Highlights on Spanish Astrophysics X, Proceedings of the XIII Scientific Meeting of the Spanish Astronomical Society held on July 16 – 20, 2018, in Salamanca, Spain. B. Montesinos, A. Asensio Ramos, F. Buitrago, R. Schödel, E. Villaver, S. Pérez-Hoyos, I. Ordóñez-Etxeberria (eds.), 2019

The catalytic role of chondrites in the prebiotic enrichment of Earth.

Josep M. Trigo-Rodriguez[1,2], and Raffaele Saladino[3]

[1] Institute of Space Sciences (CSIC), Campus UAB, c/Can Magrans s/n (Bellaterra), 08193 Cerdanyola del Vallès (Barcelona), Catalonia, Spain
[2] Institut d'Estudis Espacials de Catalunya (IEEC), C/ Gran Capità, 2-4, desp 201, 08034 Barcelona, Catalonia, Spain
[3] Biological and Ecological Department (DEB), University of Tuscia, 01100 Viterbo, Italy.

Abstract

The carbonaceous chondrites are among the most primitive materials arrived to the Earth's surface, and they are associated with undifferentiated bodies. Their chemical and mineralogical content reveal that they probably accreted far from the Sun and formed part of transitional asteroids and comets, both C and water-rich. Formed by fine-grained aggregates at relatively low-encounter velocities, they ended as porous bodies that retained significant amounts of water, organics and volatile compounds that were available in the outer protoplanetary disk. These bodies participated actively in the delivery of volatiles to the planets, particularly during the so-called Late Heavy Bombardment, but we should take into account that also preserved and transported highly reactive minerals to planetary bodies at different moments of their evolution. The catalytic properties found of these meteorites suggest that the arrival of these minerals to planetary surfaces with abundant water and N-bearing species could have promoted organic complexity. .

1 Introduction

The scientific interest of understanding the physico-chemical properties of the accretionary materials available in the protoplanetary disk is out of doubt. Meteoritica give us an amazing opportunity because mother nature offers in every meteorite fall rocks arrived from remote, but typically unknown, bodies. Then, it is not surprising that the currently ongoing sample return missions, Hayabusa 2 and OSIRIS REx, have primitive carbonaceous asteroids as targets, respectively named 162173 Ryugu and 101955 Bennu.

The growing interest of the scientific community can be understood given that the carbonaceous chondrite meteorites (hereafter CCs) have being identified as pristine materials with a primordial chemical content and specific unique properties [12] and [1]. The key role of these materials in the origin of life was envisioned many decades ago [14], but it is now reinforced by new discoveries about aqueous alteration ago [9], and [25]. CCs formed in the outer regions of the protoplanetary disk and accreted crystalline and amorphous minerals, plus organics, ices and hydrated minerals. Being formed so far away as part of relatively small asteroids that never melted, the CCs available in meteorite collections are fine-grained rocks that we could consider a kind of fossil sediments of creation. Being highly porous and fragile, these fascinating meteorites share unusual properties with their undifferentiated parent bodies: low conductivity and thermal inertia, weak magnetism and low tensile strength. CCs can be considered good proxies of the materials forming C-rich asteroids, but still can be considered rocks biased by the nature, as they have arrived to the Earth's surface after many destructive processes. Then, not only similar properties, but also spectral signatures point that small asteroids and comets are formed by CCs. Being small and fragile [22] remnants of creation, at the very beginning were scattered all over the solar system and subjected to collisions, and fragmentations [2]. In particular, close approaches experienced to planets could have induced the fragmentation of these fragile objects. As a natural consequence of being weakly compacted and collisionally fragmented objects, I envision that they were easily disrupted and arrived to different planetary bodies as a rain of meteoroids [22]. Such processes could have being necessarily intense during the Late Heavy Bombardment. By comparing with the measured projectile Lunar flux over time, we estimated that the early Earth was subjected to a meteoritic flux that could have been at least about 5-6 orders of magnitude larger than the current one [20]. It obviously traduces in huge amounts of chondritic materials reaching the Earth's surface about 4 Ga ago, at an annual rate of thousands of billions of metric tons [20]. Consequently the amount of volatiles delivered under such high-flux circumstances are also very significant, playing a key role in fertilizing the Earth's surface [5]. Then, the reactive minerals forming CCs reached the surface of Earth and other planetary bodies, being exposed to a warm, and water-rich environment that was probably promoting the first steps towards the origin of life [20]. To support the previously outlined hypothesis we have recently made a significant progress in understanding the role of chondrites in prebiotic evolution. In a previous paper we analyzed the catalytic effect of six CCs. Here we will focus in the main implications of our previous discovery [16] concerning the catalytic properties of the rock-forming chondritic minerals.

2 Technical procedure

We developed an experiment to know the reactivity of CCs that was previously described [16]. The procedure started with $\sim$50 mg of each selected stone that were ground in an agate mortar. Then, the extraction of the meteorite powder to remove endogenous organics is carried out in two steps as previously reportedmarty12. Mass spectrometry was performed by the following program: injection temperature 280°C, detector temperature 280°C, gradient 100°C×2min, 10°C/min for 60 min. To identify the structure of the products, two strategies were followed. First, the spectra were compared with commercially available electron mass spectrum libraries such as NIST (Fison, Manchester, UK). Secondly, GC-MS analysis was repeated with standard compounds. The results clearly indicate that carbonaceous chondrites catalyze the synthesis of natural nucleobases, carboxylic acids, and amino acids from mixtures of NH2CHO and water at 140°C. Two general scenarios were analyzed: thermal water (TW) and seawater (SW), both tested in the presence of formamide for six CCs that are listed in Table 1.

Table 1: Antarctic carbonaceous chondrites used in the experiments described

Meteorite name	Group and petrologic type	Discovery year
Allan Hills 84028	CV3	1984
Elephant Moraine 92042	CR2	1992
Miller Range 05024	CO3	2005
Larkman Nunatak 04318	CK4	2003
Grosvenor Mountains 95551	C-ung	1995
Grosvenor Mountains 95551	C2-ung	1995

3 Discussion

The results of our experiments were presented in [16]. They confirm that carbonaceous chondrites in presence of warm water and formamide catalyze the synthesis of natural nucleobases, carboxylic acids, and amino acids from mixtures of NH2CHO and water at 140°C (see Fig. 1). This experimental evidence supports a parent body origin for the complex organic compounds found in CCs, probably coming from hydrated asteroids as previously suggested [25]. Secondary minerals being the product of such primordial aqueous alteration were originated in a first stage of water release due to radiogenic heating [1], and show evidence of static aqueous alteration with limited water availability producing complex organic chemistry [17];[11]. Still in such restrictive conditions the reactive minerals could act as catalyzers and promote increasing organic complexity in chemical evolution, tens of millions of years before to be completed the formation of Earth [16]. These results shape a prebiotic scenario consisting of CCs debris reaching the Earth's surface and acting as catalysts, particularly in a volcanic-like environment. Such scenario could be favoured by the fact that the the flux of chondritic materials was probably very high in the remote past. We have suggested that chondritic materials reaching the Earth's surface about 3.8 Ga ago during the so-called Late Heavy Bombardment, may have reached an annual rate of thousands of billions of metric tons [20]. Such amounts could have increased as consequence of the disruption of fragile C-rich transitional objects scattered by the inwards migration of the giant planets probably occurred 3.8 Ga ago [3].

In view of our results, we think that new experimental and theoretical approaches are needed to understand the role of certain reactive minerals in promoting the catalytic reactions. For example, the interaction of organic compounds with water and chondritic silicate surfaces has been recently explored using quantum chemical periodic simulations [15]. Often we get clues on the required experiments when we study the nature of aqueous alteration minerals

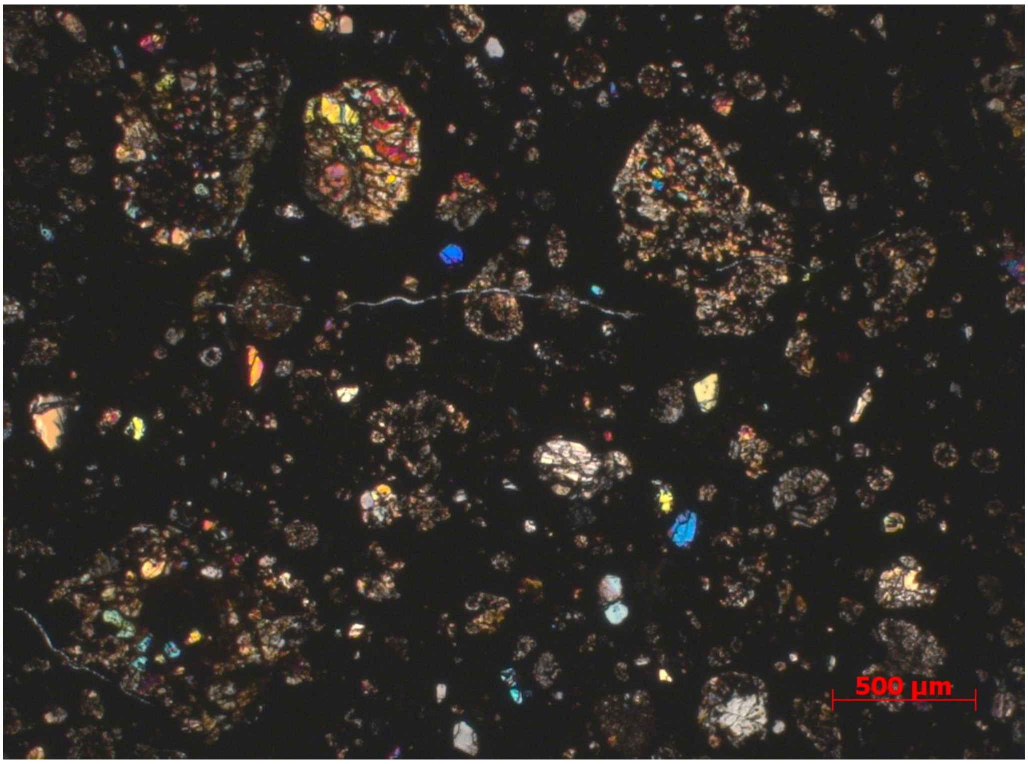

Figure 1: Prebiotic synthesis of biomolecules from the selected meteorites and water in the presence of formamide. Experimental conditions: 1% meteorite, 59% NH2CHO, 40% water, 140 °C, 24 h. The meteorite shown as example is GRO95551 in a NASA image containing a cubic cm as scale.

in the matrices of carbonaceous chondrites (see Fig.2). We notice that water played a major role in mobilizing certain elements initially present in the interiors of the chondrules, sulphide and metal grains of carbonaceous chondrites [18]. In some groups, like e.g. CM and CR chondrites, the action of water was pervasive, and participated in the partial or complete replacement of mineral grains located in the matrix. Minerals preferentially grew in the pores available in the matrix of carbonaceous chondrites [21]. In general, we can say that liquid water availability was very limited, and dependent of the primordial heat produced by the decay of short-lived nuclides. This is consistent with the dated aqueous alteration minerals, formed during the first 10 Ma after parent body accretion, see e.g. [8]. Then, we can conclude that aqueous alteration was localized and static [24]. Consequently, even when we found that chondritic minerals are extremely reactive, we think that planetary bodies are far better candidates to catalyze complex organics over long time scales. That point is not a big issue given the continuous delivery of chondritic minerals to the surface of Earth and other solar system planetary bodies [4].

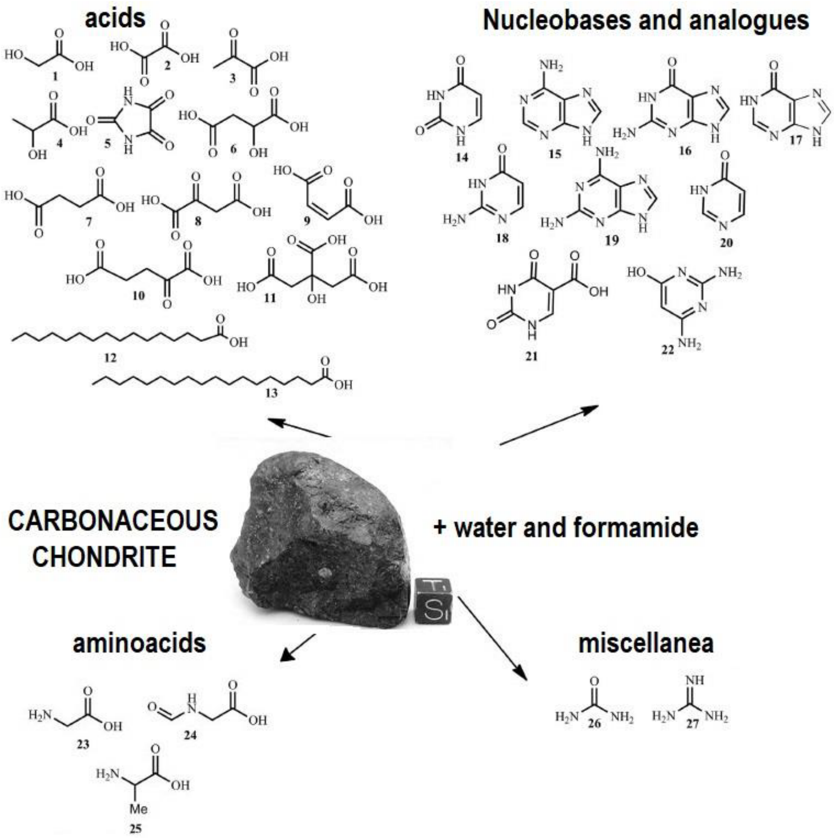

Figure 2: Transmitted image of the pristine CO3 chondrite Allan Hills 77307. The fine-grained organic-rich matrix of carbonaceous chondrites was a perfect place to retained hydrated minerals, and ices during parent body accretion. Crystalline silicate chondrules share their boundaries with the matrix and participate in the elemental mobilization.

Table 2: The products listed in Fig. 1 of the thermal condensation from NH2CHO/water mixtures in the presence of the powders of selected carbonaceous chondrites. For more details see: [16].

Product #	Compound
1	Glycolic acid
2	Oxalic acid
3	Pyruvic acid
4	Lactic acid
5	Parabanic acid
6	Malic acid
7	Succinic acid
8	Oxaloacetic acid
9	Fumaric acid
10	Ketoglutaric acid
11	Citric acid
12	Palmitic acid
13	Stearic acid
14	Uracil
15	Adenine
16	Guanine
17	Hypoxanthine
18	Isocytosine
19	2,6-Diaminopurine
20	4 (3H)-pyrimidinone
21	Uracil 5-carboxylic acid
22	2,4-diamino-6-hydroxypyrimidine
23	Glycine
24	Formyl glycine
25	Alanine
26	Urea
27	Guanidine

4 Conclusions

We have performed a series of laboratory experiments with carbonaceous chondrites that demonstrate that these meteorites can actively and selectively catalyze the formation of biomolecules from formamide in aqueous media and under presence of formamide. The presence of a N-bearing specie like formamide was found to be an important premise to catalyse organics [19]. In our new experiment we found specific catalytic behaviours, depending on the origin and composition of the chondrites and on the type of water present in the system (activity: thermal > seawater > pure). In any case, we reported in the one-pot synthesis of all the natural nucleobases, of aminoacids and of eight carboxylic acids (forming, from pyruvic acid to citric acid, a continuous series encompassing a large part of the extant Krebs cycle). See Figure 1, and Table 2 for a short list of the main products found in our experiments.

As it was previously explained in discussion, having into account the intense meteoritic flux extracted from the study of the Moon surface [20], we envision a general prebiotic scenario consisting of carbonaceous meteorite debris reaching the Earth's surface and acting as catalysts in a volcanic-like environment providing heat, thermal waters and formamide. Obviously that scenario can be extended to other planetary bodies, particularly those who had water- and N-rich environments. Consequently, other potential planetary bodies could have experienced a significant delivery of carbonaceous chondrite materials, like e.g.: Mars, Europe or Titan [20]. Our scenario is particularly favourable for Mars, which has been exposed to the continuous infall of chondritic materials over the eons, and with a extremely thin atmosphere. It is also remarkable that atmospheric changes in Mars were regional or even global, involved in brine evolution and the formation of evaporites during the Amazonian era [7]. The interaction of water with the Mars surface is demonstrated by the presence of aqueous alteration minerals found in old Martian meteorites, like e.g. the carbonates formed in the fractures of Allan Hills 84001 orthopyroxenite about 4 Ga ago [13]. Over time, varying rock/soil compositions could have produced water fluids with different PH levels, so some specific environments could have being more favourable to organic catalysis. In fact, recent discoveries of organic matter preserved at Gale crater and other Martian environments are particularly promising [6], and could be used to encourage the search of older sediments not exposed to the extreme surface environment.

Consequently, we think that our discovery of the unique catalytic properties of the minerals forming chondritic meteorites could open a debate about the ability that these rocks have to produce favourable prebiotic scenarios in other worlds different to our own. Future exploratory missions of solar system planetary bodies should try to identify old terrains, carrying instrumentation to dig, collect and characterize the organic compounds present in sequential layers, and also including specific experiments to study the reactivity of the sampled minerals under the presence of hot water and formamide.

We have performed a series of laboratory experiments with carbonaceous chondrites that demonstrate that these meteorites can actively and selectively catalyze the formation of biomolecules from formamide in aqueous media and under presence of formamide. The presence of a N-bearing specie like formamide was found to be an important premise to catalyse organics [19]. In our new experiment we found specific catalytic behaviours, depending on

the origin and composition of the chondrites and on the type of water present in the system (activity: thermal > seawater > pure). In any case, we reported in the one-pot synthesis of all the natural nucleobases, of aminoacids and of eight carboxylic acids (forming, from pyruvic acid to citric acid, a continuous series encompassing a large part of the extant Krebs cycle).

Acknowledgments

We thank the NASA Meteorite Working Group for providing the samples that were studied in the framework of two Spanish research projects (AYA2011-26522 and AYA2015-67175-P, PI: JMTR) to identify pristine meteorites, and study their properties. Chemical analyses were supported by the Italian Space Agency (ASI) project "Esobiologia e Ambienti estremi: dalla chimica delle Molecola allaBiologia degli estremofili" Number 2014-026-R.0 (CUP: F 92I14000030005).

References

[1] Alexander, C.M.O'D., McKeegan, K.D. and Altwegg, K. (2016) Space Sci. Rev. 214, 36.

[2] Beitz E., Blum J., Parisi M.G., and Trigo-Rodríguez J.M. (2016) Ap.J. 824, art.id.12, 29 pp.

[3] Bottke W.F., Vokrouhlicky D., Minton D., Nesvorny D., Morbidelli A., Brasser R., Simonson B., and Levison H.F. (2012) Nature 485, 78-81.

[4] Brownlee, The origin and properties of dust impacting the Earth, in: Accretion of extraterrestrial matter throughout Earth's history, B. Peucker-Ehrenbrink and B. Schmitz Eds. Kluwer Academic/Plenum Publishers, New York, USA, 2001, pp. 1–12.

[5] Court R.W. and Sephton M. A. (2014) Geoch. Cosmoch. Acta, 145, 175.

[6] Eigenbrode J. L. et al. (2018) Science 360, 1096-1101.

[7] Fairén A.G., Schulze-Makuch D., Rodríguez A.P., Fink W., Davila A.F., Uceda E.R., Furfaro R., Amils R., McKay C.P. (2009) Plan. Space Sci., 57, 276-287.

[8] Fujiya W., Sugiura N., Sano Y., and Hiyagon H. (2013) Earth Planet. Sci. Lett. 362, 130-142.

[9] Glavin D. P. and Dworkin J. P. (2009) PNAS 106, 5487-5492.

[10] Martins, Z., Alexander, C. M. O'D., Orzechowska, G. E., Fogel, M. L., and Ehrenfreund P. (2007) Meteoritics & Planetary Science 42, 2125.

[11] Martins, Z., Price M.C., Goldman N., Sephton M.A., and Burchell M.J. (2013) Nature Geoscience volume 6, pages 1045–1049.

[12] Marty B. (2012) Earth Planet. Sci. Lett. 313-314, 56-66.

[13] Moyano-Cambero C.E., Trigo-Rodríguez J.M., Benito M.I., Alonso-Azcárate J., Lee M. R., Mestres N., Martínez-Jiménez M.; Martín-Torres F.J., and Fraxedas J. (2017) Meteorit. Planet. Sci. 52, 1030-1047.

[14] Oró J. (1961) Nature 190, 389-390.

[15] Rimola, Trigo-Rodríguez J.M., and Martins Z. (2017) Phys. Chem. Chem. Phys., 2017, 19, 18217

[16] Rotelli L., Trigo-Rodríguez J.M., Moyano-Cambero C.E., Carota E., Botta L., Di Mauro E. and Saladino R. (2016) Scientif. Rep. 6, doi:10.1038/srep38888

[17] Pizzarello S. and Cronin, J.R. (2000) Geoch. Cosmoch. Acta 64, 329-338.

[18] Rubin A.E., Trigo-Rodríguez J.M., Huber H., and Wasson J.T. (2007) Geoch. Cosmoch. Acta 71, 2361-2382.

[19] Saladino, R., Crestini, C., Cossetti, C., di Mauro, E., Deamer, D. (2011) Origins of Life and Evolution of Biospheres 41, 437-451.

[20] Trigo-Rodríguez J.M., Llorca, J. and Oró, J. (2004) In Life in the Universe: from the Miller experiment to the search for life in other worlds. Seckbach J., Chela-Flores J., Owen T. y Raulin F. (eds), Kluwer Publishers, Dordrecht, Holland, pp. 201-204

[21] Trigo-Rodríguez J.M., Wasson J.T., and Rubin A.E. (2006) Geoch. Cosmoch. Acta 70, 1271-1290.

[22] Trigo-Rodríguez J.M., and J. Blum (2008) Plan. Space Sci., 57, 243.

[23] Trigo-Rodríguez J.M., and J. Martín-Torres (2012) Plan. Space Sci., 60, 3-9.

[24] Trigo-Rodríguez J.M. (2015) In Planetary Mineralogy, EMU Notes in Mineralogy 15 pp. 67-87.

[25] Zolensky, M.E., Krot, A.N., Benedix, G. (2008) In: Oxygen in the Solar System (G.J. MacPherson, D.W. Mittlefehldt, J.H. Jones & S.B. Simon, editors). Reviews in Mineralogy & Geochemistry, 68. Mineralogical Society of America, Washington, D.C., pp.429-462.