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Organic matter formed from hydrolysis of metal carbides of the iron peak of cosmic elemental abundance

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Abstract: This work is a modern revisitation of an old idea of great chemists of the past such as Berthelot, Mendeleev, Cloez and Moissan: the formation of organic matter under pre-biotic conditions starting from the hydrolysis of metal carbides. This idea was originally proposed for the formation of petroleum in the Earth and was extended to other bodies of the solar system by Sokolov at the end of the 19th century. The reason for this revisitation lies in the fact that complex organic matter resembling a petroleum fraction may exist in certain protoplanetary nebulae. The present work starts with a survey of the theory of the inorganic origin of petroleum and reports on current evidence for its derivation from residues of formerly living matter, but also considers theories that admit both a biogenic and an abiogenic origin for petroleum. By considering the cosmic abundance of elements and the evidence concerning the presence of carbides in meteorites, we discuss the formation, structure and hydrolysis products derived from the metal carbides of the iron peak of cosmic elemental abundance. Chromium carbide (Cr_3C_2) has then been used as a model compound for all the key carbides of the iron peak of the cosmic abundance (Cr, Fe, Ni, V, Mn, Co) and it has been hydrolysed under different conditions and the hydrocarbons formed have been analysed using electronic spectroscopy, high-performance liquid chromatography with a diode-array detector (HPLC-DAD) and by Fourier-transform infrared (FT-IR) spectroscopy. Methane, a series of about 20 different alkenes with single and conjugated double bonds have been detected. Paraffins are formed simultaneously with the alkene series but no acetylenic hydrocarbons have been detected. This study confirms early works considering the easy hydrolysis of the carbides of Cr, Fe, Ni, Mn and Co with the formation of H_2, a series of alkanes including methane and a series of alkenes including ethylene. The peculiar behaviour of copper carbide (copper is inside the iron peak of the cosmic abundances) has been discussed as well. A survey of the hydrolytic behaviour of other carbides has been included so that all lanthanides and actinides are considered as well as carbides of the second and third groups of the periodic table of elements and highly refractory carbides such as those of Ti, Zr, Ta and W have been briefly discussed. Furthermore, the hydrolysis of mixed metal carbides and nitrides is discussed, which gives a mixture of extremely interesting molecules that are considered the raw materials for the formation of the molecules of life: guanidine, methyl hydrazine, formic acid, hydrogen cyanide, urea, cyanamide, methylamine and formaldehyde. The hydrolysis of metal carbides has also been discussed within the framework of other reactions that are well considered in the present day in an astrochemical context: the ion–molecule reaction, the Miller–Urey and the Sagan–Kaare synthesis as well as the catalytic Fischer–Tropsch synthesis and the radiation-driven Fischer–Tropsch synthesis.

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Introduction

In a previous work we have discussed the possibility that the carrier of the unidentified infrared bands (UIBs) of the interstellar medium and especially of the emission spectra of the protoplanetary nebulae, could be represented by certain petroleum fractions (Cataldo *et al.* 2002a, b). Furthermore, we have shown that it is possible to change and increase the degree of aromatic content of the petroleum fractions by using Stoll's reaction (Cataldo & Keheyan 2003). This reaction is analogous to that occurring over geological timescales on organic matter under the action of heat and pressure. We have also addressed our discussion to the possible formation of petroleum fractions or petroleum-like organic matter, which could exist both in the interstellar medium and in the protoplanetary nebulae. Although petroleum and other organic matter present in Earth sediments appears today to be formed from the degradation and processing of formerly living organic matter, we have proposed an inorganic origin for the petroleum-like organic matter present in the interstellar medium, in the protoplanetary nebulae and also in certain carbonaceous meteorites.

It is now commonly accepted by the scientific community that petroleum (and coal) in the Earth originate from both organic sediments derived from living matter that has undergone an initial diagenesis under the action of certain microorganisms and catagenesis processes under different degrees of burial conditions at moderate temperatures (Durand 1980; Proskouriakov & Drabkine 1983; Barker 1985; Van Krevelen 1993). There are a number of experimental pieces of evidence that are used as proof of this interpretation; the most useful ones to mention here are:

- the optical activity of petroleum and petroleum fractions, which was discovered by Biot in 1835 (Oakwood *et al.* 1952);
- the presence of biological markers such as isoprenoids (derivatives of phytol and pristane) as well as sterols and hopanoids, porphyrins (chlorophyll and hemin derivatives);
- the *n*-alkanes in petroleum occur preferentially with odd-number carbon atoms, while the natural fatty acids are currently made from even carbon atoms. Therefore it is reasonable to think that the decarboxylation reaction of the natural fatty acids leads to the formation of alkanes with odd numbers of carbon atoms in the chains.

In particular, phytol is diterpene having an alcoholic end group and an α, β insaturation in its chain of the phytane type and occurs as an ester in chlorophyll. It is present in all green plants (Steglich *et al.* 2000). The phytyl group constitutes the lipophilic part of vitamins E and K_1. Pristane is a parent compound of phytol but it is a saturated terpenic hydrocarbon, which is widely distributed in nature occurring in shark and herring as well as in plankton (Steglich *et al.* 2000). Hopanoids are derivatives of hopane, which is a triterpene hydrocarbon. Hopanoids are widely distributed in organic sediments in the Earth and occur in many microorganisms (bacilli, cyanobacteria but not in archeabacteria), where they can replace cholesterol in bacteria cell walls. These bacteria degrade the young organic matter during the diagenesis and when they die they leave hopanoids in the sediments (Steglich *et al.* 2000). Sterols are cholesterol derivatives (Durand 1980; Steglich *et al.* 2000).

It was due to the discovery of these biological markers and also to a series of geological and geochemical considerations that, at least on Earth, the evidence for an organic origin for sedimentary organic matter is overwhelming (Durand 1980; Proskouriakov & Drabkine 1983; Barker 1985; Van Krevelen 1993).

The general view is that the petroleum may have originated mainly from marine organic sediments, while coal is most probably derived from terrestrial organic sediments (essentially from ancient flora and forests).

However, if we go back to the 19th century when our knowledge was much more limited than today, we can find theories that assumed an inorganic origin for petroleum and other organic sediments. These theories were proposed, for instance, by the famous French chemist Berthelot in 1866 who supposed that the hydrocarbons present in petroleum were formed by the hydrolysis of metallic carbides formed in the terrestrial crust under the action of water at different temperatures. The main product of this hydrolysis, acetylene, may have undergone a series of condensation reactions, which may have produced a variety of hydrocarbons, including petroleum and kerogen. The hypothesis of Berthelot was accepted and extended by Mendeleev (1877a, b). The hypothesis was based on the idea that the rocks of early Earth were also composed of iron carbides and other carbides. These carbides were the result of the reaction between carbon and iron at high temperature during the formation of the primordial Earth from the solar nebula or could be even more primitive. Experimentally the Berthelot hypothesis was tested by Cloez between 1874 and 1879, showing that by the action of acids or steam on iron carbides, on cementite (Fe_3C) and on non-stochiometric mixtures of iron and carbon it was possible to prepare a mixture of hydrocarbons. Further interesting support to the Berthelot's theory derived from Moissan's (1896) studies on the formation of saturated and unsaturated hydrocarbons by the action of water or acids on a number of different metal carbides. In 1908 Brun, Steiger and Becker made further studies on the formation of hydrocarbons by the action of ammonium chloride and water over iron carbide (Mellor 1928).

The hypothesis of the inorganic origin of petroleum was also adopted by scientists, who were instead interested in the origin of life. For instance, Oparin (1924), in the first edition of his famous book on the origin of life reported and extended the ideas of Mendeleev that the basic organic matter was formed from the hydrolysis of carbides. Prior to Oparin, also W. Sokolov in 1892 launched the 'cosmic hypothesis' of the origin of the hydrocarbons (Proskouriakov & Drabkine 1983) by considering the fact, already known at the time, that methane was present in certain bodies in the solar system. In any case, the hypothesis of an inorganic origin for petroleum is today considered somewhat outdated. However, there still exist dualistic theories incorporating both biological and inorganic aspects of the origin of the petroleum and other organic matter (Robertson 1963; Robinson 1966; Porfir'ev 1974). In the opinion of the writer, these theories appear to be more equilibrated and able to cover the topic from a more interdisciplinary point of view. Of particular interest for its large breath and interdisciplinary approach is the article written on this specific subject by Sir Robert Robinson (1966), Nobel laureate in 1947, where the discussion concerning the origin of petroleum by incorporating both biological and inorganic aspects leads the scientist to enter into the merit of the origin of life.

Concerning the formation of organic matter in the interstellar, circumstellar medium and in the molecular clouds, the most well-known and accepted theory involves ion–molecule chemistry (Herbst 1995, 1998) where ions collide with simple molecules building more complex products. The ion–molecule chemistry is now well established and there are also experimental observations that support its validity in explaining the formation of simple organic molecules up to the polycyclic aromatic hydrocarbons, but it cannot be employed to explain the formation of much more complex organic molecules.

Complementarily, the Fischer–Tropsch (FT) synthesis has been proposed especially in protoplanetary and solar nebulae. The FT synthesis occurs only in the presence of catalysts and needs CO and H_2 as raw materials. CO and H_2 are known to be abundant in molecular clouds. Hayatsu & Anders (1981) have shown that the FT synthesis can occur in conditions resembling those of the early solar nebula in the presence of catalysts such as magnetite, Ni–Fe alloys and other materials commonly found in meteorites. The FT synthesis at about 350 K (the temperature at which it is thought that the C1 chondrites are formed) and at low or very low pressure produces a mixture of linear and branched alkanes and other products. The distribution of alkanes produced by the FT synthesis is very similar to that found in the Murray meteorite and in shale oils. However, the FT reaction fails in giving aromatics while in the carbonaceous chondrite extracts a large amount of aromatic hydrocarbons are usually found in the form of kerogen. Hayatsu & Anders (1981) have shown that the FT products, which are initially a mixture of alkanes and alkenes, are partially converted into aromatics by prolonged contact with the catalyst, which caused the hydrogenation of carbon monoxide. The FT synthesis has been shown to be superior to the Miller–Urey (electric discharge in CH_4, NH_3, H_2O, H_2) and the Sagan–Kaare synthesis (ultraviolet- (UV) radiation-driven Miller–Urey synthesis) in explaining the presence of aliphatic and aromatic hydrocarbons in carbonaceous chondrites. Furthermore, it has been shown (Hayatsu & Anders 1981) that the FT synthesis is also a suitable reaction in producing a plethora of oxygenated compounds such as alcohol, aldehydes and ketones but especially the long chain fatty acids which have been easily detected in Orgueil and other seven different carbonaceous chondrites. Even in the formation of the purine and pyrimidine bases, the FT synthesis in the presence of ammonia and montmortillonite appears once again to be superior to the Miller–Urey synthesis. However, the Miller–Urey synthesis is much better than the FT one in producing amino acids that are found in meteorites (Hayatsu & Anders 1981).

In addition or as an alternative to the ion–molecule reaction and the FT synthesis, at least the aromatic hydrocarbons can be formed by the pyrolysis of methane (a reaction originally studied by the great French chemist Berthelot). This reaction is very attractive because it produces through acetylene (which is an early intermediate product together with ethylene and H_2) a plethora of different aromatic compounds, a large number of which are found in meteorites (Hayatsu & Anders 1981). The pyrolysis presents some limitation since it requires temperatures as high as 1150 K and it can only occur in the circumstellar medium. However, it has been shown that the photolysis and the radiolysis of methane can produce (at low temperatures) a very complex mixture of products, including polycyclic aromatic hydrocarbons (Cataldo 1996). This chemistry has also been proposed to explain the haze in the atmosphere of Titan, Saturn's giant moon (Cataldo 1994 and 1997).

Table 1. *Comparison of the elemental composition of kerogen and petroleum*

Meteoritic Kerogen (Hayatsu) (%)	Kuwait Raw petroleum (%)	Mexico Raw petroleum (%)
C = 76.5	85.5	83.0
H = 4.5	11.0	11.0
N = 2.4	0.7	0.5
S = 4.3	1.2	4.3
O = 12.4	1.6	1.2

Meteoritic kerogen represents about 80% of the organic matter present in a carbonaceous chondrite and is characterized by the fact that it is completely insoluble in any solvent. From this fact its crosslinked and high molecular weight nature has been deduced. It can be partially compared in its constitution to that of a petroleum or better, to shale oil (Hayatsu & Anders 1981). A comparison of the elemental composition is presented in Table 1.

Meteoritic kerogen is characterized by the presence of an excess of nitrogen, sulphur and oxygen in comparison to normal petroleum. Owing to its high molecular weight and crosslinked nature, it can be compared more with coal than petroleum. To be more precise, kerogen can be better compared with a relatively low-rank coal based on its elemental O/C and H/C ratio. The FT synthesis when it is prolonged for a 6 month period also has the merit of producing an aromatic fraction resembling in some instances meteoritic kerogen (Hayatsu & Anders 1981). In fact, its pyrolizate matches the pyrolysis products of meteoritic kerogen, while subtle but important chemical differences have been found in comparison with a coal or lignin pyrolizate.

In this introduction, we have started from the observation that petroleum fractions may exist in certain protoplanetary nebulae. How may this complex organic matter be formed? We have reviewed very briefly the old theories of the inorganic origin of petroleum and shown that these theories can no longer be applied in the interpretation of the origin of the organic sedimentary matter present in the Earth, although the most equilibrated theories appear to be those that incorporate both aspects, organic and inorganic, to explain the origin of petroleum on Earth. Only by accepting these dualistic theories such as those of Robinson (1966) and Profir'ev (1974) can we give an explanation of the inorganic origin of the organic matter present in the protoplanetary nebulae and in certain bodies of the solar system.

We have then reviewed the reactions and theories that are today more or less accepted in explaining the formation of organic matter under abiotic conditions in the solar nebulae, in the molecular clouds and in the interstellar medium. We have seen that the most accepted theory for the formation of simple organic matter in space is that involving the ion–molecule reaction, although the FT synthesis also presents many interesting and attractive results so that recently this reaction has been the subject of renewed interest, especially in explaining the formation of complex organic matter in solar nebulae (Kres & Tielens 2001; Zolotov & Shock 2001; Llorca & Casanova 1998). The pyrolysis of methane and mixtures of H_2 and CO/H_2O is also attractive for its possibility to produce aromatic hydrocarbons and other products from simple molecules (Zolotov & Shock 2001). The Miller–Urey and Sagan–Kaare reactions appear to be more limited in their application and it may be that they only play a major role in planetary surfaces and atmospheres in producing, for instance, amino acids rather than in the protoplanetary nebulae.

Among these reactions, we would like to refocus attention on the hydrolysis of metal carbides as a source of hydrocarbons, using the old ideas of Berthelot, Mendeleev, Cloez, Moissan, Sokolov and Oparin. Thus, the precise aim of this paper is to summarize and re-analyse this old hypothesis within the framework of the new knowledge we have on this specific matter.

Experimental

Chromium carbide (Cr_3C_2) was purchased from Aldrich. All solvents were high-performance liquid chromatography (HPLC) grade from Aldrich or Fluka. The electronic spectra were recorded on a Shimadzu UV160A spectrophotometer on the hexane extract of the Cr_3C_2 hydrolysis products. The same procedure as used in previous works for the analysis of the hydrolysis products of Cu_2C_2 has been adopted (Cataldo 1998, 1999).

The HPLC-DAD (HPLC analysis with a diode array detector) was performed on an Agilent Technology LC model 1100 on column Zorbax Eclipse XDB-C8 using a mobile phase of methanol/water in the ratio 80/20 or acetonitrile/water in the ratio 90/10 at a flow rate of 0.8 ml min^{-1}. The raw extract was filtered through a PVDF membrane (Acrodisc 13LC with 0.2 μm pore size).

The FT-IR analysis of the gases and volatiles evolved during the hydrolysis of Cr_3C_2 was made by collecting the hydrolysis gases and volatiles inside a 10 cm path IR cell and recording the spectra of the gases in an FT-IR spectrometer (Nicolet IR300). In addition, in this case a consolidated procedure has been adopted (Cataldo 2000).

Hydrolysis of Cr_3C_2 in water

About 500 mg of Cr_3C_2 was placed in a flask with 35 ml of distilled water and 10 ml of *n*-hexane. The mixture was shaken and stirred with a magnetic stirrer at room temperature. Periodically samples of *n*-hexane were taken to record the electronic spectrum of the evolved hydrocarbons, which were trapped in the solvent, and to run the HPLC analysis.

The same run as described above was repeated by heating the mixture under stirring in a water bath and collecting the hydrocarbons evolved in *n*-hexane, which were then used for the subsequent analysis.

Hydrolysis of Cr_3C_2 in diluted HCl

The same procedure adopted for the hydrolysis of Cr_3C_2 in water was repeated in the presence of 35 ml of 1:1 solution of concentrated HCl in distilled water at room temperature. With the acid solution the evolution of gases was much more evident and the speed of hydrolysis greatly accelerated. The hydrocarbons trapped in *n*-hexane were analysed using electronic spectroscopy and HPLC-DAD.

Hydrolysis of Cr_3C_2 for the FT-IR analysis

The hydrolysis of Cr_3C_2 (500 mg) was conducted in pure distilled water (35 ml) with few drops of concentrated HCl. The mixture was stirred and heated at 80 °C in a water bath. Obviously, *n*-hexane was not used in this run. The flask containing the reaction mixture was instead connected with silicon tubing to an IR gas cell. The gases and volatiles evolved were accumulated into the cell, which was then used to record the FT-IR spectra of the evolved hydrocarbons.

Results and discussion

Metal carbides and cosmic abundances

The cosmic abundance of the elements is related to the cycles of thermonuclear reactions occurring in stars and to the stability of the nuclei formed in terms of bond energy per nucleon. From hydrogen and helium all the other elements are formed due to the thermonuclear reactions occurring in the stars (Burbidge *et al.* 1957). Depending on the mass of the stars, after the consumption of H, He is used as a nuclear combustible to produce C, O and N and then heavier elements are produced up to Fe. If we look at the graph of the cosmic abundances (Fig. 1) (Cameron 1973), we find that iron is the most abundant element together with the elements with Z between 23 and 30 (Cr, Fe, Ni, V, Mn, Co, Cu). The excess of iron in the cosmic abundance exceeds the expected value by about 1000 times based on the degrading trend of the cosmic abundance of elements after O (Ne, Mg, Si, S, Ar, Ca, Ti, see Fig. 1). This is due to the fact that thanks to its stability (high bonding energy per nucleon) it is the end product of the nuclear fusion of the light elements and it is not easily depleted by photodegradation and spallation reactions as happens for lighter and heavier elements, which are less stable.

The topic of cosmic abundance is important since we will focus our discussion mainly on the properties of the carbides of the transition metals belonging to the iron peak of cosmic abundance.

The present work is based on the idea that being abundant, elemental carbon can combine with Cr, Fe, Ni and Mn, Co, Cu to give carbides that then are incorporated in chondrules and then may enter into the composition of meteorites, cometary and planetary bodies. Krot *et al.* (1997) and Llorca & Casanova (1998) have discussed the formation and presence of carbides in meteorites. In particular, Krot *et al.* (1997) focused their attention on certain carbides such as cohenite [$(Fe,Ni)_3C$] and haxonite [$(Fe,Ni)_{23}C_6$] and other carbides, which have been found in different types of meteorites. Furthermore, Krot *et al.* (1997) have discussed the possible formation of these carbides by the action of CO according to the

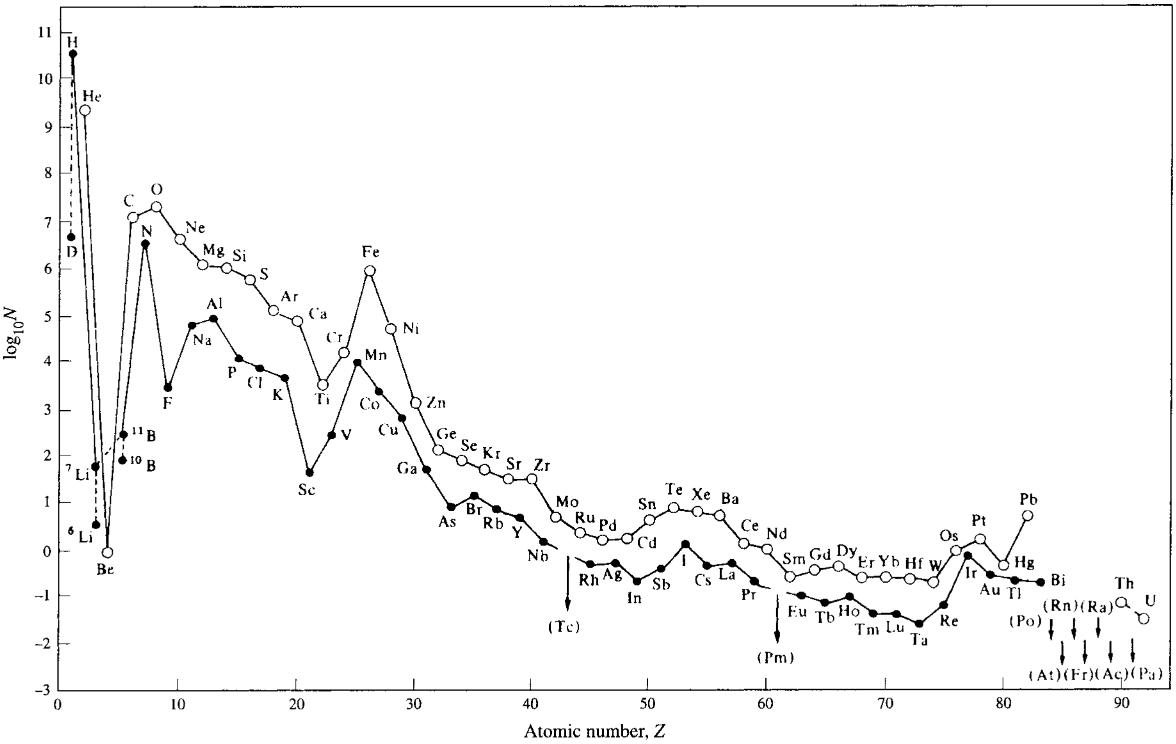

Fig. 1. The cosmic abundance of the elements (after Cameron 1973).

following reactions:

$$15\,\mathrm{Fe(s)} + 4\,\mathrm{CO(g)} \rightarrow 4\,\mathrm{Fe_3C(s)} + \mathrm{Fe_3O_4(s)}$$

or

$$3\,\mathrm{Fe(s)} + 2\mathrm{CO(g)} \rightarrow \mathrm{Fe_3C(s)} + \mathrm{CO_2}$$

and have also considered the action of water on the iron carbide. A reaction which will be rediscussed in further detail in the following paragraphs of this section and which leads to a mixture of hydrocarbons, not just to H_2. In fact, the water present in the meteoritic and cometary bodies may reach the liquid or vapour state during their long history causing a slow hydrolysis and release of hydrocarbons and other products.

In addition to iron group carbides, carbides of Ti, Mo and W have also been found in meteorites together with silicon nitrides and carbides (Norton 2002).

The carbides of the 'iron peak' in the cosmic abundance curve

Mellor (1928) reports the experience of Cloez (1874, 1877) concerning the hydrolysis of iron containing about 3.0% total carbon. Cloez used 200 kg of cast iron and its dissolution produced a mixture of hydrocarbons in sufficient quantity to allow separation, fractionation and partial identification. The attack was made by diluted sulphuric acid and the result was the production of (the percentages are calculated on the initial mass of the iron employed in the study):

0.32% organic oil (presumably a mixture of condensed olefins),
0.27% olefins,
0.27% paraffins,
1.7% elemental carbon,
0.2% extractables from elemental carbon (presumably an aromatic/naphtenic fraction).

The paraffins consisted of the complete series of C_nH_{2n+2} with $n = 10$, 11, 12, 13, 14, 15 and 16, which were isolated by fractionated distillation. The analysis of Cloez was directed to the identification of the liquid and solid organic matter but not the volatile. Moissan (1896), as reported by Mellor (1928), has instead shown that the acid hydrolysis of cementite (an iron carbide Fe_3C) yields mainly H_2 (up to 75% of the gas evolved) together with CH_4, CH_3—CH_3, CH_3—CH_2—CH_3 (about 15%), with the remainder being alkenes such as propenes, butenes and butadienes. For the hydrolysis reaction, Mellor (1928) has proposed the following schemes:

$$\mathrm{Fe_3C} + 6\,\mathrm{HCl} \rightarrow 3\,\mathrm{FeCl_2} + \mathrm{CH_4} + \mathrm{H_2}$$

$$3\,\mathrm{Fe_3C} + 18\,\mathrm{HCl} \rightarrow 9\,\mathrm{FeCl_2} + 6\,\mathrm{H_2} + \mathrm{CH_3{-}CH{=}CH_2}.$$

Of course, other similar reactions may be postulated to explain the formation of other hydrocarbons. The action of heated water over Fe_3C has been reported by Mellor (1928) to produce only a slow decomposition, which is strongly accelerated under hydrothermal conditions. Hydrogen, hydrocarbons, iron oxides and carbon appear to be the final products of water attack of Fe_3C. A similar distribution of products has been reported by Emeleus & Anderson (1960) and by Greenwood & Earnshaw (1984) for the hydrolysis of cementite, the main product being H_2 followed by methane, ethane, ethylene, liquid and solid higher hydrocarbons (waxes), saturated and unsaturated, as well as some free elemental carbon.

Iron can also form several mixed carbides with other metals but we limit our discussion on the hydrolysis of other pure carbides present in the 'iron peak' of the cosmic abundance curve. For instance, several manganese carbides have been prepared and their hydrolysis products studied. Mn_3C (Hiroyatsu *et al.* 1985), Mn_7C_3 (Bohumil *et al.* 1983) and $Mn_{23}C_6$ (Pavel & Bohumil 1986; Pavel *et al.* 1987) on water hydrolysis produce a mixture of H_2, CH_4, $CH_3—CH_3$, propane, butane, higher alkanes and alkenes. For higher alkanes and alkenes we intend specifically $C_5—C_8$ mainly linear chain hydrocarbons. Similarly, complex carbides also containing group III metals with the general formula Mn_3MC, where M=Al, Ga, In, Sn, produce the same mixture of alkanes and alkenes mentioned previously for the pure Mn carbides under hydrolytic conditions. The addition of a metal belonging to group III of the periodic table of elements causes an increase in the yield of CH_4 and this is not a surprise since it is known (Bailar *et al.* 1973) that Al_2C_3 and Be_2C (Be is in group II of the periodic table) usually produce almost pure methane with traces of H_2 and other hydrocarbons under hydrolysis with water. Concerning the group II carbides, apart from Be_2C, it is important to mention MgC_2 and CaC_2. The former rearranges under thermal treatment into another carbide Mg_2C_3 with liberation of carbon (Bailar *et al.* 1973). The action of water on Mg_2C_3 produces almost exclusively propyne $CH_3—C{\equiv}CH$, while CaC_2 is the well-known (industrial) source of acetylene. Depending on the hydrolysis conditions, the acetylene produced from CaC_2 may polymerize directly into higher hydrocarbons.

Returning to the carbides of the iron peak, we should mention Ni_3C, Co_3C and Co_2C as well as Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$, which are analogous to Fe_3C and Mn_3C, at least in their hydrolytic behaviour in the sense that they hydrolyse very easily under the action of water to yield H_2 and hydrocarbons (Greenwood & Earnshaw 1984). It is worth mentioning here that Ni, Co and Cr carbides are less stable than Fe_3C (Bailar *et al.* 1973; Emeleus & Anderson 1960) and even more prone to yield H_2 and hydrocarbons under hydrolytic conditions. The distribution of hydrocarbons formed by hydrolysis of Ni_3C and Co_3C is analogous to that discussed for cementite (Bailar *et al.* 1973; Emeleus & Anderson 1960). It is interesting to remind the reader here that all the carbides belonging to the iron peak of cosmic abundance can be formed by a carburizing process involving the action of carbon monoxide on the subject metal (Storch *et al.* 1955) in agreement with the proposal of Krot *et al.* (1997).

Since the behaviour of all the carbides belonging to the iron peak of cosmic abundance is more or less analogous, we have selected Cr_3C_2 as a model carbide to study its hydrolysis products. The results will be discussed in the next section.

The important remark we have to make here is that all the metals in the iron peak of cosmic abundance form carbides easily under the direct action of elemental C at high temperature or by a carburizing reaction with CO under relatively mild conditions. All of these carbides are able to produce a mixture of gaseous, liquid and solid hydrocarbons under the action of simple liquid water even at low temperatures. This fact is of importance in explaining the presence of hydrocarbons in carbonaceous chondrites since the hydrolysis of these metal carbides can be a process alternative and competitive both to the Fischer–Tropsch reaction and other reactions proposed to explain the formation of hydrocarbons in the primitive solar nebula. In contrast to the metals of the iron peak of cosmic abundance, the other metals that lie 'around' the iron peak, namely Ti, Zr, Hf, V, Nb, Ta, Mo and W instead form very stable carbides, which are called interstitial carbides and have the property of being completely resistant to any hydrolytic process (Emeleus & Anderson 1960; Bailar *et al.* 1973; Greenwood & Earnshaw 1984). These carbides are really refractory materials and some of them, such as TaC and WC, have also found technological applications for their special properties. Ti, Mo and W carbides have been found in meteorites together with silicon nitrides and carbides (Norton 2002). They are considered primordial grains and seeds of interplanetary dust; because of their extreme stability and inertness they remained unaltered for billions of years. The conditions, which have caused the formation of these carbides, are the same that could have also formed the carbides of the iron peak. However, the latter, because of their hydrolytic instability may have undergone a liquid water metamorphosism, which should have changed the carbides into H_2 and hydrocarbons. The hydrocarbons may have undergone radiation processing, which may have transformed them into a mixture of aromatic hydrocarbons and even kerogen. This could be one of the reasons for their rarity. The water hydrolysis of the iron peak metal carbides may also be the source of the abundant hydrocarbons we know to be present, for instance, in the atmosphere of Titan, the giant moon of Saturn, in Triton which is one of the satellites of Neptune and in several known transneptunian objects such as Pluto and Charon, as well as Chiron and other Kuiper belt objects known under the general name of 'Centaurs' (Weissmann *et al.* 1999).

Copper carbide or acetylide

Notwithstanding that copper is within the iron peak of cosmic abundance (Fig. 1), its behaviour with carbon is completely different from the other carbides just discussed. First of all the copper carbide, better known as copper acetylide (Cu_2C_2) does not form at high temperature by synthesis from the elements or by the action of CO as in the case of the other metals. Cu_2C_2 is formed only by the action of acetylene on copper or, much better, by the action of acetylene on a solution of Cu^+ ions. The constraints for its formation in the solar nebula are too demanding so it cannot be formed at all under those conditions. Furthermore, copper acetylide is too unstable and explodes if it is heated in air but under vacuum it decomposes explosively into elemental carbon and copper (Cataldo 1998, 1999, 2001; Cataldo & Capitani 1999). The elemental carbon also contains domains of carbyne, a carbon allotrope made by carbon chains with the general structure $—(C{\equiv}C—C{\equiv}C)_x—$ (Cataldo & Capitani

1999; Cataldo 2001). Under water and acid hydrolysis copper acetylide produces essentially acetylene. However, the presence of Cu^{2+} ions in the hydrolysis medium or the partial oxidation of Cu_2C_2 even in the solid state causes coupling of the $C{\equiv}C^{2-}$ ions present in its crystal lattice, producing (under subsequent hydrolysis) a mixture of acetylenic hydrocarbons having the general formula $H{-}(C{\equiv}C)_n{-}H$, where n an integer from 1 to 14 (Cataldo 1998, 1999) together with carbonaceous matter containing carbyne (Cataldo & Capitani 1999; Cataldo 2001). Since copper carbide (or acetylide) cannot be produced at high temperatures, as in the case of all other carbides discussed in the previous paragraph, and considering its high instability above 100 °C, we could postulate its possible formation only by starting from the free metal at low temperature in the presence of water and acetylene. As mentioned the constrains are too stringent, but the hydrolysis products are of extreme interest because of the presence of highly unsaturated molecules, which are analogous to the cyanopolyynes $H{-}(C{\equiv}C)_n{-}CN$, which have already been detected in interstellar molecular clouds and because of the presence of carbyne, a carbon allotrope found in certain carbonaceous meteorites.

Other carbides that produce hydrocarbons

There are two interesting series of metals that form carbides which under hydrolysis produce mixtures of hydrocarbons. These series are, respectively, the lanthanides and the actinides. The lanthanides were known as rare earths and in fact their cosmic abundance is low (see Fig. 1), probably the lowest among all elements, although in the Earth the rare earths are not as rare as in the cosmos. The actinides are also very rare in the cosmic abundance table (Fig. 1).

Despite their rarity, both lanthanides and actinides form a series of carbides, which under hydrolysis produce a very rich and complex mixture of hydrocarbons, even richer and more complex than the mixture of hydrocarbons obtained from the hydrolysis of the metals present in the iron peak of cosmic abundance. Examples of hydrocarbon mixtures derived from hydrolysis of lanthanides and actinides carbides are reported in Table 2. In contrast with the carbides of the iron peak, which produce exclusively H_2, alkanes and alkenes but not acetylenes, the lanthanide carbides produce mainly acetylenes with acetylene as the principal component, although H_2 and mixtures of paraffins and alkenes are not lacking (see Table 2). The actinides in turn yield much more alkanes and H_2 rather than acetylene and other alkynes although the latter are always present and this again is in contrast with the behaviour of the carbides of the iron peak.

Although rare, these elements may also have made a contribution to the formation of organic matter, which we can observe in the carbonaceous chondrites and in the atmospheres and surfaces of certain bodies of the solar system.

Some special observations on the hydrolysis of carbides

Practically all authors who have studied the structure of the metal carbides and the hydrolysis products agree in considering that the mechanism of formation of the hydrocarbons involves a radicalic mechanism where acetylenic radicals and methyl radicals couple together forming alkenes and alkanes (see, for instance, Pollard *et al.* 1964; Pavel & Bohumil 1986; Pavel *et al.* 1987; Gesing & Jeitschko 1995; Jeitschko & Gesing 1996; Gesing *et al.* 1997). The high abundance of H_2 in all the carbide hydrolysis considered also causes continuous hydrogenation reactions where the metal part of the carbide acts as a hydrogenation catalyst to produce alkanes and alkenes. In any case, the crystal structure of the carbide plays a key role in driving the synthesis of the resulting hydrocarbons. For instance, in Al_2C_3 the hydrolysis yields exclusively methane because in the crystal structure of this carbide the carbon atoms occur as individual atoms and not as acetylide $C{\equiv}C^{2-}$ ions as in the case of calcium carbide and copper carbide, for instance. Copper carbide yields higher acetylenic hydrocarbons when its crystal structure has been allowed to weather and to cause a coupling reaction between the acetylide ions. In the case of Mg_2C_3 the main product is propyne because the carbon ions in its crystal lattice are in the form of allenides, i.e. with a $H_2C{=}C{=}CH^-$ structure, which rearranges to $CH_3{-}C{\equiv}CH$ during hydrolysis (Bailar *et al.* 1973). Alternatively, a coupling reaction between acetylide and individual carbon atoms should be advocated. Concerning the structure of Cr_3C_2, the carbide we have used as a model compound to study the hydrolysis products, it has been shown that the C—C bond length in its crystal structure is only 0.165 nm. This distance is only a little longer than normal aliphatic chains and indicates that the carbon atoms may be regarded as existing in chains within the metal lattice. The Cr atoms are inserted between the chains such that each carbon atoms is surrounded by six Cr atoms at the corner of a distorted trigonal prism. The Cr—C bond length being 0.202–0.207 nm. Because of the distorted structure, the carbides react easily with water (Bailar *et al.* 1973). During the hydrolysis again a free radical mechanism should be advocated for the reaction.

Examples of hydrolysis which produces other precious organic matter other than only hydrocarbons

Up to now we have reviewed the hydrolysis of metal carbides and shown that the general reaction products are H_2 and hydrocarbons of various nature that depend on the nature of the metal present in the carbide and also on the crystal lattice structure of each individual carbide. Oparin in his book (1924) talked about the possible formation of ammonia by hydrolysis of certain metal nitrides in early Earth. The ammonia may have then undergone a series of condensation reactions with hydrocarbons to produce precious nitrogen-containing organic molecules. This exact view of Oparin could be considered outdated today. However, in this context it is interesting to mention here a nuclear reaction studied by Yankwich & Cornman (1956). They started from Be_3N_2, which was neutron bombarded to cause the following nuclear reaction:

$$^{14}N + n \rightarrow {}^{14}C + {}^{1}H.$$

Of course not all nitrogen present in the nitride was converted into carbon, only a certain part, but the beryllium nitride after

Table 2. *Hydrolysis products from lanthanides and actinides carbide*

Carbide	A_3MC	$Ln_2O_2C_2$	Ln_4C_5	Ln_4C_7	$YC_{1,4}$	LaC_2	LaC_2	LaC_2	CeC_2	CeC_2	CeC_2	NdC_2	GdC_2	ThC_2	ThC_2	UC	UC_2
	A = Ln M = Al, G, In, Tl, Sn, Pb	Ln = La, Ce, Pr, Nd	Ln = Y, Ho	Ln = Ho, Er, Tm, Lu													
Hydrolysis	Water	Water	Water	Water	Water	In H_2SO_4	Water	Water	Water	Water	Water	Water	Water	Water	In NaOH	Water	Water
Temperature	25 °C	25 °C	25 °C	25 °C	100 °C	25 °C	25 °C	100 °C	25 °C	100 °C	200 °C	100 °C	100 °C	25 °C	25 °C	25 °C	25 °C
Hydrogen					2.5	17.9		5.6		1.8		2.2	5.1	33	36	9.16	0.54
Methane	84–97		X	X	4.5	0.2		0				0.3	0.14	4	4.8	79.05	27.21
Ethane			41	X	8.45		24.3	11.1	19.7	13.8	11.2	12.7	12.35	27	29	5.5	44.31
Propane		X	16		5.71	1.4	0.22			0.06	13.5	0.72	0.06	7	1.6	1.36	6
Butane					0.32	0.2	0.52	0.4	2.8	0.69	2	0.42	0.51	2.8	3.2	1.4	5
Isobutane													0.02				
C5–C8 alkanes							0.1			0.01	3.2			0.6	0.4		
Higher alkanes	4–13		X	X	0.3		2.2	2.3		0.9		1.94	0.41			0.07	0.7
Waxes																	
Ethylene			X	X	7.15	8.8	8.4	7.4	6.6	8.7	39.6	9.2	8.48	4.5	4.6	0.43	9.23
Propene			X		0.93		0.1		0.1	0.01	12.4		0.02			0.57	2
1-butene		X			1.35	0.2		1.8		0.45		2.1	1.33	5.7	5.3	0.86	4
2-butene (CIS)					0.01	0.5	0.72	0.5	0.9	0.92	3.7	0.6	0.65			0.31	
2-butene (trans)					0.34	0.6	0.66	0.5	0.8	0.87	3.6	0.64	0.65			0.31	
Isobutene							1.1		1.4		2.4						
‘1,3-butadiene’					0.83	2.6	0.1	2.4	0.1	1.74	3.6	2.7	2			0.42	
‘1,2-butadiene’						0.2	0.4		0.2	0.01	4.3	0.03	0.02				
C5–C7 alkenes														1.7	1.3		
Higher alkenes	1–3			X													
Acetylene					67.3	67.4	61.5	67.7	67.3	69.7	0	66.5	68.2	7.5	9	0.57	0.6
Propyne		X		X	0.71									1.8	1.8		
1-butyne					0.01			0.2		0.32		0.02	0.03	4.2	2.8		
2-butyne										0.06		0.01					
l-esyne														0.2	0.2		
Total					100	100	100	100	100	100	100	100	100	100	100	100	100
Reference	Gesing	Pavel	Bailar	Emeleus	Pollard	Greenwood	Palenik	Pollard	Palenik	Pollard	Palenik	Pollard	Pollard	Bradley	Bradley	Pollard	Pollard

the bombardment was converted partially into beryllium carbide, which we have discussed in the preceding paragraph. The astonishing thing is that the hydrolysis of the resulting mixed beryllium nitride and carbide yielded the following products (Yankwich & Cornman 1956):

methane	26%
CO_2	14%
guanidine	19%
methyl hydrazine	11%
formic acid	8%
hydrogen cyanide	7%
urea	6%
cyanamide	5%
methylamine	4%
formaldehyde	2%.

This is a perfect prebiotic synthesis, which yields guanidine, urea, cyanamide and hydrocyanic acid and other interesting organic substances, which are already recognized as the key building blocks for the formation of purine and pyrimidine bases and many other organic compounds, which are important for building the molecules of life. The experience of Yankwich & Cornman (1956) is important because it can occur in a natural environment over geological times under the action (bombardment) of cosmic rays. Suppose that we have some Be_3N_2 (or another hydrolizable metal nitride) in a meteorite and suppose that this meteorite is bombarded in the space for millions or billions of years. Part of the nitride has been transformed into carbide by the simple action of cosmic rays! In fact, the reaction $^{14}N+n \rightarrow {}^{14}C+{}^{1}H$ occurs in the upper atmosphere due to cosmic ray bombardment and leads to the formation of $^{14}CO_2$, which then is absorbed by vegetal flora and inserted into the cycle of living matter. Once the meteorite enters into contact with water after billions of year of radiation processing, it can release its extremely precious organic matter.

Once formed the metal nitride can be bombarded by cosmic rays without radiation dose limits. Excess or defects of bombardment will only affect the amount of precious organic matter that will be formed under subsequent (it may be millions or billions of years after the continuous bombardment) hydrolytic conditions, but will not have an influence on the stability of this matter. In fact, the criticism, which is sometimes made against the abiotic synthesis of the organic building blocks of life, is that the electromagnetic radiation that causes the formation of certain key molecules, may also cause their destruction after their formation. Instead in the case of the nitride–carbide, the bombardment will have no effect on the resulting organic matter when it arises from inorganic matter during a hydrolysis episode in a protected environment certainly different from that which caused the formation of the mixed nitride and carbide and after geological or cosmic timescales. Furthermore, the organic matter formed is so simple that it can undergo further condensation and polymerization reactions either under the catalytic action of rocks and metals and/or with the aid of electromagnetic radiation. Elsewhere (Cataldo 1996, 1997, 2002) we have talked about the destiny of cyanogens, acetylene and ethylene under the action of UV radiation. Many important new molecules can be derived, some of which are extremely important for life.

The case of chromium carbide (Cr_3C_2) hydrolysis

As discussed in the previous paragraphs, we have selected Cr_3C_2 as a model compound to study the products evolved from its hydrolysis, bearing in mind that its behaviour towards hydrolysis is analogous and comparable to the other carbides of the iron peak of cosmic abundance.

As described in the experimental section, the Cr_3C_2 was initially hydrolysed in distilled water at room temperature and the evolved hydrocarbons and gases were collected in *n*-hexane, which was then used to study the electronic spectrum and to run an HPLC analysis. Fig. 2(a) shows the electronic spectrum of the hydrocarbons produced from the hydrolysis in cold water. The electronic spectrum is characterized by four absorption bands at 200, 223, 253 and 283 nm. It must be clarified that with electronic spectroscopy it is not possible to detect saturated alkanes since their electronic transition lies in the vacuum UV and is far beyond the spectral window accessible to our spectrophotometer. For instance, ethane has a $\sigma \rightarrow \sigma^*$ transition due to the excitation of the electrons of the C—C bond at 135 nm (Rao 1961). Therefore what we can detect in the electronic spectra are only alkenes and acetylenes in the present context. In fact, these compounds show absorption bands in the UV due to the excitation of the π electrons of the double or triple bonds. The band at 200 nm in Fig. 2(a) can be assigned to the $\pi \rightarrow \pi^*$ transition of a single or isolated double bond such as, for instance, ethylene, propene, butenes, pentenes, hexenes, etc. (Gillam & Stern 1954; Rao 1961). The following band at 223 nm can be assigned to dienes. Among the most common dienes, 1,3-pentadiene (also known as piperylene because it derives from the Hofmann degradation of piperidine, a component of the alkaloid present in black pepper also called *Piper nigrum*) has its absorption band just at 223 nm (Gillam & Stern 1954; Rao 1961). The following maximum at 253 nm can be assigned either to a cyclic diene such as, for instance, 1,3-cyclohexadiene or to a triene such as 1,3,5-hexatriene (Gillam & Stern 1954; Rao 1961). Among the two possible assignments it is more reasonable that we are dealing with the 1,3,5-hexatriene since its spectrum is also characterized by additional absorption bands at 263 and 275 nm, which may explain both the broad and relatively noisy maximum at 253 nm and can contribute to the following maximum at 283 nm, which in any case could be assigned to a tetraene such as 1,3,5,7-octatetraene, for instance.

Thus, from Fig. 2(a) it is confirmed that the hydrolysis of Cr_3C_2 in addition to the production of H_2, CH_4 and straight-chain higher alkanes C_nH_{2n+2}, which we cannot detect in our analysis but that have been found in previous works (Emeleus & Anderson 1960; Bailar *et al.* 1973; Greenwood & Earnshaw 1984), it also gives a series of essentially straight chain alkenes having a single double bond, two conjugated double bonds as well as three and four conjugated double bonds.

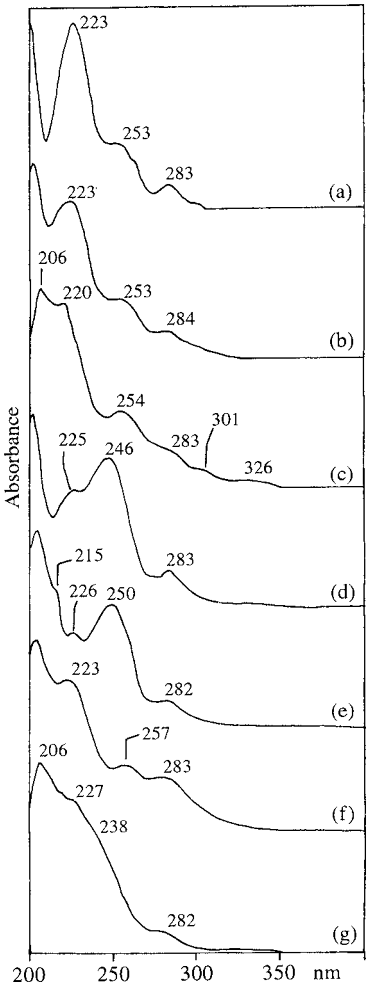

Fig. 2. Electronic spectra of the hydrolysis products of Cr_3C_2. (a) The *n*-hexane extract of the hydrocarbons produced by the hydrolysis of Cr_3C_2 in cold water. Spectrum recorded after a few minutes from the beginning of hydrolysis reaction. (b) Same as (a) but after 30 min of hydrolysis. (c) The *n*-hexane extract of the hydrocarbons produced by the hydrolysis of Cr_3C_2 in warm water (80 °C). (d) The *n*-hexane extract of the hydrocarbons produced by the acid hydrolysis of Cr_3C_2 in cold HCl solution. Spectrum recorded after a few minutes from the beginning of the hydrolysis reaction. (e) Same as (d) but after 15 min of hydrolysis. (f) Same as (e) but after being contacted with a montmorillonite KP10 clay at 80 °C. (g) Same as (d) but after having been left in contact with Cr^{3+} and HCl solution for 5 days.

Using the tabulated molar extinction coefficient ε (expressed in $M^{-1}\,cm^{-1}$) for isolated double bonds $\varepsilon = 10\,000$ for two conjugated double bonds $\varepsilon = 25\,500$, for three conjugated double bonds $\varepsilon = 50\,000$ and for four conjugated double bonds $\varepsilon = 69\,600$ (Gillam & Stern 1954; Rao 1961) and inserting these values in the Lambert–Beer law:

$$C = A/(\varepsilon b),$$

where C is the molar M concentration (in mol l^{-1}), A is the absorbance or optical density measured in the spectrum and b is the path length of the cell in centimetres, it is possible to calculate the ratio among the insaturated hydrocarbons. For instance, for the spectrum of Fig. 2(a) this ratio is

alkenes with isolated double bonds	= 100
dienes	40
trienes	6
tetraenes	1.5.

The total concentration of alkenes in the spectrum of Fig. 2(a) obtained on a sample collected some minutes after the hydrolysis from Cr_3C_2 in cold water started at 1.5×10^{-5} M. After 15 min the total alkene concentration reached a value of 4×10^{-5} M. The spectrum after 30 min is shown in Fig. 2(b). Now the ratio of alkenes with an isolated double bond over dienes is now 100:30, while the ratio with the higher homologues is unchanged with respect to the initial conditions.

Fig. 2(c) refers to the *n*-hexane extract of the hydrocarbons evolved from a Cr_3C_2/water mixture heated at about 80 °C in a water bath. Apart from the fact that after a few minutes of hydrolysis the alkene concentration in the *n*-hexane phase is at least one order of magnitude higher than the case of hydrolysis in cold water (confirming that higher temperatures exert the effect of accelerating the hydrolysis), the ratio of single, double, triple and quadruple double bonds is practically the same as observed in hydrolysis in cold water:

alkenes with isolated double bonds	= 100
dienes	36
trienes	7.5
tetraenes	2.5.

Thus, the hydrolysis at relatively higher temperatures does not change the distribution of products too much, although we may notice a slight increase in the higher homologues. Another feature of the spectrum in Fig. 2(c) is the presence in the spectrum of additional bands at 301 and 326 nm, which may be due to a thermal rearrangement of the hydrolysis products. This means that the products may cyclize, condense together forming small amounts of aromatic compounds.

The spectra of Figs 2(d) and (e) refer to the hydrocarbons evolved under acid hydrolysis of Cr_3C_2 in cold diluted HCl. Fig. 2(d) is the spectrum taken after a few minutes of hydrolysis, while spectrum Fig. 2(e) was taken after 15 min. The most interesting point is the fact that the acid hydrolysis leads to an enhancement in the content in the trienes and tetraenes and a reduction of dienes:

alkenes with isolated double bonds	= 100
dienes	22
trienes	16
tetraenes	2.5.

However, when the *n*-hexane extract is left in contact at 80 °C with a catalyst such as montmorillonite KP-10, which is able to catalyse isomerization and cracking reactions, the content of the dienes returns to the usual values we have observed for cold water hydrolysis of Cr_3C_2 (see Fig. 2f). Since the temperature employed is rather low, one could argue that the spectral change could be due to some selective absorption of trienes and tetraenes rather than to a real reaction.

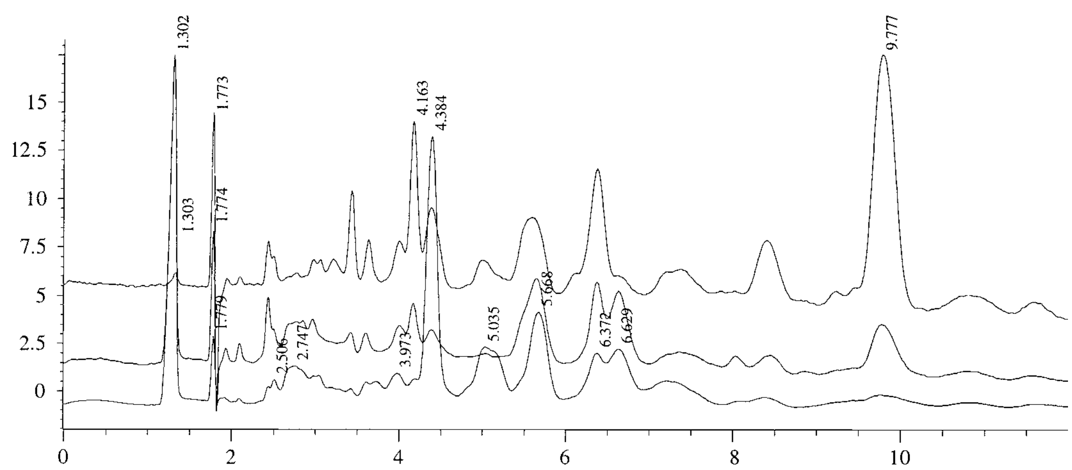

Fig. 3. Typical HPLC chromatogram of the hydrocarbon mixture. The diode detectors were set at wavelengths of 220, 235 and 260 nm.

Hayatsu & Anders (1981) have shown that the mixture of hydrocarbons obtained from the Fischer–Tropsch reaction tends to isomerize to aromatic hydrocarbons when it is left in contact with the catalyst used for the synthesis. They have shown that the aromatic content increased significantly after very long contact times (of the order of months). We have left the hydrocarbons evolved from the hydrolysis of Cr_3C_2 in contact with the inorganic hydrolysis products, including the Cr^{3+} ions formed from the hydrolysis and the HCl. After 5 days the spectrum changed into Fig. 2(g). The spectrum is completely changed in comparison with the pristine spectra discussed previously and although it is still possible to distinguish the absorption bands due to dienes, trienes, etc., new bands appear to have developed, which have changed the original spectral pattern. Based only on the electronic spectrum we cannot demonstrate the aromatization reaction but this will be the subject of a further study.

A typical HPLC chromatogram for the products derived from Cr_3C_2 hydrolysed in warm water is shown in Fig. 3. Each individual peak corresponds to an alkene. Alkanes cannot be detected with this technique because the diode array detector is a device that records the UV spectrum of each individual molecular species that has an electronic spectrum in the spectral window between 190 and 400 nm. Thus, as mentioned previously, paraffins cannot be detected, only olefins and other species giving absorption bands in the mentioned spectral range can be 'seen'. From Fig. 3 it can be deduced that about 20 different individual molecules have been separated. In some cases, the separation is not complete and the peak appears somewhat broad. In any case, the electronic spectrum on each individual peak has been recorded and analysed. As expected, the spectra of Fig. 2 are the sum and overlap of the individual spectra of the eluted molecular species. In fact, the peaks with shorter retention times show mainly absorption bands, essentially at 204 and 220 nm. The peaks having increasing retention times instead show absorption bands at 220, 250 and 280 nm as expected.

Electronic spectroscopy is a powerful tool for the detection of molecules having electronic transitions in the ultraviolet and in the visible range. We have already interpreted all the spectra reported in Fig. 2 and re-analysed, using the HPLC-DAD technique, in terms of a mixture of olefins. However, the absorption bands in the electronic spectra could also be due to acetylenic and aromatic hydrocarbons. We have then applied FT-IR spectroscopy on the hydrocarbons evolved from the hydrolysis of Cr_3C_2 to verify that only alkenes and alkanes, and not acetylenes and aromatics are evolved in the hydrolysis reaction, thus confirming the correctness of our interpretation of the electronic spectra of Fig. 2. The vapour phase FT-IR spectrum of the mixture of hydrocarbons evolved from Cr_3C_2 in water (see the experimental section) is shown in Fig. 4. First of all we can confirm that no acetylenic hydrocarbons are present in detectable amounts since their eventual presence should cause the absorption at about 3300 cm^{-1} due to the $\equiv$C—H stretching as well as absorption at 2100–2250 cm^{-1} due to the triple bond stretching (Lin-Vien *et al.* 1991). These bands are completely absent in the spectrum of Fig. 4. Furthermore, the characteristic IR bands of pure acetylene, which occur in the gas phase at 3311 and 3268 cm^{-1} (Cataldo 2000) are also not present in the spectrum of Fig. 4. The possible presence of aromatic hydrocarbons can be phased out owing to the fact that the spectrum of Fig. 4 lacks all the characteristic aryl C—H wagging vibrations that occur in the range of 700–900 cm^{-1}. Thus, all the bands present in the IR spectrum of Fig. 4 are due to aliphatic and olefinic hydrocarbons with the exclusion of the bands at 2361 and 2342 cm^{-1}, which are due to carbon dioxide CO_2. In the early literature the formation of CO_2 from the hydrolysis of carbides and especially Cr_3C_2 has never been reported. However, the hydrolysis of the mixed carbide and nitride of beryllium also produces CO_2 (Yankwich & Cornman 1956). The presence of olefinic hydrocarbons is underlined by the $=CH_2$ asymmetric stretching at 3085 cm^{-1} and by the symmetric $=CH_2$ stretching at 2968 cm^{-1} (Lin-Vien *et al.* 1991). Further indications concerning the olefinic nature of the evolved hydrocarbons are derived from the C=C stretching band at 1647 cm^{-1} and the alkenic rocking bands at 1338 and 1264 cm^{-1}, respectively, due to *cis* asymmetric rocking and *cis* symmetric rocking (Lin-Vien *et al.* 1991). Furthermore, olefins present the =CH wagging bands

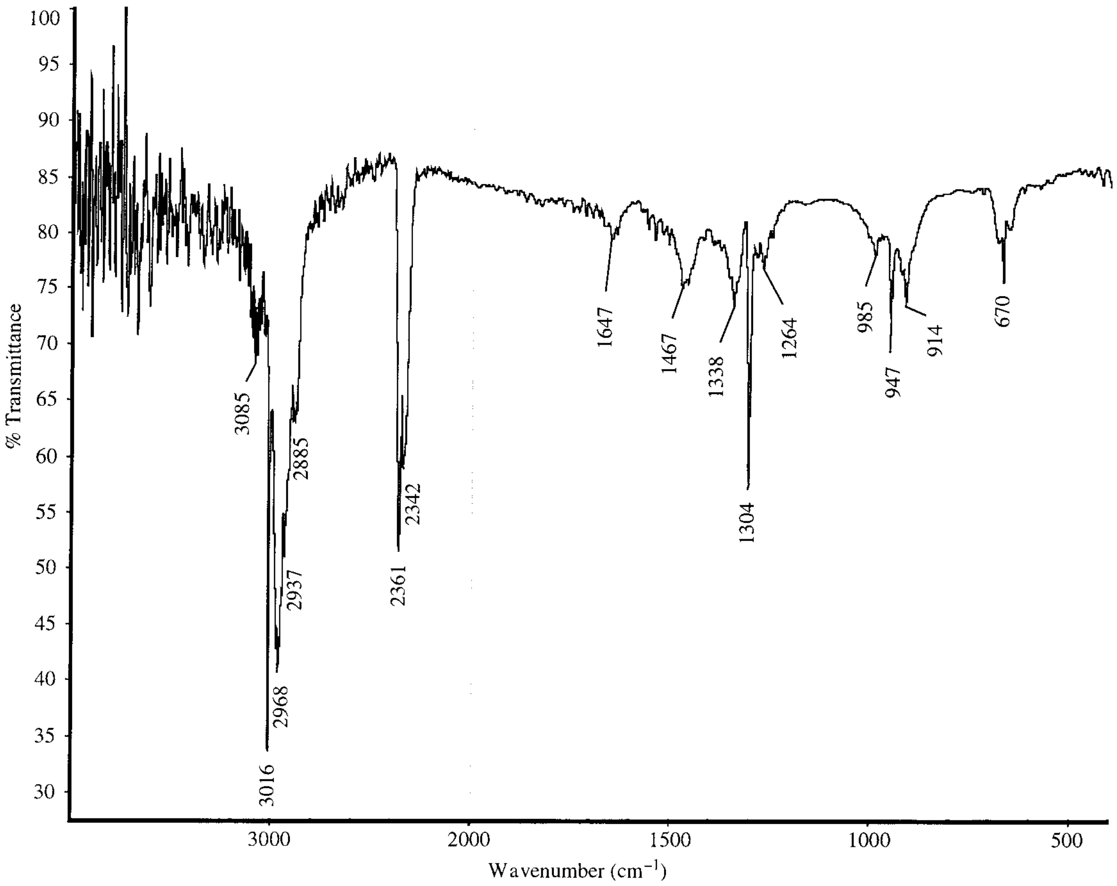

Fig. 4. Gas-phase FT-IR spectrum of the hydrocarbon mixture evolved from the hydrolysis of Cr_3C_2.

in the region below 1000 cm^{-1}, where in Fig. 4 we can distinguish three bands at 985, 947 and 914 cm^{-1}. For comparison, 1,3-pentadiene shows three wagging bands at 1000, 950 and 900 cm^{-1} (Lin-Vien *et al.* 1991) and an automatic search in the library spectra of our spectrometer Nicolet IR300 recognizes this spectrum as 1,3-pentadiene, although with not a very high degree of confidence. The low degree of confidence is obvious since the spectrum of Fig. 4 is not pure 1,3-pentadiene but a complex mixture of hydrocarbons where 1,3-pentadiene is present together with other dienes and olefins already detected by electronic spectroscopy. Therefore the FT-IR spectroscopy has fully confirmed our interpretation of the electronic spectra and the HPLC-DAD analytical results. Concerning the nature of the alkanes evolved together with the olefins, the spectrum of Fig. 4 provides clear and strong evidence concerning the presence of methane (CH_4). In fact, the two strong bands at 3016 and at 1304 cm^{-1} are due to methane (Avram & Mateescu 1972). The intensity of these bands in the spectrum of Fig. 4 suggests a high abundance of this hydrocarbon in line with the results of earlier investigations we have discussed in the paragraph of the hydrolysis products of the carbides of the iron peak of abundances. Higher alkanes evolved together with methane are present in the mixture as deduced for the bands at 2937 and 2885 cm^{-1} assigned to the asymmetric and symmetric stretching of saturated C—H (Lin-Vien *et al.* 1991). Also the band at 1467 cm^{-1} is due to the scissoring deformation of the paraffinic CH_2.

Conclusions

This work has shown that the old ideas of some great chemists of the past can be reconsidered in an astrochemical and astrobiological context. The key points of the present work are the following.

- The metals in the iron peak of cosmic abundance are all able to form carbides, which are hydrolizable.
- The possibility of formation of these carbides is high since other hydrolytically stable carbides such as TiC and WC have been found in meteorites (Fe–Ni carbides have also been found in meteorites).
- The hydrolysis of the carbides of the iron peak of cosmic abundance produces H_2, CH_4 and a series of alkanes and alkenes.
- In the present work we have verified and confirmed early conclusions concerning the hydrolysis products of the mentioned carbides by hydrolysing Cr_3C_2 selected as model carbide for all the carbides of the iron peak of cosmic abundance.
- The products of hydrolysis of metal carbides may have played a key role in the formation of hydrocarbons that have been found in meteorites and which have been detected in several bodies in the solar system, including the atmospheres and the surfaces of Titan, Triton, Pluto, Charon and several Centaurs.

- The hydrolysis of metal carbides can be considered to be a reaction in direct competition or complementary with the Fischer–Tropsch synthesis which is thought to have occurred in the early solar nebula. In fact, the hydrolysis of carbides gives a mixture of hydrocarbons (mainly aliphatic and olefinic), which are similar to those formed from the Fischer–Tropsch synthesis. Furthermore, the process of metal carbide formation may involve carbon monoxide and its hydrolysis involves the release of hydrogen. CO and H_2 are the key molecules for Fischer–Tropsch synthesis.
- The formation and hydrolysis of metal carbides has some merit over the Fischer–Tropsch reaction, which has several drawbacks a low temperature (Hayatsu & Anders 1981). It may be that at low temperature the Fischer–Tropsch reaction is radiation-driven and not catalyst-promoted as is commonly thought. Lind *et al.* (1961) have reported that the irradiation of CO and H_2 with α particles produces a wax-like substance (high molecular weight paraffins) and with electron bombardment produces a mixture of high molecular weight alcohols and aldehydes.
- If the metal carbides are mixed with metal nitrides their hydrolysis produces a series of organic molecules, which are considered to be the basis for the abiotic synthesis of purin and pyrimidin bases as well as amino acids and sugars. The mixed metal carbide and nitride may be formed by cosmic ray bombardment of metal nitrides.

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