To use the biological metaphor for the last time: even if the list of all currently recognized orders of living organisms does not represent all of nature's biological richness, it is certainly a convenient approximation to the current state of knowledge. A broader critical perspective on the method used is found in Section 7.

Here, all 176 level-V subclasses of four level-III classes relevant for the study of the growth of natural chemistry ("544 Physical chemistry", "546 Inorganic chemistry", "547 Organic chemistry" and "577 Material basis for life. Biochemistry. Molecular biology. Biophysics") are used. Two level-III classes ("542 Practical laboratory chemistry" and "543 Analytical chemistry") and 2 level-V classes ("544.18 Quantum chemistry" and "544.42 Formal kinetics") of chemical nature were excluded, because they specifically describe human activities related to chemistry, and not natural chemical phenomena. Also, for this group the translation of class names to names of chemical phenomena and a physico-chemical interpretation of their novelty are highly non-trivial – which will be commented further in Section 4.6.

Some of the resulting classes (given, for clarity, without class numbers and in plain text, from now on being treated as names for chemical phenomena, not names for subfields of science[1]) are: atomic and molecular spectra; combustion and explosion; plasma chemistry; colloid chemistry; phosphorus and its inorganic compounds; rare earths; unsaturated hydrocarbons; phenols and aromatic alcohols in general; trinuclear systems. The purpose of this study is to track the appearance of entities and processes denoted by these class names throughout the cosmic history with a proper appreciation of the relevant cosmological, astrophysical and geological context.

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[1] It should be noted that this procedure – the transition from a list of fields of study to the list of natural phenomena – which *in theory* may sound tricky (and from a philosophical perspective means moving from epistemology to metaphysics), proved *in practice* to be immediate and straightforward.

3. The big picture of cosmic evolution

The presentation of the development of chemical phenomena throughout cosmic time will follow in Section 4, but first some preliminary explanations are in place. The big picture of cosmic evolution that serves as a background for chemical evolution is presented in Fig. 1.
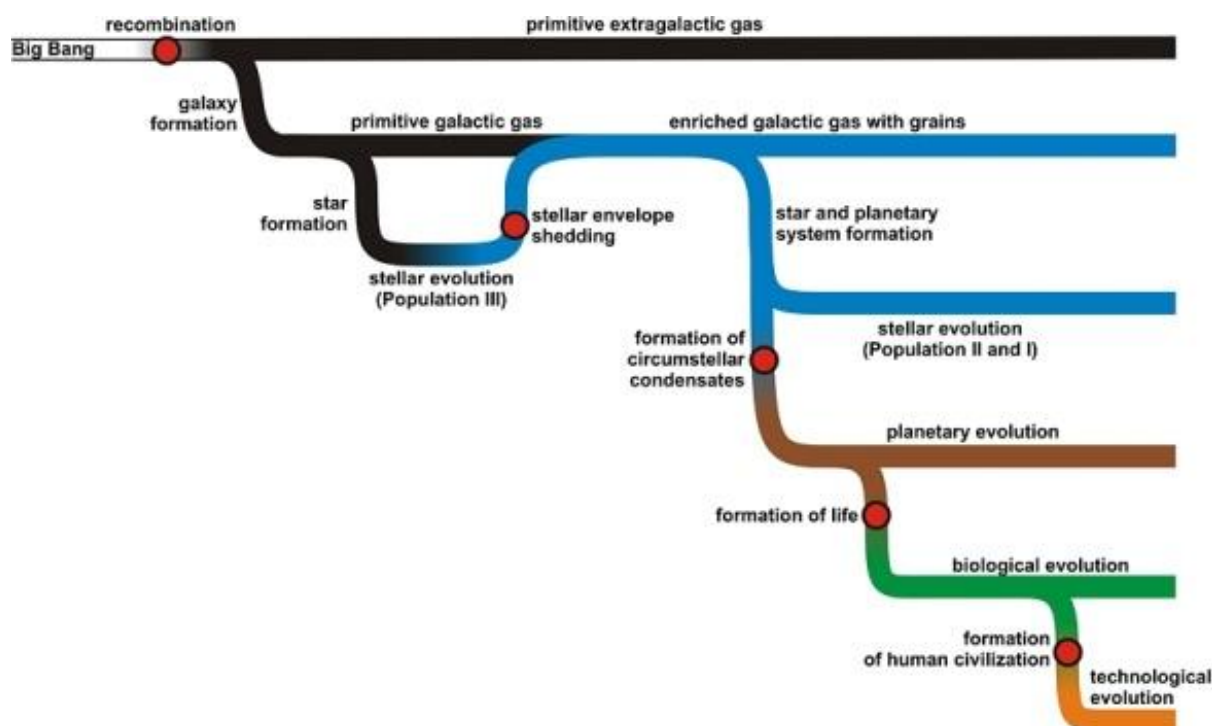

Fig. 1 *The big picture of cosmic evolution, time runs from left to right. Six phases of cosmic chemical evolution described in the article are symbolized by six colors and red spots indicate areas and processes in the Universe that lead to the emergence of new such phases. More information in text*

All elements of the scenario described below are now generally agreed on and well corroborated by observations. The interested reader may find more details on the general history of cosmos in numerous sources (e.g. Liddle 2003; Pagel 2006; Tolstikhin and Kramers 2008). The terms in **boldface** refer to the terms used in Fig. 1.

The universe started out in a state precluding any form of chemistry, with temperatures not only exceeding ionization thresholds, but also levels enabling the existence of atomic nuclei in the first place. The gradual cooling of that **prestellar gas** led to the emergence of rudimentary chemistry (based on H, He and Li only) and the collapse of matter into overdensities which eventually led to galaxy and **star formation**. The gas that did not participate in galaxy and star formation (**primitive extragalactic gas**) is a largely unstudied reservoir, although it slowly becomes observable (Simcoe et al. 2012). The **stellar evolution** of first stars (termed, slightly confusingly, Population III) led to the nucleosynthesis of all heavy elements and culminated in the ejection of enriched gas (**stellar envelope shedding**) that condensed into a small but solid population of chemical and mineralogical species.

From this moment on, the galactic gas is being steadily cycled through the nuclear machinery of stars, leaving behind an increasingly more **enriched interstellar gas with grains** and a growing population of stellar remnants (not pictured). Our Sun is one of those stars that formed from a gaseous reservoir containing not only the dominating H+He component, but also a small admixture of heavier elements which initiated **planetary system formation**. Around the young star condensation of matter

occurs, forming a reservoir that might be termed **circumstellar condensates**. This includes comets, asteroids, planetoids, planets and dwarf planets, their satellites, interstellar dust particles and other objects orbiting the Sun, primarily composed of condensed matter and a primitive stellar-like gas. **Planetary evolution** ensues. On at least one planet chemical systems turn into living systems, initiating the phase of **biological evolution**. Human civilization is but one of the numerous "special cases" of biological evolution; from a chemical perspective a rather spectacular one, too – but that will be discussed in further detail in Section 4.5.

This complex history may be schematically divided into six segments ("phases"), sequentially discussed in Section 4. Each phase is initiated by a dramatic, intensive and usually rapid pulse of chemical creativity and each leads to a closed and mostly static repertoire of chemical phenomena. What is especially important, and graphically illustrated in Fig. 1, is that the new chemical revolutions always concern only a small portion of cosmic matter and that up to this day there are "primitive" reservoirs in the Universe that are relatively simple and do not demonstrate chemical phenomena typical for more "advanced" chemical phases. This is yet another similarity of chemical to biological evolution, where the evolution of new biological groups does not necessarily lead to the extinction of the ones from which they evolved.

4. The six phases of cosmic chemistry

In the following section, phrases in **boldface** refer to terms present in the UDC classes under consideration or in their subclasses. Some results discussed in this section are presented graphically in Fig. 2.
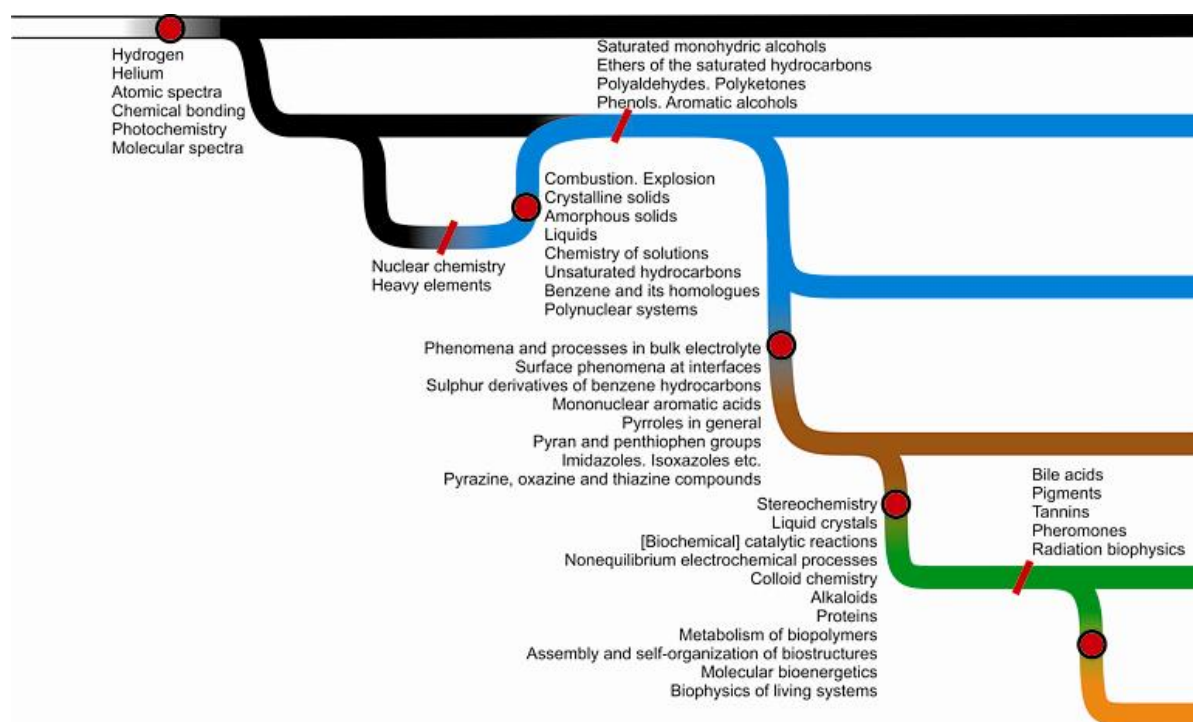

Fig. 2 The appearance of major chemical innovations throughout cosmic history. The "flow diagram" used as background is described in Fig. 1. All names come from the UDC. More information in text, including the discussion of possible controversies or uncertainties and the references to relevant literature

4.1. The Phase of No Chemistry: from the beginning to recombination

The universe began with no chemistry whatsoever. The gradual cooling of matter led to a series of transformations, the most important of which, at least from the perspective of this article, is the phase of primordial nucleosynthesis which took place within the first three minutes of Big Bang. This Big Bang Nucleosynthesis is responsible for the well-known mixture of **hydrogen** and **helium** in mass proportions of approximately 0.75-0.25 and a tiny admixture of **lithium** and an even tinier – of heavier elements (all elements heavier than helium are in cosmology called *metals*, hence *metallicity* as the measure of the concentration of metals). Because of high temperatures the matter was still fully ionized and no chemistry *sensu stricto* was present.

4.2. The Phase of Prestellar Chemistry: from the recombination to the first stars

About 300000 years after Big Bang recombination took place and first neutral atoms appeared. This enabled collisional or radiative **excitation**, de-excitation **and ionization** with concurrent **absorption** or **emission.** This in turn brought **atomic spectra** (including the astronomically important **hyperfine emission** of H at 21 cm) to the radiation field. This rudimentary chemistry, in a rare and hot (ambient temperatures around 2000-3000 K) gas persisted for only a couple million years.

Around 2-5 million years after Big Bang first molecules started to form; given the simple elemental composition[2], this included H_2 (and H_2^+, plus HD and HD^+), LiH (and LiH^+) and – which may be more surprising – a microscopic amount of HeH, whose relative abundance was estimated to be ca. 10^{-14} (Maoli et al. 1994). The first appearance of **covalent chemical bonding** also brought **rotational** and **vibrational spectra**. Note that the repertoire of vibrational spectra included only a tiny subset of known modes because the largest molecules at that time were 2-atomic (no scissoring, wagging, twisting etc.).

This mostly neutral gas slowly began to collapse and about 30-50 million years after the Big Bang massive haloes (10^5-10^6 M_Θ, where M_Θ is the mass of the Sun) formed. These haloes, which can be thought of as the building blocks of protogalaxies, separated from the rare surrounding gas that would not participate in further chemical revolutions – which is presented graphically in Fig. 1 as the first divergence between the primordial extragalactic gas and the primitive interstellar gas. Although this almost-zero-metallicity gas has not yet been unequivocally observed, promising signs of such detection do exist (Simcoe et al. 2012). Based on tentative cosmological calculations, up to 90% of all (baryonic) matter may be currently tied up in such an extragalactic gas of negligible metallicity (Fukugita et al. 1998; Fukugita and Peebles 2004) typical for the Second Phase – although such calculations should be treated with great care. The haloes soon fragmented into the first population of stars, termed for historical reasons Population III stars.

4.3. The Phase of Galactic Chemistry: from the first stars to planetary systems

The following stages of cosmic evolution are all related to the star formation cycle, where galactic gas of suitable density and composition undergoes gravitational collapse, forms a star accompanied (in case of later populations of stars, symbolized at Fig. 1 by the second blue loop) by a planetary system, and is finally either quietly extinguished (in case of very low mass stars) or more or less violently expelled (in case of heavier stars) leaving behind a compact remnant. These local events are in stark contrast to the global events described in the previous section – all the stages of stellar and

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[2] Some authors (see e.g. Vonlanthen et al. 2009) include the microscopic amounts of even heavier elements suspected to form in the Big Bang Nucleosynthesis to calculate the abundances of molecules such as CH (relative abundance on the order of 10^{-19}), NH (10^{-25}) or HF (10^{-29}), however this is speculative.

planetary evolution, with the emergence of all related chemical phenomena, happen all the time in billions of slightly different variants throughout the universe.

From the chemical point of view, the most important process in stellar evolution is nucleosynthesis – responsible for the proportions of elements produced – and the late stages responsible for the return of those elements to the interstellar medium with the concurrent creation of a considerable richness of chemical and mineralogical species. Because of the high temperatures of stars, even after heavy isotopes are synthetized the resulting gas is chemically "primitive" until it cools down below the recombination threshold, analogous to the above-mentioned situation during the Big Bang.

Stellar evolution is a vast and rich area of study, but for the purposes of this article two basic observations seem most important:

(A) All elements heavier than hydrogen are produced in stars in varying proportions, but the resulting mixture is dominated by O, C, Ne, N, Fe, Si, Mg and S; together with H and He these 10 elements currently add up to 99,9988% of all baryonic matter in the Universe (by number, not mass; calculated from the data in: Palme and Jones 2003, 44-5). Excluding the chemically inert Ne, carbon and oxygen account together for ca. 85% of all "metals" in the interstellar medium, and become two major players in astrochemistry.

(B) After the enriched stellar envelope is ejected, a sequence of condensation events take place, whose outcome is determined primarily by the proportion of C to O. Depending on which of these elements is more abundant, a vastly different chemical and mineralogical mixture forms, because the less abundant element of the two will be invariably tied up in the stable CO molecule, leaving only the surplus of the more abundant one to undergo further chemical processes.

It is in stellar envelopes and in the interstellar medium, where a considerable proportion of known chemical processes and classes of compounds first appears. Out of 66 classes of organic molecules found in the UDC, 28 (42%) have been detected in the interstellar medium (for a recent review of astrochemistry, see e.g. Shaw 2006). All compounds mentioned in round brackets belong to this group.

On the oxygen side, various **oxides** form, including compounds of N, S and P, but also mineral-forming oxides, especially Al_2O_3 (corundum) and TiO_2. These are later incorporated into minerals in a complex sequence of chemical and physicochemical processes, leading through rare mineral species such as gehlenite $Ca_2Al[AlSiO_7]$ and akermanite $Ca_2Mg[Si_2O_7]$ to more well-known ones such as enstatite $MgSiO_3$ or diopside $CaMgSi_2O_6$ (Davis and Richter 2003). Tiny grains of material incorporated into meteorites but formed before the Solar System – so-called presolar grains – also contain spinel $MgAl_2O_4$, olivine $(Mg,Fe)_2SiO_4$ and other major rock-forming minerals. Iron is partly incorporated into oxide minerals, but mostly forms a metallic alloy with nickel (known as kamacite or taenite, depending on proportions). Some numerical simulations (Lattimer et al. 1978) suggest that this sequence of mineralogical processes involves certain mineral phases for which the ambient temperature is above the liquidus – these should for a short period of time form tiny droplets: the first **liquids** in the Universe.

On the carbon side, there are chain radicals and ions (C_8H^-, C_5N^- and such) and **saturated** or **unsaturated hydrocarbons** (methane to hexane, acetylene, triacetylene) and later their simple derivatives, such as **ethers** (e.g. dimethyl ether), **monohydric alcohols** (methanol, ethanol), **carboxylic acids** (formic acid) and cyclic hydrocarbons, both **aromatic** (benzene) and **alicyclic**

(cyclopentane), likely including their derivatives such as **phenols**. Further reactions between benzene and its derivatives lead first to the formation of **binuclear** and **trinuclear** aromatics, later **polycyclic aromatic hydrocarbons (PAHs)** and their weakly bound aggregates, then particles of soot and microscopic particles of graphene and graphite. Also, **carbides** such as SiC, TiC or MoC can be found in spectra of many giant stars and later become condensation nuclei and cores of aggregating interstellar grains. Naturally, grains of "pure" carbon also form, consisting of **graphite** or **diamond**, depending on conditions. This growth of solids is accompanied by a fascinating transition from line to continuum spectra which can be thought of as an illustration of the transition from chemistry to solid state physics and is beautifully illustrated by the evolving spectra of PAHs of increasing size (Bakes & Tielens 1994).

The whole process involves, for the first time, the (almost) full richness of **reaction types** (addition, elimination, substitution, rearrangement) and **mechanisms** (e.g. multistage reaction with highly reactive intermediates), plus related physicochemical processes (**nucleation**, formation of **solutions**). **Metallic bonds** (hinted in **metallic clusters** and fully developed in alloys) and **weak bonds** (e.g. in stacking interactions between PAH molecules) emerge for the first time which – accompanied by the above-mentioned enrichment in vibrational modes – leads to a more complex energy landscapes of molecules and the resulting growth in the complexity of spectra. In the high-energy environment typical for the late stages of stellar evolution **photochemical** and **radiochemical** processes become important.

Finally, the resulting mixture of gaseous and solid-state products cools down and is incorporated into the interstellar medium. There, on the scale of hundreds of millions of years, they attain equilibrium with the fluctuating radiation and cosmic ray field. The interstellar grains undergo slow evolution, reaching through collisions and aggregations an equilibrium size distribution with a maximum at about 100 nm and not exceeding 1-2 μm (Tielens 2010, p. 159). The surfaces of grains host **solid surface chemistry**, including first instances of rudimentary **catalysis** such as the very effective surface-catalyzed formation of H_2 from H (Dyson and Williams 1997, p. 72). Because of the importance of gas cooling to astrophysical structure formation, this particular catalytic reaction is of prime importance to astronomy.

Currently, about 23% of galactic mass is in the form of interstellar medium, 63% resides in active stars, and 14% in stellar remnants, with only a negligible amount (0,03%) in planetary systems (Fukugita et al. 1998). Because stars themselves host only a very limited repertoire of non-specific chemical phenomena (see e.g. Sinha 1991), to complete the "chemical picture" of galaxies at the Third Phase, only stellar remnants are left. Their interiors are too dense and hot to host any form of chemistry and their surfaces and atmospheres host a poor-known repertoire of chemical phenomena, likely but not necessarily similar to ones found in normal stars (Gaur et al. 1988). However, the effect that stars and stellar remnants have on their environment is not to be underestimated from a chemist's point of view. Just recently, an entirely new class of chemical bonding was implicated in ultra-strong magnetic fields such as those around white dwarfs (Lange et al. 2012). Any census of chemical processes or entities relevant for this phase of cosmic evolution should leave some place for the likely unusual high-energy phenomena related to compact objects.

Had for some reason stellar formation ceased after Population III stars, the above-mentioned suite of chemical processes would be all there is in the universe. Luckily, further generations of stars are steadily created up to the present day. These, however, incorporate not only the bare primordial gas, but also the "metals" that condense, aggregate and ultimately form planetary systems.

4.4. The Phase of Planetary Chemistry: from planetary systems to the emergence of life

Planetary systems are, in astrophysical scale, minor additions to stars. In the current mass budget of the Solar System, only 0,14% of mass belongs to the planetary system, the rest being locked up in the Sun (calculated from the data in: Cole and Woolfson 2002). After accounting for the fact that most of the planets' total mass rests in the gas giants' gas – which has an essentially stellar composition – there remains only a tiny admixture of "heavy" elements to form all the ices, rocks and metals and the fantastic abundance of soft matter and chemical systems that we know from Earth.

Let's quickly review what we know about the growth of chemical complexity that occurred with the formation of our planetary system.

First, looking from the perspective of the (largely organic) ices formed during the Third Phase, through their irradiation, heating and fractionation many large groups of organic compounds appeared for the first time, especially numerous heterocycles – **pyrroles** and **pyrans** (Cody et al. 2011), **pyrazines, imidazoles** and **carbazoles** (Remusat et al. 2005), **aromatic acids** (Martins et al. 2006) and alicycles including **cyclohexane** (Pilling et al. 2011) and **spiranes** (Whittet 1997, 69). Life, from a chemical perspective, may basically seem like a very specialized and incredibly innovative segment of that chemistry – this will be discussed in the following section.

Second, looking from the perspective of the "rocks", from the first moments the interstellar gas is heated by the young star, novel minerals and their associations form (Davis and Richter 2003). Thus, in short time, the initial repertoire of ca. 15 minerals found in interstellar grains grows to the estimated 250 present in primitive meteorites that did not go through planetary evolution (Hazen et al. 2008).

From the earliest stages of planetary volcanism certain geologically interesting molecules are created, including the infamous **chlorofluorocarbons** (CFCs) responsible for ozone depletion in the 1970s and 80s and other **halogeno derivatives of hydrocarbons** (Gribble 1994) which are present in volcanic gases. Later stages of geological evolution bring mostly mineralogical innovations which, because of their spectacular nature, deserve a short mention. It is estimated that from the 250 or so minerals present at the formation of Earth, the planet's mineral repertoire grew to a stunning 4300 (Hazen et al. 2008).

4.5. The Phase of Biological Chemistry: from the emergence of life to humans

Out of the 176 chemical phenomena distinguished for the purposes of this article, 43 are specific for the biological world. This may be little or a lot, depending on the perspective. Lacking a definite theory of abiogenesis, we may not safely discuss the amount and scope of physicochemical innovation necessary for the creation of life, but several general observations remain valid and several main biochemical novelties are well known. Let's list all the "usual suspects" which can be found in any cell biology or biochemistry textbook.

First of all, there are three main classes of complex biopolymers specific to biology: **proteins**, **carbohydrates** and **nucleic acids**. There are also other well-known large classes of biomolecules, either chemically well-defined, such as **lipids** and **alkaloids,** or ill-defined, such as **pigments** or **hormones**. Several smaller groups of compounds are found only in certain groups of living organisms:

sterols are typical for eukaryotes and as such are sometimes used as biomarkers in paleontology[3]; **lignins** and **tannins** are plant-specific; **chitin** is present only in fungi and certain groups of animals and **collagen** in animals only. An amusing example of evolution's ability of penetrate unusual segments of chemical creativity is the emergence of the ability to produce ultrasounds in certain groups of marine mammals which induces a range of novel biomechanical and **sonochemical** effects (Krasovitski 2011).

Second, the formation of life was related to a plethora of new chemical and physicochemical processes and properties, such as **stereoselectivity**[4] or the development of **disperse phase** and **colloid chemistry**. Lipid membranes are a rare example of natural **liquid crystals.** Biological systems exhibit high degree of control over **polymerization** and **depolymerization** under various chemical regimes. Cellular metabolism requires high-specificity **catalysis** including first true organic **enzymes** (unlike the generally low-specificity catalysis exhibited by mineral surfaces), exhibits instances of **autocatalysis** (e.g. in hammerhead ribozymes) and is based on a tightly controlled network of **chemical cycles** and **pathways**. Finally, the coordinated oxidation-reduction reactions in living cells and the very existence of ion pumps can be interpreted as **electrochemistry**.

4.6. The Phase of Human Chemistry

The purposeful activity of humans leads to the progressing penetration of all imaginable avenues of chemistry, from our first experiments with fire to modern analytical chemistry.

On the structural side, a bewildering array of atomic, molecular and supramolecular creations has been prepared in human laboratories whose appreciable stability or even the very existence seems very unlikely in nature. This is usually achieved by attaining right temperatures (especially ultralow temperatures), ultrapure substances or protective non-reactive atmospheres, whereas in typical natural environments thermal fluctuations, defect-causing admixtures or a highly reactive environment would stop these phenomena from manifestation. Out of the plethora of possible examples, this is a small selection just from the previous year selected to represent different levels of chemical organization, from nuclear and atomic, through molecular and macromolecular to biophysical:

- synthesis of several nuclei of element-113 (Morita et al. 2012) which does not occur naturally[5];
- observation of Bose-Einstein condensate-like processes in a molecular system (Stuhl et al. 2012) – an OH preparation which had to be cooled to few milikelvin;
- stabilization of boron-boron triple bonds (Braunschweig et al. 2012) by tailor-made bulky side groups;
- preparation of whole new classes of protein fold patterns not found in nature (Koga et al. 2012) achieved by computer-aided rational design of secondary structure sequences;
- creation of colloids exhibiting valence and directional bonding (Wang 2012) that were prepared through the careful design of asymmetrical colloid particles.

On the process side, all analytical techniques and tools of chemistry are obviously human inventions – from spectroscopy and mass spectrometry, to chromatography and gel electrophoresis. It is however disputable whether basic physico-chemical processes utilized in such methods are not at

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[3] Although this is sometimes disputed and sterol synthesis has been implicated in some prokaryotic groups, notably actinobacteria (Donova 2007).
[4] Spectroscopic signatures of homochirality are often suggested as a test for the presence of life in the context of astrobiology (Caglioti et al. 2006)
[5] Although it might be formed during explosive nucleosynthesis in supernovae (Botvina and Mishustin 2010).

work throughout the universe. For instance, the differential action of magnetic fields on ions of different charge – the physical basis for mass spectrometry – is clearly a process expected to be active in many astrophysical settings. It would be probably much harder to find a natural equivalent of gel electrophoresis, where a heterogeneous population of particles is separated in a homogeneous medium through the action of an electric potential. The complicated nature of chemical technology which involves the application of straightforward physico-chemical processes in complex and innovative procedures would require a separate study on its own.

5. The similarity of cosmic chemical transitions to phase changes

As already hinted in Section 3, the six phases described in the article are separated by short-lived episodes of intensive change which may be likened to phase changes. This should probably not be seen as surprising, as thermodynamics often permeates discussions of cosmic evolution (e.g. Prigogine and Stengers 1984; Kaufmann 1996; Schneider and Sagan 2006).

Four properties of such transition periods are especially suggestive of a similarity to classic phase changes known from elementary thermodynamics:

- the rapid nature of the transition,
- the intensity of ongoing changes,
- nucleation-like dynamics,
- the "freeze-out" of physical conditions at the time of transition.
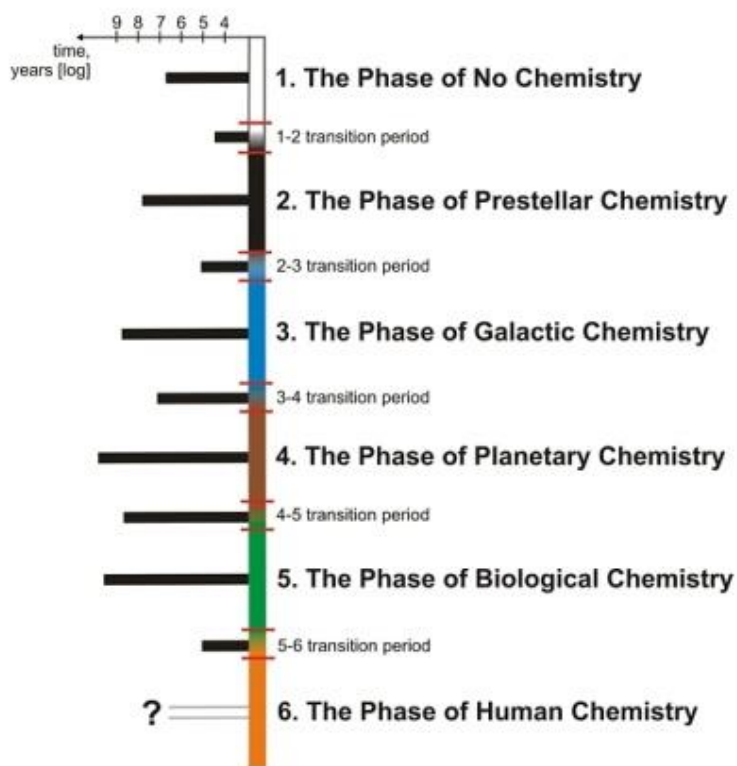
Let's take a look at these properties in some detail.

Fig. 3 *The summary of all major phases of cosmic chemical evolution with corresponding transition periods. The duration of these phases and "phase transitions" is indicated by the length of the black bars. More information in text*

5.1. The rapidity of transitions

The major constituent of the **1-2 transition** – the transition[6] from the H^+ to the H-dominated Universe – took about $1.6 \cdot 10^4$ years (Stiavelli 2009, p. 12), while the preceding **Phase of No Chemistry** lasted for about $4 \cdot 10^6$ years and the following **Phase of Prestellar Chemistry** lasted for about $5 \cdot 10^7$ until first stars collapsed (Stiavelli 2009, p. 24).

Further phases, as it has already been indicated, do not simply occur successively at well-defined moments of cosmic history, but are being constantly initiated locally, so one cannot determine their duration unambiguously. One cannot say, for instance, how long the Phase of Planetary Chemistry was, because planets still evolve after the formation of life. However, all the processes involved happen on typical timescales and the transition periods have their typical durations.

A natural timescale for the evolution of stars ranges from 10^7 to 10^{10} years. The **2-3 transition** occurs during the late stages of stellar evolution and it takes about 10^5 years from the moment heavy elements are first ejected into cooling stellar envelopes to the time when they have mostly condensed and reacted with each other (Herwig 2005). The **galactic chemistry** evolves on a timescale similar to the stellar evolution timescale: for instance, it takes Milky Way's interstellar gas around $5 \cdot 10^7$ years to travel between two star-forming regions which marks episodes of increased chemical enrichment, compression, heating and irradiation (Pagel 2006), interstellar grains have lifetimes on the order of 10^8 years (Jones 2004) and global enrichment of interstellar medium's metallicity takes ca. 10^9 years (Lineweaver 2001). Thus, 10^8 years will be assumed here as a natural timescale for this phase.

The interstellar medium undergoes the **3-4 transition** during the formation of planetary systems and it takes about 10^7 years from the moment interstellar matter enters the protoplanetary disk to the time when most chemical and mineralogical processes mentioned in Section 4.3. have occurred and planets are essentially formed (Trieloff and Palme 2006). It is more difficult to put a time limit on the **Phase of Planetary Chemistry** and the **Phase of Biological Chemistry**. We do not know how long planets and life can evolve, but this seems largely dependent on the timescale of their central stars' lives. Earth's chemistry has evolved unimpeded for ca. $4.6 \cdot 10^9$ years and the biosphere only slightly shorter, so, for lack of more data, this lower limit may be used as a first approximation.

We have no knowledge whatsoever of how long did it take for Nature to perform the **4-5 transition** (abiogenesis). It is generally assumed that first signs of life have appeared ca. $3.5\text{-}3.8 \cdot 10^9$ years ago (see e.g. Wacey et al. 2011), and only $4 \cdot 10^9$ years ago was our planet cool enough and safe from planetary-scale impacts to permit a stable hydrosphere (Williams 2007), so $5 \cdot 10^8$ years for the whole transition is a reasonable upper limit. If the rapid nature of large chemical transitions is in fact a regularity of Nature, it can be predicted that abiogenesis took considerably less time than that.

Human chemical creativity had its first episode of growth as soon as thermal processing of food and materials has been invented. However, large-scale experimentation with numerous levels of chemical organization is limited to modernity, with the rise of alchemy and the Industrial Revolution being probably two good examples of considerable advances in our conquering of the chemical universe. The timescale of **5-6 transition** can be thus estimated to be anywhere in the range of $10^4\text{-}10^5$ years. We have no reasonable way of estimating just how much future is left for the human race, with seriously published estimates ranging from 100 years (Rees 2003) to infinity (Dyson 1979), so I shall not attempt to estimate the duration of the Sixth Phase. Also, one may wonder whether the ongoing explosive growth of our chemical creativity should not be understood as suggestive of the transition

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[6] Where the word "transition" is used to denote the period in which the matter's ionization dropped from 99% to 1%.

phase, not of the plateau-like phase itself. Because human-related chemistry is not central to this article and because of the methodological issues raised by it, this last transition period and the last phase will not be included in the following calculations.

In summary, it is clear that transition periods are short in comparison to timescales typical of the chemical reservoirs created during these transitions (average duration of $1.3 \cdot 10^8$ and $2.1 \cdot 10^9$ years, respectively).

5.2. The intensity of changes

The importance of transition periods for the chemical evolution of the universe was described in detail in Section 4, but it might be helpful to gather in one place the quantitative side of the discussion, i.e. the number of UDC classes describing phenomena appearing at a given stage of cosmic evolution (Tab. 1). The larger concentration of chemical evolution in transition periods than in phases is clear (average number of innovations per million years of 333 and 0.004, respectively).

The stage of cosmic evolution (1)	Number of chemical innovations (2)	Duration/ timescale in years (3)	Innovations per million years (4)
1. The Phase of No Chemistry	0 (0%)	$4 \cdot 10^6$	0
1-2 transition period	8 (5%)	$1.6 \cdot 10^4$	500
2. The Phase of Prestellar Chemistry	0 (0%)	$5 \cdot 10^7$	0
2-3 transition period	83 (47%)	$1 \cdot 10^5$	830
3. The Phase of Galactic Chemistry	15 (9%)	$1 \cdot 10^8$	0.015
3-4 transition period	23 (13%)	$1 \cdot 10^7$	2.3
4. The Phase of Planetary Chemistry	4 (2%)	$4.6 \cdot 10^9$	0.00087
4-5 transition period	22 (13%)	$5 \cdot 10^8$	0.044
5. The Phase of Biological Chemistry	15 (9%)	$4.6 \cdot 10^9$	0.0032
5-6 transition period	*6 (3%)**	?	-
6. The Phase of Human Chemistry	*0 (0%)**	?	-
Total	176 (100%)		

Tab. 1 The summary of the results discussed in the text. The column (2) is calculated as the number of UDC classes describing phenomena appearing at a given stage of cosmic evolution. The asterisk refers to the stages involving human-related UDC classes which have been partly excluded from the analysis for reasons described in Section 2 and Section 4.6. In cases of controversy mentioned in Section 5.1, column (3) always contains the "pessimistic" number, i.e. the one least favorable for the hypothesis described in the text. Column (4) is calculated as $10^6 \cdot (2) \cdot (3)^{-1}$, although this "measure" must obviously be taken with a grain of salt

5.3. Nucleation-like dynamics

All transitions in the early universe are normally treated as phase transitions (Kibble 1982) and are expected to involve nucleation and even "bubble formation" (Liu et al. 1992). The localized initiation of all other phases of cosmic chemistry has already been described in Section 3. For instance, the ongoing transition from The Phase of Primitive Gas to the Phase of Enriched Gas takes place in individual stars and only later the high-metallicity gas with grains is spread throughout the galaxy.

5.4. The freeze-out of physical conditions

The "freeze-out" of certain physical conditions is best-known from those classical phase transitions which involve a symmetry break. For instance, during the crystallization of liquid water, a macroscopically isotropic liquid turns into an anisotropic solid, and the momentary configuration of water molecules at the point of nucleation determines the orientation of the ice crystal lattice. Which is

especially important, once the optical axis has been "chosen", it is stable and will not change unless dramatic physical processes occur. Similar processes also discussed in cosmology (where momentary conditions of the Universe during phase transitions may have quite dramatic consequences, see e.g. Smolin 1995).

This effect, applied to the evolution of cosmic chemistry, is probably best documented in the emergence of planetary chemistry and will be described in some detail in the following section. It will be shown there that the momentary composition of the protoplanetary disk at the moment of the formation of a given planetary body will strongly determine its future chemical evolution. Because our knowledge of living systems is limited to a single example, we can only speculate on how much a slightly different composition of Earth at the moment of abiogenesis would change the chemistry of life (Bains 2004).

There is no convincing evidence that the local state of interstellar matter during the planetary system formation influences its further evolution, although the injection of short-lived radioactive nuclides which dramatically influenced the evolution of Solar System bodies (Trieloff and Palme 2006, p. 77) may be thought of as a suggestive example of a process that contains a strong element of randomness. Also, the irreversible nature of the "choice" is well illustrated by the relative isolation of planetary systems which will be discussed in the following chapter.

6. The importance of planetary systems for chemical evolution

The cosmological importance of planetary systems may seem difficult to assess, as we know in detail only one such system. To put the problem in a proper perspective, let's note that a recent evaluation of the Kepler data revealed that ca. 23% of all stars should harbor a close-in Earth-mass planet (Howard 2010), which gives a conservative number of 50 billion planetary systems similar to ours in the Milky Way alone. However, even our limited sample of one can yield valuable insights. Consider the following facts.

First, let's note that the interstellar matter is relatively well-mixed (De Avillez and Mac Low 2008), so all planetary systems can be approximately treated as starting with a similar chemical composition. Also, because of the pressure of stellar winds and the shielding properties of heliospheric electromagnetic currents (Burgess 1997), planetary systems develop with little external influx of matter.

Second, the early stages of planetary system evolution act to separate this initial homogeneous matter into a number of heterogeneous planetary-size reservoirs. This is mostly achieved by the orchestrated action of two groups of processes (Trieloff and Palme 2006). 1) Temperature gradients and gravitational forces fractionate elements and chemical compounds by condensation point and mass, respectively. This works both in protoplanetary disks (leading to the existence of metal- and rock-rich, gas-rich and ice-rich sectors of Solar System) and later in individual planets (leading to the existence of metallic cores, rocky mantles, atmospheres and cryospheres). 2) Gravitational interactions in the protoplanetary disk lead to the formation and migration of planets and their smaller companions.

Third, these processes create a very diverse population of objects. In our Solar System, there are ca. 30-40 bodies large enough to have been rounded by gravity[7]. Even a cursory look at them reveals considerable diversity, even based on coarse orbital, thermodynamic, geophysical or

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[7] It is a simple criterion used sometimes in planetary science to distinguish "small" from "big" bodies and appears currently in the IAU's definition of a "planet" (Soter 2006).

geomorphological criteria (see e.g. Taylor and McLennan 2008; Melosh 2011; Watters and Schultz 2012). Were there only a limited number of ways in which protoplanetary evolution can partition the solar nebula into planetary-size bits, we should expect duplicates in our sample of 30+ such bodies. This is definitely not the case. Also, even our limited knowledge of extrasolar planetary systems shows that there are vast variations in their general architecture (Marcy et al. 2006), including the now confirmed discovery of planets orbiting binary systems (Doyle et al. 2011).

Fourth, even tiny variations of such general planetary parameters translate to peculiar chemical phenomena. The colorful appearance of Jupiter's Io, for instance, is caused by the temporary break-up of the familiar cyclo-octal sulfur compound S_8 into unusual chain forms (Geissler 2003) which are highly unstable on Earth. For similar reasons related to elemental concentrations, a rich chlorine chemistry operates on Venus (Zhang et al. 2012). On Saturn's Titan, the lack of atmospheric oxygen led to peculiar chemical phenomena, including the hypothesized oxygen-less biochemistry with familiar molecules having their "ammono analogs", such as "ammono-ribose" with amines instead of hydroxyls and a nitrogen heteroatom in the ring (Raulin 1997).

Note that these local effects are not just curiosities of little cosmological importance. It is on the surfaces of the planets that a large part of the universe's chemical creativity seems to unfold. Out of the 176 chemical phenomena studied here, 52 occur only in the context of planetary systems, and a more detailed analysis would almost certainly increase this proportion even further. The special case of life serves only to accentuate that point.

Therefore, planetary systems may be seen as "atoms" of cosmic chemical creativity: isolated laboratories where an initial homogeneous mixture is, through a highly efficient randomizing procedure, fractionated and subjected to various physical influences to yield a rich repertoire of chemical (and physical, mineralogical, geological…) phenomena. Based on what has been said above, it seems clear that our planetary system does not represent all of the cosmic chemical creativity. The 30% of all chemical phenomena studied here that are specific to planetary systems represents only a very limited sample of one, whereas spectroscopic observations of interstellar matter give us data from multiple spots, including extragalactic sources. To put it differently, an inclusion of only one planetary system to the census of chemical phenomena increased its size by a half – and there are literally billions of other planetary systems out there which may be reasonably suspected to host their own novel "chemistries". If this perspective is valid, an increasing penetration of extrasolar planetary systems should bring a growing appreciation of the peculiar, local and accidental nature of the chemistry that we know of.

7. Conclusion

The method described in the article was designed to shed light on the complex relationships between chemistry and other natural sciences, but not in a static, "nomothetic" (roughly: law-based) sense, but in the "idiographic" (again, roughly: fact and event-based; for the source of this dichotomy, see: Windelband 1894) perspective of cosmic evolution. The evolution of galactic, stellar, planetary and biotic systems proceeds with concurrent evolution of chemical phenomena, and chemistry (understood as the totality of phenomena studies by chemical sciences) can be seen as a key element in the functioning of the cosmic organism, from its simple "embryonic" stage to the present moment.

It is vital to clearly understand the place of chemistry in natural sciences. Unfortunately, this issue is usually seen through the "static" perspective of theoretical reductions, i.e. the reduction of chemistry to physics, the reduction of biology to chemistry etc. Even a cursory look at the literature

shows that the problem of reduction is still one of the major open issues in philosophy of chemistry (Vihalemm 2001, Earley 2004, Ostrovsky 2005, Scerri 2007, Boeyens 2008: p. vi.) and the reduction of chemistry to quantum mechanics seems to be one of the defining issues for the identity of chemical sciences. This "nomothetic" perspective, as I have already argued elsewhere (Lamza 2010), conceals the fact that chemistry seen as part of the "idiographic" study of the history of the Universe is no more reducible to physics than physics to chemistry. In fact, this article intended to demonstrate that it is virtually impossible to understand the early Universe, the galaxies, stars, stellar envelopes, protoplanetary systems or planets themselves without a proper appreciation for the growth of chemical complexity through time. From a "cosmo-historical" perspective, the reduction of chemistry to physics is simply an absurd proposition; the most one could hope to prove is the reduction of a very tiny subset of chemical sciences – the study of small molecular systems – to a very tiny subset of physical sciences – the quantum theory; and even that is still controversial (see the references above).

However, for this to be adequately appreciated, a very broad look at chemistry is needed. In philosophy of science chemistry is too often represented as a computational science concerned with calculating, to the n-th decimal place, the bond lengths and angles of small molecules. The dizzying richness of chemical phenomena – which includes colloids, flames, electrochemistry and liquid crystals – is intimately intertwined with the richness of the evolving Cosmos, and in that perspective the traditional "big" issue of intertheoretic reduction seems irrelevant and marginal for the identity of chemistry as part of the landscape of natural science. This led to the decision to use a library catalogue as a source of inspiration for describing "chemistry as such" – a source which aims to contain a broad and rationally organized catalogue of all conceivable issues which are traditionally regarded as part of "chemistry".

I believe that there is a large and as yet unrecognized philosophical potential in library catalogues. After all, they are probably the best shot that humanity has had at compiling exhaustive and detailed lists of issues relevant for any conceivable topic – even if created without a particular philosophical agenda, with the praxis of cataloguing books as a stated goal. The UDC catalogue's section 5 is in fact a well-thought, cleverly organized list of "all things that scientists write books about" – and is thus as good a starting perspective on the subject of "all things chemical" as one can hope for. This article intends to demonstrate this potential in the study of the "cosmic history of chemical phenomena" – where the assembled list of 176 chemical phenomena is not treated as a final word on "what chemistry is", but as a starting point that should give the reader a feeling that at least a fair sample of topics in chemistry has been included. It should be noted that some subjects that might be considered parts of chemistry are outside the main "chemical" UDC classes listed in Section 2 (e.g. "550.4 Geochemistry").

Overall, it is clear that this method has limitations; after all, library catalogues are primarily created to help librarians, not to shed light on cosmic order. One good choice for future research of this point would be to try to supplement the list drawn from the UDC with a number of other sources, such as comprehensive lists of astromolecules, published classification of organic molecules etc.

Some philosophically interesting results that are systematically exposed by the method described in the article were already alluded to, such as:

- the causal relationship between the formation of chemical structures and the growing complexity of electromagnetic spectra;
- the role of solid-state catalysis for large-scale astrophysical phenomena;

- the dependence of the formation of important classes of materials, such as solids, gels, colloids or liquid crystals, on the preceding chemical processes;
- the role of human creativity in the development of cosmic chemistry.

That may be seen as another contribution to the unraveling of the complicated relationship between physics and chemistry, which is not limited to the reduction of chemistry to physics. Currently the inclusion of all 185 physics-related level-V UDC classes to the scheme described in this article is underway and it can be estimated that about 80% of physical processes denoted by those classes are directly causally linked to the preceding evolution of chemical phenomena[8].

A final advantage of the method may be now discussed: it naturally allows one to discuss the universe's repertoire of chemical phenomena within a framework that is equally well suited for chemistry as it is for astrophysics, mineralogy, geology or biology. This brings us even closer to see all natural sciences as a single science concerned with a single object – the evolving Cosmos. In fact, preliminary results show that the inclusion of further 717 level-V UDC classes representing the rest of natural sciences shows considerable similarity of the patterns of cosmic evolution regardless of the type of system under consideration. Also, with a tool of that sort it can be shown in detail how physical, chemical, biological and geological innovations co-occur throughout the past 3 billion years of our planet's evolution (the great atmospheric oxidation event of 2.4 billion years ago being a particularly beautiful example) and what is the place of chemical phenomena in that process. Thus, chemical phenomena may be consistently described as part of the general architectonics of the universe, as exemplified by the use of the formalism of phases and phase transitions in Section 5.

Thus, this "cosmohistorical" perspective on chemical phenomena may make it easier to appreciate the "function" of chemistry in the world, i.e. to try to understand what chemistry *does* as part of the evolving organism of the Cosmos, in unison with cosmological, astrophysical, geological, atmospheric, biological or technological phenomena.

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[8] It is important to remember that the – admittedly very tenuous – quantitative flavor to this estimation is not intended as a demonstration of an objective measure, but rather as a stimulation to further discussion.

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