

**BULLETIN N° 167**  
**ACADÉMIE EUROPEENNE**  
**INTERDISCIPLINAIRE**  
**DES SCIENCES**



**Séance du mardi 11 septembre 2012:**

**Conférence de Marc OLLIVIER**

**Astronome à l'Institut d'Astrophysique Spatiale d'Orsay**

**Directeur du programme interdisciplinaire du CNRS**

**"Environnements Planétaires et Origines de la Vie" (EPOV)**

**«Exoplanètes et Recherche de la vie»**

**Prochaine séance :**

**mardi 9 octobre à 17h30 Maison de l'AX 5 rue Descartes 75005 Paris**

**Conférence de François ROBERT**

**Directeur de recherche au CNRS**

**Directeur de l'UMR 7202 CNRS –MNHN.**

**LMCM : Laboratoire de Minéralogie et Cosmochimie du Muséum**

**Président du Programme National de Planétologie – CNRS**

***"Comment reconstituer la synthèse organique dans le système solaire primitif ?"***

# ACADEMIE EUROPEENNE INTERDISCIPLINAIRE DES SCIENCES

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septembre 2012

# N°167

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### Prochaine séance:

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***"Comment reconstituer la synthèse organique dans le système solaire primitif ?"***

***ACADEMIE EUROPEENNE INTERDISCIPLINAIRE***  
***DES SCIENCES***  
**Fondation de la Maison des Sciences de l'Homme, Paris.**

**Séance du**  
**Mardi 11 septembre 2012**

**Maison de l'AX 17h30.**

La séance est ouverte à 17 h30 sous la Présidence de Victor MASTRANGELO et en la présence de nos collègues Gilbert BELAUBRE, Gilles COHEN-TANNOUDJI, Françoise DUTHEIL, Michel GONDRAN, Irène HERPE-LITWIN, Pierre MARCHAIS, Jean SCHMETS.

Etaient excusés François BEGON, Bruno BLONDEL, Michel CABANAC, Alain CARDON, Daniel COURGEAU, Claude ELBAZ, Jean -Pierre FRANCOISE, Robert FRANCK, Walter GONZALEZ, Gérard LEVY, Jacques LEVY, Saadi LAHLOU, Valérie LEFEVRE-SEGUIN, Emmanuel NUNEZ, Pierre PESQUIES, Alain STAHL.

**I) Après que présentation par notre Président de notre nouveau Collègue, Jean Schmets, Professeur de Mathématiques à l'Université de Liège en Belgique et après avoir consacré une minute de silence à notre Collègue Marie-Louise LABAT, décédée le 14 juillet dernier, la séance est dédiée à la Conférence de Marc OLLIVIER, Astronome à l'Institut d'Astrophysique Spatiale d'Orsay**

**«Exoplanètes et Recherche de la vie»**

**Notre Président nous présente notre conférencier:**

**Marc OLLIVIER** est Astronome à l'Institut d'Astrophysique Spatiale d'Orsay, directeur d'EPOV, responsable instrument de la mission spatiale **CoRoT du CNES**, et **très impliqué dans la préparation de la mission EChO (Exoplanet Characterization Observatory)** proposée à l'ESA et en cours d'étude pour un vol en 2024. Sa thèse de doctorat en 1999 portait sur l'étude d'un démonstrateur en laboratoire d'un concept nouveau d'interféromètre permettant la spectroscopie des exoplanètes dans le cadre de l'étude d'une mission qui s'appelait à l'époque DARWIN et qui pour l'instant n'est plus étudiée à l'ESA.

## La parole est donnée à notre Conférencier:

Notre Conférencier nous présente le plan de son exposé : " **Exoplanètes et Recherche de la vie**" qui peut se schématiser ainsi:

### A) La diversité des systèmes planétaires

- Introduction historique
- Description statistique des exosystèmes
- Comment compléter la description
- Comprendre la structure des exoplanètes

### B) Comment rechercher la vie sur les exoplanètes ?

- Définir la vie
- La zone d'habitabilité des exoplanètes
- La recherche de bio-signatures

### A) La diversité des systèmes planétaires

Il nous expose les caractéristiques des planètes du système solaire en les présentant par ordre de distance croissante au soleil:

Planète	Diam.Equat(km)	Masse ( $M_{\oplus}$ )	Distance(u.a.)	Période (ans)
Mercure	4850 (0.38)	0.0554	0.3871	0.2409
Vénus	12140 (0.95)	0.815	0.7233	0.6152
<b>Terre</b>	<b>12756 (1.0)</b>	<b>1.00</b>	<b>1.000</b>	<b>1.000</b>
Mars	6790 (0.532)	0.1075	1.5237	1.8809
<b>Jupiter</b>	<b>142600 (11.18)</b>	<b>317.83</b>	<b>5.2028</b>	<b>11.8623</b>
Saturne	120200 (9.42)	95.147	9.5388	29.4577
Uranus	49000 (3.84)	14.54	19.1819	84.0139
Neptune	50200 (3.93)	17.23	30.0578	164.793
<b>Pluton</b>	<b>6400 (0.52)</b>	<b>0.17</b>	<b>39.44</b>	<b>247.7</b>

Concernant les **exosystèmes**, il nous donne les dates des observations récentes, sachant qu'au début seuls des objets de masse très importante sont détectés comme dans le cas de Berman en 1931 qui a détecté une étoile de faible masse ayant 18 fois la masse de Jupiter ( $M_j$ ) ....Jusqu'en 1995 on ne détectait aucune planète de masse inférieure à 3 fois la masse de Jupiter autour de 21 étoiles. Jusqu'à une époque très récente la détection des exoplanètes s'est révélée extrêmement difficile.

Il nous explique quelles sont les **méthodes de détection des planètes hors systèmes solaire**:

La présence d'une exoplanète modifie la vitesse, l'orbite d'une étoile par des effets gravitationnels. **Plusieurs milliers d'étoiles ont ainsi été surveillées en vitesse radiale**. Grâce à la coordination et à l'affinement des technologies, ont été découverts:

- 660 systèmes planétaires
- 837 planètes (~500 par mesure de la vitesse radiale)
- 124 systèmes multiples :dont 2 sextuples, 1 quintuple

L'augmentation de la **découverte d'exoplanètes** suit une courbe remarquablement ascendante : alors que 3 exoplanètes étaient découvertes en 1992, 196 l'ont été en 2011....

De même on a trouvé des planètes partout:

- Autour des étoiles de toutes tailles Type solaire : ex HD 209458 (G0V)
- Géantes : ex HD 47536 )□(K1 III : 23.5 R
- Naines : ex Gl 581 (M4)
- Autour des étoiles en fin de vie Pulsar : ex PSR 1257+12
- Naines blanches : ex V 391 (naine SdB)
- Autour des objets jeunes : ex 2MASS 1207 (naine brune 5 Mans)
- Dans les systèmes en formation : ex Fomalhaut
- Dans les disques de débris : ex Béta Pic

La distribution des masses des exoplanètes découvertes (exprimée en Mj- masse de Jupiter) est telle qu' on commence à observer de plus petites planètes et situées à de moindres distances de l'étoile.

Il nous rappelle également **quelques principes concernant la formation des planètes**:

La planète se forme dans un disque de gaz. Ensuite, se déclenchent des migrations d'orbites avec transfert de moment angulaire entre une planète et un disque. L' Interaction avec le disque keplerien dans un rayon de Hill autour de la planète peut se manifester comme suit:

- Le **Gaz interne** est plus rapide que la planète, il cède du moment angulaire à la planète, tombe vers l'étoile et accélère sa rotation.
- Le **Gaz externe** est moins rapide que la planète ,il prend du moment angulaire à la planète, s'éloigne de l'étoile et ralentit. Au bilan net : la planète perd du moment angulaire.

Il nous décrit ensuite les mécanismes de migrations d'orbite et ce qui régit l'excentricité des exoplanètes. Celle-ci induit elle-même des phénomènes tels que des effets de marée pour les orbites proches comme la lune sur la Terre.

Un autre paramètre est très important pour la formation des planètes: **la métallicité des Etoiles**.

La métallicité des étoiles permet de mesurer leur compositions respectives en H (X), He (Y), et les métaux (Fe ou Z) : Z : métallicité. **Une métallicité élevée semble favorable à la formation de planètes**. Cette observation serait compatible avec un modèle par **accrétion de planétésimaux et formation de planètes géantes**. **On ignore cependant son rôle dans la formation des planètes telluriques**.

La recherche d'**exoplanètes de type tellurique** pousse à rechercher de "**petites planètes**". Comment les **détecter**? En observant leurs transits autour des étoiles . Cela ne concerne que les systèmes observés par la tranche, pour lesquels les planètes peuvent occulter partiellement leur étoile centrale

Il nous présente à ce propos en bref **le projet COROT auquel il participe activement:**

- "Petite" mission CNES (MO) + Belgique +Allemagne +Brésil +ESA
- 3ème mission Proteus (minisat)
- Double programme: astérosismologie et Recherche de planètes extrasolaires
- Lancement 27 décembre 2006: Soyouz Starsem 2b depuis Baïkonour
- Orbite polaire circulaire à 896km d'altitude
- durée nominale : 3ans

Il nous explique quelques étapes du projet dans lequel sont mesurés **des variations de flux lumineux** liés à la présence de planètes. Pour mieux comprendre **la structure des exoplanètes**, il nous explique à ce propos **l'intérêt de la spectroscopie**. Cette dernière permet de connaître **la nature chimique de l'atmosphère** (CH<sub>4</sub>, H<sub>2</sub>O, NH<sub>4</sub>..) de la planète en réalisant une spectroscopie en transmission des transits lumineux. La **Spectroscopie de l'atmosphère** (Spectroscopie en transmission) permet une identification de CH<sub>4</sub>(et H<sub>2</sub>O).

Il en résulte **le projet EChO : spectroscopie des planètes en transit**

- Projet en cours à l'ESA
- Spectroscopie des planètes dans la gamme 0.6-11(16)microns
- sélection fin 2013, vol en 2022

## B)•Comment rechercher la vie sur les exoplanètes? habitabilité des exoplanètes

- **Comment définir la vie?** la vie est un système structuré ( contient de l'information), reproductif, évolutif (modification aléatoire et sélection du plus performant). Certes, mais comment **la caractériser à distance (détection, analyse)?** On utilise d'abord l'hypothèse selon laquelle la vie doit se développer à l'échelle de la planète et **modifier son environnement pour être détectable.**

### - Quelle(s) forme(s) de vie envisager ?

Un codage chimique de l'information basé sur la **Chimie du carbone** avec l'existence de 2 formes: C réduit(CH<sub>4</sub>) et C oxydé(CO<sub>2</sub>) et tous les nombres d'oxydation intermédiaires. La Chimie du carbone **est une chimie universelle**: Au laboratoire: 10<sup>7</sup>molécules (hors ADN) : 10<sup>5</sup>non carbonées. Dans le milieu interstellaire: plus de 80 % des molécules organiques ont été identifiées.

C'est également **une chimie en solution dans l'eau liquide** (Brack93) qui est un **solvant polaire ionisant et solvatant**, capable d'induire des liaisons par **pont hydrogène**, un solvant à activité **modérée** (hydrolyse), un solvant **résistant aux UV** (photodissociation: formation de O<sub>3</sub>).

Donc **pour définir une planète comme habitable** il faut:

- 1) la **présence d'une grande quantité d'eau liquide**
- 2) la présence d'une **quantité importante de carbone (CO<sub>2</sub>, CH<sub>4</sub>, molécules organiques extraplanétaires).**

**Néanmoins ces conditions sont nécessaires mais non suffisantes.** Il faudrait encore ajouter par exemple la

présence d'un champ magnétique pour protéger l'atmosphère.

La présence d'une grande quantité d'eau liquide va dépendre **de la distance de la planète à son étoile** comme le montre l'exemple du système solaire où à une distance inférieure à celle de la Terre l'eau est gazeuse et gelée à trop grande distance.

### - Comment étudier l'habitabilité effective des exoplanètes ?

On peut déjà comme dans l'**expérience d'Urey et Miller** essayer de **modéliser** la synthèse des acides aminés à partir d'une atmosphère abiotique "primitive" réductrice comportant de l'ammoniac de l'hydrogène, du méthane, de l'eau, de l'énergie. On aboutit à la formation de nombreuses molécules organiques complexes en une semaine. *(PB : ne marche que si l'atmosphère primitive est réductrice et acide, mais OK si c'est neutre)*

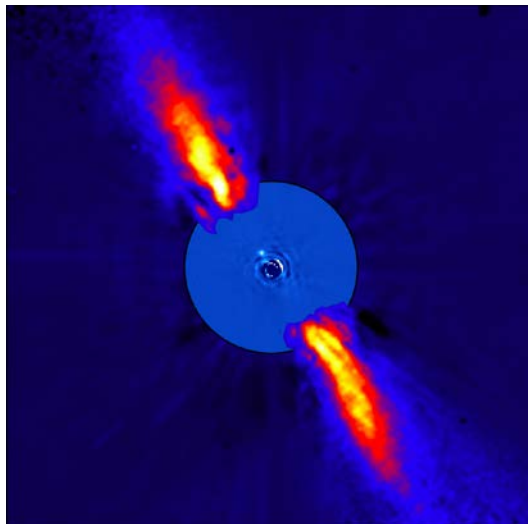
### - Comprendre les processus conduisant à la vie

Les difficultés de l'approche analytique sont liées à :

- 1) une **inconnue sur la nature exacte de l'atmosphère primitive (composition + conditions physico-chimiques)**
- 2) une **difficulté à passer des briques organiques aux premiers organismes vivants,**
- 3) l'interrogation sur **l'unicité des processus**, sur leurs rôles dans l'évolution (**longue durée ou catastrophiques**) et à une information parcellaire et parfois biaisée.

Une autre **approche est observationnelle**, fondée sur des **critères d'habitabilité effective**. Elle s'appuie sur **une recherche d'espèces hors équilibre i.e. qui ne subsistent pas ensemble simultanément comme par exemple méthane + oxygène, méthane + eau ..**

Pour tester **l'habitabilité effective** il faut observer la composition atmosphérique au premier ordre avec un spectre d'une haute résolution. Notre conférencier nous montre également des exemples de détections directes d'exoplanètes comme Lagrange et al. en 2009:



Lagrange et al. 2009

Il faut essayer d'**observer directement des planètes "telluriques"** en les imageant, On peut essayer d'obtenir par ordre croissant de résolution:

- 1) une caractérisation morphologique des grosses structures (continents -oceans) avec une résolution spatiale "pauvre" : 16x16 px
- 2) Une observation des structures géologiques, météorologiques et biologiques (montagnes - mers et océans -nuages -forêts)avec une résolution spatiale "faible" : 128x128 px
- 3) Observation des grandes structures technologiques (cités) avec une résolution spatiale "médium": 1024 x 1024 px
- 4) **une observation de la vie in-situ** (réseaux de communication, constructions artificielles, animaux) avec une **résolution spatiale "élevée" > 10000 x 10000 px**

D'autres méthodes consistent encore à détecter les modifications physico-chimiques, thermodynamiques, photosynthèse,...imputables à la vie dans l'environnement de la planète. Cela nécessite la construction d'instruments dédiés.

**Pour conclure** notre conférencier déclare que:

- Les exoplanètes et les exo-systèmes existent en grand nombre
- La diversité des systèmes a permis un nouveau regard sur la planétologie
- De nouveaux mécanismes ont été identifiés (migration d'orbite...)
- A ce jour, aucune exoplanète n'est assurément habitable et encore moins habitée,
- Une analyse chimique au premier ordre est envisageable à moyen terme
- L'observation directe de la surface des exoplanètes est illusoire.

Après quoi, notre séance prend fin,

Irène HERPE-LITWIN



# Comptes-rendus de la section

## Nice-Côte d'Azur

*Il y a une grandeur dans l'Homme qui se révolte devant le fait que la nature ne comprend pas, pour ainsi dire, la grandeur de ce qu'elle a fait.*

Prof. Gustave Martelet, théologien.

### Compte rendu de la séance du 21 juin 2012

(160<sup>ème</sup> séance)

#### Présents :

Pierre Bourgeot, Patrice Crossa-Raynaud, Guy Darcourt, René Dars, Jean-Pierre Delmont, Pierre Gouirand, Yves Ignazi, Jacques Lebraty, Maurice Lethurgez.

#### Excusés :

Jean Aubouin, Richard Beaud, René Blanchet, Maurice Papo, Jean-Marie Rainaud.

#### 1- Approbation du compte rendu de la 159<sup>ème</sup> séance.

**Le compte rendu est approuvé à l'unanimité des présents.**

#### 2- Accueil de M. Pierre Bourgeot.

Nous accueillons aujourd'hui notre nouveau membre, M. Pierre Bourgeot. Celui-ci exprime sa satisfaction et revient sur quelques-uns des faits marquants de sa carrière.

#### 3- Le mois écoulé.

Patrice Crossa-Raynaud : il n'est pas de meilleur révélateur des différences économiques entre les nations que l'écoute de leurs musiques. Comparons celles du 19<sup>ème</sup> siècle.

Les Allemands se projettent constamment dans le temps long (Wagner, Mahler, Brahms) alors que les Français privilégient l'instant, le résultat immédiat, la subtilité des accords successifs, la concision (Debussy, Satie,

Messiaen). C'est un habit d'arlequin sonore alors que la musique allemande est basée sur le développement, à partir d'un ou deux thèmes qui peuvent être très simples : deux notes pour le 1<sup>er</sup> mouvement de la 5<sup>ème</sup> symphonie de Beethoven, 4 notes pour le Requiem de Mozart.

On retrouve ces caractéristiques dans la politique économique. Le Chancelier Schroeder a mis en route des réformes en 2003, en se fixant un agenda 2010. On va au bout, on fait une symphonie. En France, nous privilégions plutôt l'instant et le résultat immédiats quand les Allemands se forment un avenir.

Yves Ignazi : à Nancy, la gare est un exemple fluide de l'art nouveau mais à Metz, construite sous l'occupation allemande, elle est prussienne.

Il faut cependant se garder de donner une échelle de valeur parce que ces deux expressions artistiques sont également admirables.

La vitesse des neutrinos : une publication récente a fait sensation. Des chercheurs du CERN ont affirmé que des neutrinos avaient dépassé la vitesse de la lumière. En fait, il s'agissait d'une erreur instrumentale que les chercheurs eux-mêmes ont admise ensuite.

Si cela avait été vrai, cela aurait bouleversé tout le modèle standard de la physique et donc cette publication erronée a eu un retentissement mondial.

On peut reprocher à ces chercheurs d'avoir publié leurs résultats révolutionnaires sans avoir pris le temps de bien les vérifier mais c'est la loi actuelle que de publier le plus vite possible, de crainte d'être pillés.

La conférence de Rio :

Patrice Crossa-Raynaud : on a constaté l'échec total de la dernière conférence internationale de Rio sur l'écologie. Cet échec fait suite à toutes les conférences précédentes : Copenhague, Durban, mais la dernière s'est caractérisée par l'absence de nombreux responsables de premier plan comme Obama, Merkel, Hu Jintao, Sing, Cameron, et signe la fin d'une certaine écologie, l'écologisme qui, depuis des années, utilise la peur comme instrument politique en prônant le naturisme, la décroissance.

En fait, elle est un succédané du communisme dont l'échec a été retentissant partout où on a voulu l'imposer. L'écologisme a été une nouvelle façon de lutter contre le capitalisme et les sociétés basées sur la liberté d'entreprendre, d'échanger, en prônant la planification à laquelle il faudrait se résoudre de gré ou de force.

L'erreur des animateurs de l'écologisme l'est d'avoir choisi de mauvaises causes.

Tout a commencé par le nucléaire très vite complété par les OGM et le réchauffement climatique. Or il n'y a eu qu'une catastrophe nucléaire, Tchernobyl. Toutes les autres centrales fonctionnent normalement et produisent, à moindre coût, l'énergie dont nous avons besoin.

Au Japon, les centrales nucléaires sont remises en route progressivement, même la troisième unité de Fukushima.

Pour les OGM, les variétés créées sont utilisées partout dans le monde sans aucun problème. Elles sont refusées en France à cause d'une campagne de dénigrement injustifiée. Or on vient de mettre au point des variétés OGM comportant des gènes qui leur permettent de produire dans des sols légèrement salés. Ces sols représentent des millions d'hectares dans le monde, dans toutes les régions où la pluviométrie ne permet pas de les lessiver naturellement.

En outre, on a constaté que les variétés OGM résistantes aux chenilles et qui ne sont donc plus traitées contre elles, hébergent des insectes auxiliaires qui luttent efficacement contre les autres parasites sans traitement.

Enfin, le fameux réchauffement climatique dont seraient responsables les hommes est mis en doute puisque la « température moyenne » (pour autant que cette notion utilisée par le GIEC ait vraiment un sens) n'a pas augmenté depuis 15 ans. La Terre se réchauffe depuis 15000 ans avec des variations. Tout le problème est de préciser le rôle de l'Homme dans le réchauffement.

Il convient donc maintenant de cesser de faire peur et de jeter l'anathème contre les hommes pour prôner une écologie véritable qui ne stérilise pas les initiatives.



*Il y a une grandeur dans l'Homme qui se révolte devant le fait que la nature ne comprend pas, pour ainsi dire, la grandeur de ce qu'elle a fait.*

Prof. Gustave Martelet, théologien.

## **Compte rendu de la séance du 19 juillet 2012**

(161<sup>ème</sup> séance)

### **Présents :**

Richard Beaud, Patrice Crossa-Raynaud, Guy Darcourt, René Dars, Jean-Pierre Delmont, Yves Ignazi, Maurice Lethurgez.

### **Excusés :**

Jean Aubouin, René Blanchet, François Cuzin, Pierre Gouirand, Jean-Paul Goux, Maurice Papo, Jean-Marie Rainaud.

### **1- Approbation du compte rendu de la 160<sup>ème</sup> séance.**

**Le compte rendu est approuvé à l'unanimité des présents.**

### **2- Le mois écoulé.**

- Le fils de notre confrère Jean-Paul Goux, qui est un spécialiste des problèmes d'énergie (Edf-Gdf) s'est révélé être un écrivain. Il a publié, avec succès, un roman –Jean-Pierre Goux : Ombres et lumières, Siècle bleu – Editions JBZ & cie, collection Hugo roman- d'une lecture agréable.

- Nicole Petit-Maire, qui a participé à notre colloque sur « Les climats de la Terre au cours des temps » vient de publier un livre qui résume toute sa très grande expérience professionnelle : « Sahara : les grands changements climatiques naturels » très largement illustré. C'est une des meilleures spécialiste du Quaternaire.

- La confirmation de la découverte du « Boson de Higgs » par le CERN à Genève est une illustration magnifique de la démarche scientifique. Certaines découvertes résultent surtout du « bricolage » : nous avons cité, le mois dernier, le transistor et le laser, mais il en est des milliers de comparables. D'autres, au contraire, ont été faites au tableau noir (la théorie de la relativité par exemple) et ont été confirmés ensuite grâce à des « bricolages ». C'est le cas pour le « boson de Higgs » qui confirme d'une manière définitive le modèle standard pour la « force faible » au départ entièrement théorique.

### **3- Prochain thème de conférences.**



## *Annonces*

### **I ) Notre Conférencier Marc OLLIVIER nous fait part de la présentation du projet EPOV "Environnements Planétaires et Origines de la Vie" :**

Le Programme Interdisciplinaire de Recherche du CNRS "Environnements Planétaires et Origines de la Vie" (EPOV) tiendra son colloque de restitution **les 29 et 30 novembre 2012** dans l'amphithéâtre Marie Curie sur le **campus Gérard Mégie du CNRS, 3 rue Michel-Ange à Paris.**

L'objectif de ce colloque est de présenter les principaux résultats des projets soutenus par le programme et de les mettre en perspective dans un contexte interdisciplinaire. Le colloque alternera des conférences par des orateurs invités de prestige (Steven Benner, T. Encrenaz, John Sutherland, Guenter Von Kiedrowski, ...) et la présentation des résultats des projets proprement dits, sous forme orale ou posters.

**Le programme du colloque ainsi que le formulaire d'inscription sont disponibles sur le site de la conférence :**

**<http://epov2012.sciencesconf.org/> L'inscription au colloque est gratuite, ouverte à tous, mais obligatoire pour des raisons de logistique (organisation du colloque) et de sécurité (campus sous plan vigipirate).**

II) Notre Collègue **Gilles COHEN-TANNOUDJI** nous fait part d'événements à la BNF:

## A) Cycle de Conférences à partir du 6 octobre 2012

### Les samedis des savoirs - Penser le vivant

Informations pratiques

samedi 6 octobre 2012

15h00-16h00

François-Mitterrand

Petit auditorium

Entrée libre

Quai François-Mauriac - Paris 13<sup>e</sup>

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#### • Que peuvent les gènes ?

Avec **Pierre-Henri Gouyon**, professeur d'écologie au Muséum National d'Histoire Naturelle et **Denis Noble**, professeur de physiologie à l'université d'Oxford (sous réserve).  
Cycle conçu et présenté par **Roland Schaer**, philosophe.

**samedi 6 octobre 2012 15h00-16h00**

- *Autres Séances*
- [Le temps de l'évolution, le temps de l'histoire](#)
- samedi 13 octobre 2012
- [Cerveaux animaux, cerveau humain, à la lumière de l'évolution](#)
- samedi 20 octobre 2012
- [Comment devenons-nous des individus ?](#)
- samedi 27 octobre 2012

Génétique, biologie du développement, neurosciences : qu'est-ce que le vivant ? Qu'est ce que l'être humain ?  
Quatre rencontres, réunissant à chaque fois deux spécialistes, nous aideront à entrer dans ce monde en pleine effervescence.

*Cycle conçu et présenté par Roland Schaer, philosophe.*

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## **B) Colloque**

### **Les nouvelles lumières**

*Comment la physique continue d'éclairer le monde*

*qui se tiendra :*

**Samedi 24 novembre 2012 de 9h à 18h**

**Bibliothèque Nationale de France,**

**Site François Mitterrand,**

**Grand auditorium,**

**hall est Quai François Mauriac,**

**75013, Paris**

Notre Collègue Gilles COHEN-TANNOUDJI nous communique les coordonnées du site <http://sfp.in2p3.fr/CP/pifn/fren13.htm> contenant toutes les informations relatives au futur colloque



III) Le Pr André BRAHIC nous fait part de la parution de son dernier ouvrage:



[Agrandir l'image](#)



## Science (La)

Une ambition pour la France

Auteur(s) : [André Brahic](#)

- **Date de parution** : 15/05/2012
- **Nombre de page** : 160 pages
- **Format** : 140 x 205 mm
- **ISBN** : 9782738128164
- [9.90 €: Acheter la version papier](#)
- [8.49 €: Acheter la version numérique](#)

« La recherche, l'éducation et la culture doivent être les priorités absolues d'un pays avancé. On ne pourra pas lutter efficacement contre la violence et contre le chômage si on ne mène pas un combat pour la connaissance.

Mon appel pour la science est destiné à tous, citoyens, hommes politiques, responsables économiques, décideurs, enseignants et chercheurs. À tous, je dis : aimons la science car elle peut beaucoup pour nous rendre heureux ! Osons la science pour préparer notre avenir !

Renouons le dialogue entre sciences et société, entre la France et ses chercheurs ! » *A. B.*

Un manifeste pour la recherche.

André Brahic est astrophysicien. Il est professeur à l'université Paris-Diderot et au Commissariat à l'énergie atomique et aux énergies alternatives. Découvreur des anneaux de Neptune, membre des équipes scientifiques des missions

Cassini et Voyager, il est l'un des principaux acteurs mondiaux de l'étude du système solaire. Il est l'auteur d'*Enfants du Soleil*, de *De feu et de glace* et, en collaboration avec Isabelle Grenier, de *Lumières d'étoiles*, qui ont été de très grands succès.

**IV) Franck VARENNE qui avait présenté ses travaux lors de notre Colloque "Théories et Modèles en science sociales" nous fait part de la parution de son dernier ouvrage:**



**Théorie, réalité, modèle**  
**Épistémologie des théories et des modèles face au réalisme dans les sciences**

Paris, Editions Matériologiques, 2012 /Collection "Science & Philosophie"  
 ISBN : 978-2-919694-13-6/ Format : 17x24 cm /Support : PDF /Publication : août 2012  
 Nombre de pages : 259 /Prix : 13 euros

Présentation :

Les théories scientifiques sont-elles vraies ? Nous donnent-elles une juste représentation de la réalité ? Ou bien ne sont-elles que des fictions commodes permettant uniquement la prédiction et le calcul ? Et qu'en est-il des modèles ? C'est toute la question du réalisme scientifique. Dans cet ouvrage, Franck Varenne pose la question du réalisme scientifique, essentiellement dans sa forme contemporaine, et ce jusqu'aux années 1980. Il s'est donné pour cela la contrainte de focaliser l'attention sur ce que devenaient sa formulation et les réponses diverses qu'on a pu lui apporter en réaction spécifique à l'évolution parallèle qu'ont subie les notions de théories et surtout de modèles dans les sciences, à la même époque. Même si, bien sûr, on ne peut pas attribuer le considérable essor des modèles au XXe siècle au projet qu'auraient eu les scientifiques de régler cette question, en grande partie philosophique, du réalisme – car les modèles scientifiques ont bien d'autres fonctions et ils proviennent de bien d'autres demandes techniques, cognitives et sociales –, son choix épistémologique a consisté à suivre la littérature contemporaine désormais classique, tant scientifique que philosophique, sur les théories puis sur les modèles afin d'une part, d'en rapporter l'évolution générale, mais, d'autre part aussi, afin de l'interroger de proche en proche, et systématiquement, sur ce qu'elle entend à chaque fois réévaluer ou remettre en débat au moyen de cette question persistante du réalisme et de la réalité en science. Au-delà de l'enquête historique, cette étude se révèle donc également comparative. Elle présente l'intérêt de mettre en évidence des similitudes de forme remarquables (identités, symétries, inversions, déplacements) entre des séquences argumentatives produites par des auteurs différents, dans des contextes distincts, au sujet de cette capacité qu'aurait – ou non – la science à rendre véritablement compte de la réalité.

Ainsi, via l'analyse épistémologique historique et comparative qu'en propose Franck Varenne, la question cruciale de la médiation du réel par nos outils conceptuels ou expérimentiels reçoit dans ce livre l'éclairage d'auteurs contemporains dont les conceptions sont, pour certaines encore, méconnues du lecteur non anglophone : Peter Achinstein, Max Black, Ludwig Boltzmann, Nancy Cartwright, Pierre Duhem, Ian Hacking, Mary Hesse, Evelyn Fox Keller, Imre Lakatos, Ernst Mach, Ernest Nagel, Henri Poincaré, Willard V.O. Quine, Bas van Fraassen, etc.

**V) Notre Collègue Christian HERVE nous donne les préprogrammes des journées du 3 et 4 décembre 2012 :**

Journée de la Société Française et Francophone d'Ethique Médicale (SFFEM)

**Lundi 3 décembre 2012**

« Les nouveaux modèles de médecine, enjeux cliniques, scientifiques et éthiques »

Personnes pressenties

8h30 : accueil des auditeurs

9h00/9h15 : Introduction par le Pr Christian Hervé, les mouvements de la pensée et l'ESi3S

9h15/9h45 : La médecine personnalisée par le Pr Eric Thervet,

10h/10h30 : La médecine palliative par le Pr Régis Aubry

10h45-11h15 : Pause Café

11h15/11h45 : La médecine de la maladie chronique par le Pr Serge Perrot

12h00/14h : Déjeuner

14h/14h30 : La médecine de solidarité interhumaine, par le Dr Marie France Mamzer

14h45/15h15 : La médecine de prévention par le Pr Jacques Blacher

15h30/16h : La précarité et les urgences médico-judiciaires par le Pr Jean-louis Pourriat

16h15/16h45 : La médecine et l'informatique, par le Pr Anita Burgun

17h00/17h30 : Audition et remise des deux prix Jean Bernard et Yves Pélicier par le Pr Patrick Berche, doyen de la faculté de médecine Paris Descartes, prix accordés aux meilleurs affiches présentées lors du congrès réalisées respectivement par un sénior et un junior.

17h30 : Conclusion par un grand témoin, Pr Sadek Béloucif

18h00 : Assemblée générale de la SFFEM.

**Journée de la Société Française et Francophone d'Ethique Médicale (SFFEM)**

**Mardi 4 décembre 2012**

Salle du Conseil, Université Paris Descartes 12, rue de l'Ecole de médecine

« Les nouveaux modèles de formation en éthique médicale »

Personnes pressenties

9h00/09h15 : accueil par le Pr le Pr Frédéric Dardel, président de l'Université Paris Descartes et par le doyen de la faculté de médecine, le Pr Patrick Berche

9h15/9h30 : Introduction : De la pluridisciplinarité et de l>IDEX à une collaboration InterPRES en Ile-de-France, par le Pr Jean François Girard, président du PRES Sorbonne Paris Cité

9h30/10h : De l'organisation, de l'éthique clinique et du management, Le concept ESi3S par Michel Daigne, Centrale Santé.

10h15/11h15 : Les patients et les formations des médecins à propos d'une formation «De l'étudiant médecin au médecin responsable, EM2R » : tels qu'ils les espèrent, Table Ronde par Patrice Marvanne, groupe des patients de l'Institut Curie, Claude Rambaud, Le lien et le CISS, Catherine Vergely, groupe des parents de l'IGR.

11h30/12h : Les différents modes de réalisation d'un corpus de connaissances éthiques pour l'enseignement et la recherche : De Rodin à E-Ethics par le Pr Christian Hervé, LEM

12h00/14h : Déjeuner

14h/14h30 : L'éthique dans le domaine de la santé à l'Assistance Publique par le Pr Emmanuel Hirsch, Espace éthique de l'APHP

14h45/15h15 : L'enseignement des travaux des membres du CCNE par le Pr Pierre Le Coz, rapporteur de l'avis n° 84 du Comité Consultatif National d'Ethique sur « La formation à l'éthique médicale »

15h30/16h30 : L'enseignement des travaux des comités internationaux par Mme Michèle Stanton Jean, Université de Montréal et le Pr Gérard Teboul, Université Paris XII à propos de la Déclaration universelle sur la bioéthique et les droits de l'homme du 19 octobre 2005 et de la convention du Conseil de l'Europe, du 4 avril 1997, pour la protection des Droits de l'Homme et de la dignité de l'être humain à l'égard des applications de la biologie et de la médecine: Convention sur les Droits de l'Homme et la biomédecine

16h45/17h15 : L'éthique et les professions de santé par Alain Cordier, Haute Autorité de Santé

17h30/18h : Synthèse par Michel Doucin, ambassadeur chargé de la bioéthique et de la responsabilité sociale des entreprises de la bioéthique et des entreprises

## Documents

Pour préparer la conférence de François ROBERT, directeur de Recherche au CNRS, "*Comment reconstituer la synthèse organique dans le système solaire primitif ?*" nous vous proposons:

p. 21: "Distinct source for lunar water" publié par François ROBERT dans Nature geoscience | VOL 4 | FEBRUARY 2011 | [www.nature.com/naturegeoscience](http://www.nature.com/naturegeoscience)

P. 24 "Model of molecular structure of the insoluble organic matter isolated from Murchison meteorite" par Sylvie DERENNE\* et François ROBERT paru dans Meteoritics & Planetary Science 1–15 (2010)

## Planetary science

### Distinct source for lunar water

The origin of water in the Earth–Moon system is an open question. Geochemical analysis of the rocks retrieved by the Apollo missions show that lunar and terrestrial water are isotopically distinct, suggesting acquisition after the Moon’s formation.

#### François Robert

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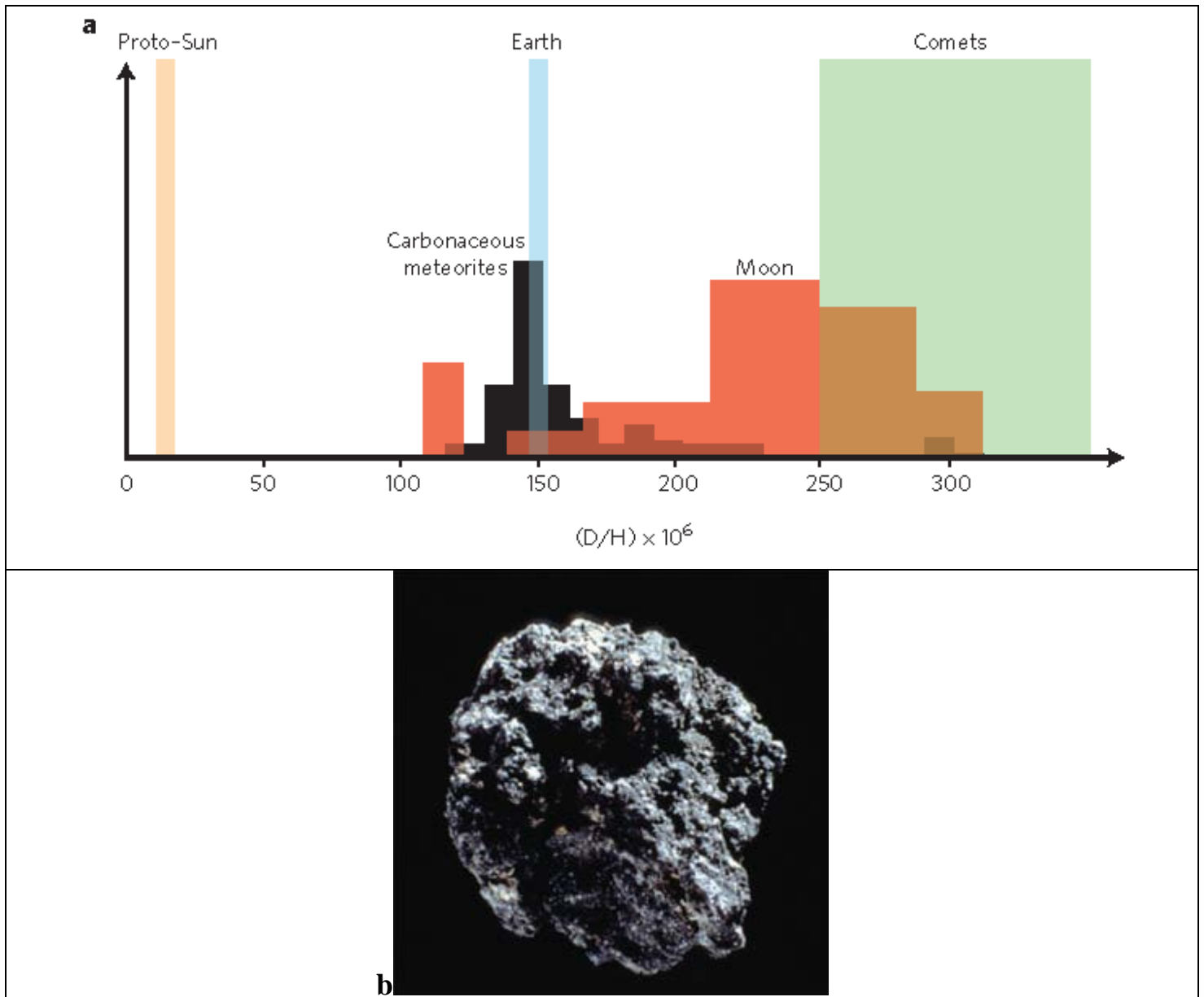
The Earth was essentially dry when it formed. Our planet’s bulk chemical and mineralogical composition shows some similarities with a group of meteorites, known as the enstatite chondrites<sup>1</sup>, that were originally hosted by small planetoids in the protosolar disk. These planetoids were free of water when they accreted. No trace of water circulation was ever detected in the enstatite chondrites. By inference, proto-Earth is assumed to have been devoid of water, too, and the existence of oceans on Earth has been a puzzle. Writing in *Nature Geoscience*, Greenwood and colleagues<sup>2</sup> report that lunar water has a substantially different isotopic composition to that on Earth, implying that our planet received its water after the formation of the Moon, probably in a few or even only a single collision that missed our nearest neighbour.

Meteorites are the most ancient rocks. They are regarded as the debris of the first planetoids that formed in the Solar System. Thus, they represent the elemental bricks from which the planets were formed. Under the conditions prevalent in the protoplanetary disk, water freezes to ice at temperatures of 200 K (ref. 3). This is well below the condensation temperature of the mineralogical compounds found in enstatite chondrites, and thus presumably of the compounds that constituted the proto-Earth. Because the gas phase was highly reduced when the accretion of enstatite chondrites took place in the solar disk, their minerals would therefore not have been altered by trace amounts of water vapour — if there was any. And had water occurred in trace concentrations in the enstatite planetoids, it would immediately have been chemically reduced on circulation on a metre scale, because of the reaction of water with the metallic minerals. The resulting molecular hydrogen would have escaped to space, leaving proto-Earth and the enstatite chondrites dry. How and when water accumulated on Earth remains unclear.

Two scientific advances have helped with unravelling these questions. First, the hydrogen isotope ratio of water, that is, the ratio of deuterium (D) to hydrogen (H), has been determined for a range of meteorites<sup>4</sup>, and was found to be characteristic of the water’s sources. For example, water found in comets has a D/H ratio that is twice that of a second class of meteorites, the carbonaceous chondrites (Fig. 1). Unlike enstatite chondrites, the carbonaceous chondrites were formed at low temperature and they were oxidized by extensive circulation of liquid water. They display a distribution of D/H ratios that corresponds roughly with that found in the bulk Earth. Therefore, it was proposed that water on Earth was added by the final impacts of water-rich planetoids — akin to carbonaceous meteorites — that formed the Earth. A further source for the water on Earth is nevertheless conceivable: comets — which are made up of up to 50% of water ice — could have contributed, too. However, the D/H ratio of cometary water was found to exhibit a value that is around twice that of the terrestrial oceans<sup>5</sup>, ruling out a significant contribution to the water budget on Earth.

Second, numerical simulations of planetary collisions have mimicked the formation of planets by successive additions of planetoids<sup>6</sup>, and result in simulated planets that have masses and orbital parameters

close to those observed in Solar System planets at present. These simulations support the geochemical scenario in several respects. First, the fraction of cometary water relative to the bulk terrestrial water reservoir is negligible. Second, the last planetoids accreted by the proto-Earth come from cold regions of the inner Solar System where carbonaceous chondrites formed. And finally, the bulk Earth is essentially composed of bodies that formed and travelled in its close vicinity. Earth would thus have been dry originally, although there is a lack of consensus on this last point<sup>7</sup>. All in all, the view emerges that water on Earth was added by the last massive impacts of planetoids, whose compositions and origins were similar to those of the carbonaceous chondrites.



**Figure 1** | Water acquisition in the Earth–Moon system. **a**, Water isotope ratios in material from the Solar System. Greenwood and colleagues<sup>2</sup> show that the ratio of deuterium to hydrogen (D/H) in lunar water (red) is distinct from the water D/H ratio found in Earth’s ocean and mantle (blue) and in carbonaceous meteorites (black). The D/H ratio for protosolar molecular hydrogen is lower (pale orange), whereas cometary water has a higher ratio (green). **b**, A piece of the Orgueil meteorite. This meteorite is often used as a reference sample for the carbonaceous chondrites. It contains around 10% water, with a D/H ratio close to that of the Earth’s oceans. The piece on the photo is about 2 cm in diameter. [Au: Please provide a figure credit.]

Greenwood and colleagues<sup>2</sup> refine this view by reporting the D/H isotope ratio of rocks from the Moon collected during the Apollo missions. They detected high D/H ratios in the rare mineral apatite, which forms during the crystallization of magma and was found in a variety of lunar mare basalts and highlands rocks. Because the detected D/H ratios of apatite (Fig. 1), contamination from Earth material can be ruled out. Water must therefore have occurred in at least a few lunar magmas when they cooled. Furthermore, the large variations in the D/H ratio of the samples from various surface locations on the Moon, and with different formation ages, suggest that — unlike on Earth — water on the Moon from different origins was never homogenized.

The isotopic contrast with the Earth is even more surprising. The lunar apatites have D/H ratios that are twice that of terrestrial water, and therefore seem to have acquired their water from comets. It seems possible that comet impacts occurred on the Moon before its basalt reached the surface. The comets' ice could then locally have contaminated the magma that later formed the sampled apatite. But if so, it is difficult to explain the absence of an isotopic signature in line with that of carbonaceous chondrites, which are the dominant source of water on Earth. It remains a conundrum how Earth and the Moon could have sampled water from different origins.

The study by Greenwood and colleagues<sup>2</sup> confirms a remarkable prediction<sup>6</sup>: although the oxygen isotopic compositions of the mantles of the Earth and the Moon are identical<sup>8</sup>, their water D/H ratios are quite distinct. Water on Earth must therefore be a late addition, resulting from only one, or at most a few collisions with the Earth that missed the Moon.

### References [Au: please check carefully as they have been renumbered]

1. Javoy, M. *et al. Earth Planet. Sci. Lett.* **293**, 259–268 (2010).
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## Model of molecular structure of the insoluble organic matter isolated from Murchison meteorite

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(Received 10 May 2010; revision accepted 28 July 2010)

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**Abstract**—The molecular structure of the insoluble organic matter (IOM) from Murchison meteorite has been investigated by our group for several years using a large set of analytical methods including various spectroscopies (Fourier transform infrared spectroscopy, nuclear magnetic resonance, electron paramagnetic resonance, X-ray absorption near-edge spectroscopy), high resolution electron microscopy, and thermal (pyrolyses in the presence or not of tetramethylammonium hydroxide) and chemical (RuO<sub>4</sub> oxidation) degradations. Taken together, these techniques provided a wealth of qualitative and quantitative information, from which we derived 11 elemental and molecular parameters on the same IOM residue. In addition to the basic elemental composition, these parameters describe the distribution of the different types of carbon, nitrogen, and sulfur atoms as well as the size of the polyaromatic units. For this molecular structure, we therefore propose a model which fits with these 11 molecular quantitative parameters. Several cosmochemical implications are derived from this structure. Based on the fact that aromatic moieties are highly substituted and aliphatic chains highly branched, it can be anticipated that the synthesis of this IOM occurred through successive additions of single carbon units in the gas-phase ending by a spontaneous cyclization for chain length  $\geq 7$  C. As a whole, these observations favor an organosynthesis in the solar T-Tauri disk.

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### INTRODUCTION

Carbonaceous chondrites are known to contain substantial amounts (up to 4%) of organic matter, most of which occurs as insoluble organic matter (IOM). Numerous studies performed since the 1970s aimed at deciphering the chemical structure of this IOM, mostly in the Murchison meteorite. Indeed, a precise knowledge of the structure of the organic macromolecule contains irreplaceable information that traces its mechanisms of synthesis and its conditions of formation. During the last 10 yr, we have participated in this work, with the aim of reconstructing the overall molecular structure of Murchison IOM. This led us to propose a preliminary model (Rémusat et al. 2007). The latter was qualitative and limited to a small number of moieties and as mentioned by the authors themselves “to draw a molecular model should be the goal of a future work.”

The main weakness of this model structure appears to be the large size of the aromatic units, which turns out to be impossible to balance with short aliphatic chains as required by molecular parameters. In this article, we propose such a more complete modeled structure that takes into account all these parameters.

The IOM, which constitutes more than 75 wt% of the bulk organic matter, is isolated from the bulk rock through water and solvent extractions to remove soluble organic compounds and successive HF/HCl treatments to dissolve most of the mineral matrix. Such acid treatments are known not to alter the IOM (Durand and Nicaise 1980). Acid insoluble residues are enriched in IOM but contain inorganic material mainly consisting of natural oxides, sulfides, and chlorides according to X-ray diffraction.

The chemical structure of IOM isolated from Murchison has been studied by both destructive and nondestructive methods. The former include thermal



and chemical degradations followed by gas chromatography/mass spectrometry (GC/MS) (Studier et al. 1972; Lévy et al. 1973; Hayatsu et al. 1977, 1980, 1983; De Vries et al. 1993; Komiya and Shimoyama 1996; Sephton et al. 1998, 2000, 2004; Remusat et al. 2005a, 2005b; Huang et al. 2007; Yabuta et al. 2007) and the latter contain mainly spectroscopic techniques (nuclear magnetic resonance [NMR], Fourier transform infrared [FTIR] spectroscopy, X-ray absorption near-edge spectroscopy [XANES], and electron paramagnetic resonance [EPR]) along with high-resolution transmission electron microscopy (HRTEM) (Cronin et al. 1987; Ehrenfreund et al. 1992; Gardinier et al. 2000; Cody et al. 2002, 2008; Cody and Alexander 2005; Binet et al. 2002, 2004a, 2004b; Derenne et al. 2002, 2005; Yabuta et al. 2005; Wirick et al. 2006). Although each technique alone cannot provide definite information on the chemical structure of such a complex material, the combination of the results can be used to reconstruct the molecular structure of the IOM. However, quantitative data are key parameters to build up such a model and to assess its validity. Therefore, we will only use the studies reporting such parameters to construct the model, and our qualitative observations will be used to support discussions. It is also important to note that variations in the bulk elemental compositions were reported in the literature (probably depending on the isolation procedures of the acid residues). To overcome this analytical bias, all the quantitative parameters used in the present work were obtained on the same residue, which contained 19% mineral matter (Gardinier et al. 2000).

The details of this structure reveal information of the conditions of the formation in space of the IOM. Therefore, the last section of the article discusses the possible organosynthetic pathways in the cosmochemical context of the formation of the solar system.

## MODELING THE CHEMICAL STRUCTURE OF THE IOM

### Analytical Constraints

Analytical methods including spectroscopic, microscopic, and degradation techniques were used to determine the analytical constraints that are discussed below. Experimental conditions for these methods were described in detail in the source papers; they are only briefly reported in the Appendix.

### *Aromatic Moieties*

The elemental composition of the IOM isolated from Murchison points to a rather high aromaticity

with hydrogen to carbon atomic ratios around 0.7 (Gardinier et al. 2000).

The aromatic nature of the IOM from Murchison was further evidenced by the occurrence of an intense band at  $1600\text{ cm}^{-1}$  in its FTIR spectrum (Gardinier et al. 2000) and of a strong absorption at 285.5 eV in C-XANES, corresponding to the  $1s\text{-}\Pi^*$  transition of the aromatic carbons as in polyaromatic hydrocarbons (Derenne et al. 2002; Wirick et al. 2006; Cody et al. 2008). Moreover, a strong aromaticity was inferred from the pioneer solid-state  $^{13}\text{C}$  NMR study, the Murchison IOM spectrum being dominated by a peak around 130 ppm in the (Cronin et al. 1987). Extensive CP/MAS  $^{13}\text{C}$  NMR studies using variable contact time and IRCP sequence (Gardinier et al. 2000) and interrupted decoupling experiments (Cody et al. 2002) revealed that most of these aromatic carbons were nonprotonated, thus leading to two hypotheses: the polyaromatic units are either very large (hence a large number of nonprotonated core carbons) or, if smaller, they must be highly substituted. The HRTEM and EPR results reported below clearly support the second assumption.

In HRTEM, aromatic layers appear as fringes. Such layers can be isolated or stacked together to form coherent domains. Image analysis was developed to derive semiquantitative data from the HRTEM images (Rouzaud and Clinard 2002). In Murchison IOM, the distribution of the fringe lengths indicates that the aromatic layers in the meteorites are of rather small size, most of them exhibiting diameter between 0.25 and 1 nm, i.e., 1–4 ring large, the average values corresponding to two to three rings (Derenne et al. 2005). In addition, a relatively low level of organization is inferred from the rather high contribution of isolated fringes (65%). This is confirmed when coherent domains are considered as more than 70% of them are made up with only two stacked layers, nearly 30% comprising three layers. Finally, the average interlayer spacing is of 0.49 nm, i.e., far from graphite (0.3354 nm).

The occurrence of aromatic moieties was also inferred from chemical degradation studies, especially oxidations using trifluoroacetic acid, nitric acid, potassium dichromate, cupric oxide, or ruthenium tetroxide as reagents (Hayatsu et al. 1977, 1980; Remusat et al. 2005a, 2005b). However, the formation of benzene hexa- and tetracarboxylic acids was first considered to reveal the occurrence of highly condensed polyaromatic units (Hayatsu et al. 1977), but this interpretation was revisited (Hayatsu and Anders 1981). Indeed, the high degree of carboxylation of the aromatic oxidation products is also consistent with a high degree of substitution of the initial aromatic units. More recently,  $\text{RuO}_4$  oxidation products pointed to less

condensed aromatic units in Murchison IOM than in high rank coals (Remusat et al. 2005a, 2005b). One- to four-ring aromatic products are extensively generated during pyrolyses with a lower abundance of the larger compounds (Studier et al. 1972; Hayatsu et al. 1977; Komiya and Shimoyama 1996; Sephton et al. 1998, 2000; Remusat et al. 2005b; Yabuta et al. 2007). As demonstrated by the above spectroscopic data, these aromatics are pre-existing in the IOM and thus are not mainly derived from secondary aromatization upon pyrolyses. Although the larger aromatics are the more difficult to detect upon GC/MS, the decrease of the abundance of the aromatic products when their size increases is consistent with the small size of the polyaromatic units derived from HRTEM. In addition, the presence of polyaromatic units containing pentagonal rings such as indene or acenaphthene was reported in several pyrolytic studies (Komiya and Shimoyama 1996; Sephton et al. 2000; Remusat et al. 2005b) and especially in Yabuta et al. (2007) although no quantification was performed and hence no relative abundance can be assessed for these compounds.

#### *Aliphatic Linkages*

Fourier transform infrared and  $^{13}\text{C}$  NMR show that aliphatic carbons contribute along with aromatic ones to the molecular structure of the IOM. Based on the  $\text{CH}_2$  to  $\text{CH}_3$  ratio, both techniques point to a high branching level in the aliphatic chains (Ehrenfreund et al. 1992; Gardinier et al. 2000). A number of chemical degradations were performed on Murchison IOM as far back as 1977 using a wide range of reagents such as trifluoroacetic acid, nitric acid, dichromate, copper oxide, and ruthenium tetroxide (Hayatsu et al. 1977, 1980; Remusat et al. 2005a, 2005b). Nitric acid did not yield any aliphatic acid but benzene polycarboxylic acids with up to three carboxylic groups (Hayatsu et al. 1977). Oxidation with dichromate mainly resulted in the formation of aromatic acids, but small amounts of aliphatic diacids ( $\text{C}_3$ – $\text{C}_5$ ) and monoacids ( $\text{C}_3$ – $\text{C}_7$ ) were also identified (Hayatsu et al. 1977), the diacids being also detected upon copper oxide oxidation (Hayatsu et al. 1980). Diacids were supposed to be derived from hydroaromatics with five- to six-membered rings (Hayatsu et al. 1977). In contrast, monoacids were considered to represent alkyl substituents or bridging groups between aromatic units. However, it was mentioned that acids lower than propionic were probably lost and that those with more than seven carbon atoms may have escaped detection due to their low-intensity molecular ion (Hayatsu et al. 1977). Trifluoroacetic acid also led to the formation of small amounts of aliphatic compounds (alkanes and alkenes, the latter being dominant), but their origin was

not clear. As a result, little information on the aliphatic linkages can be derived from these chemical degradations.

In contrast, ruthenium tetroxide is a mild and selective oxidizing agent that preferentially destroys aromatic rings converting them into  $\text{CO}_2$ . The aliphatic and acyclic structures released appear as carboxylic acids. These carboxylic functional groups mark either points of attachment in the kerogen or positions of labile functional groups, such as carbon–carbon double bonds and ether links (Stock and Wang 1986). This method was shown to be especially efficient to investigate the aliphatic structures in kerogens (Boucher et al. 1990). This oxidation reveals the short length of the chains (less than three carbons for side chains born by aromatic moieties and from two to seven carbons for aliphatic bridges between aromatic units) (Remusat et al. 2005a, 2005b; Huang et al. 2007). The short length of these chains is consistent with the lack of *n*-alkane/*n*-alk-1-ene doublets upon pyrolysis GC-MS as they are usually detected for carbon numbers higher than eight. However, when gases released upon pyrolysis are studied, alkanes and alkenes from methane to  $\text{C}_4$ -compounds are indeed identified (Remusat et al. 2005b). Aliphatic linkages released through  $\text{RuO}_4$  oxidation also exhibit a high branching level, with substitution by methyl or ethyl groups. These substitutions are randomized as there is an isomeric diversity. Moreover, the occurrence of aliphatic chains linking several aromatic units (Remusat et al. 2005a, 2005b) is consistent with the high degree of cross-linking evidenced by solid-state  $^{13}\text{C}$  NMR.

#### *Oxygen Localization*

Besides carbon and hydrogen, oxygen is the most abundant element of the IOM. Spectroscopic analyses reveal several forms of oxygen-containing functional groups. Indeed, C-XANES spectra exhibit a strong absorption at 288.9 eV (Wirick et al. 2006).  $1s\text{-}\Pi^*$  transition of carbons in carbonyl groups is known to occur at approximately 289 eV but C–H\* resonances typical of  $\text{sp}^3$ -coordinated carbons with a high content of hydrogen have been reported at 289.2 eV. The XANES peak in the meteorite spectra thus suggests the presence of oxygen-containing functions. Solid-state  $^{13}\text{C}$  NMR confirmed the presence of low amounts of carbonyl groups (resonance at 200 ppm) and revealed substantial amounts of carbon linked to oxygen (as in ether or aliphatic alcohols, at 55 ppm) and involved in carboxylic groups (acids and/or esters, around 168 ppm) (Gardinier et al. 2000; Cody et al. 2002). The presence of these groups is further supported by a high yield in  $\text{CO}_2$  and CO upon vacuum pyrolysis of the IOM. The production of these gases reflects

Table 1. Summary of the chemical and molecular parameters of Murchison IOM used to model the chemical structure.

	Parameter	Experimental value	Analytical techniques	Other literature data
1	Aliphatic CH <sub>2</sub> /aliphatic CH <sub>3</sub>	2.0 ± 0.2 <sup>[1]</sup>	<sup>13</sup> C NMR, FTIR	1.57–1.79 <sup>[2]</sup>
2	Nonprotonated aromatic C/protonated aromatic C	2.80 ± 0.28 <sup>[1]</sup>	<sup>13</sup> C NMR	2.33 <sup>[2]</sup> ; 1.86–2.70 <sup>[3]</sup>
3	Aromatic C/aliphatic C	3.0 ± 0.3 <sup>[1]</sup>	<sup>13</sup> C NMR	2.76 <sup>[2]</sup> ; 3.08–3.28 <sup>[3]</sup> ; 1.82–2.17 <sup>[4]</sup>
4	Acid C/total C	0.070 ± 0.014 <sup>[1]</sup>	<sup>13</sup> C NMR	0.074 <sup>[2]</sup>
5	Thiophenic S/aliphatic S	3.17 ± 0.31 <sup>[5]</sup>	S-XANES	
6	N as nitriles/total N	0.15 ± 0.05 <sup>a[5]</sup>	<sup>15</sup> N NMR	
7	Average number of rings (2-D)	2.3 ± 0.3 <sup>[6]</sup>	HRTEM	
8	H/C	0.70 ± 0.04 <sup>[1]</sup>	Elemental analysis	0.70 <sup>[7–9]</sup> ; 0.71 <sup>[10]</sup> ; 0.38 <sup>[11]</sup> ; 0.52 <sup>[12]</sup> ; 0.48 <sup>[13]</sup> ; 0.53 <sup>[14]</sup>
9	O/C	0.22 ± 0.02 <sup>[15]</sup>	Elemental analysis	0.16 <sup>b[7]</sup> ; 0.12 <sup>[10, 13]</sup> ; 0.25 <sup>[14]</sup>
10	N/C	0.03 ± 0.006 <sup>[5]</sup>	Elemental analysis	0.031 <sup>[7]</sup> ; 0.027 <sup>[10, 16]</sup> ; 0.015 <sup>[12]</sup> ; 0.012 <sup>[13]</sup> ; 0.034 <sup>[8]</sup> ; 0.044 <sup>[17]</sup> ; 0.029 <sup>[14]</sup> ; 0.035 <sup>[18]</sup> ; 0.039 <sup>[9]</sup>
11	S/C		Elemental analysis	0.021 <sup>[10, 13]</sup>
	Small aromatic units		EPR, <sup>13</sup> C NMR, HRTEM	
	Short chains		<sup>13</sup> C NMR, oxidation-GC-MS	
	Highly branched aliphatics		FTIR, <sup>13</sup> C NMR, oxidation-GC-MS	
	Highly substituted aromatics		FTIR, <sup>13</sup> C NMR, pyrolysis GC-MS	

Note: NMR = nuclear magnetic resonance; FTIR = Fourier transform infrared; XANES = X-ray absorption near-edge spectroscopy; HRTEM = high-resolution transmission electron microscopy; EPR = electron paramagnetic resonance; GC-MS = gas chromatography–mass spectrometry.

[1] Gardinier et al. (2000); [2] Cody et al. (2002); [3] Cody and Alexander (2005); [4] Yabuta et al. (2005); [5] Remusat et al. (2005b); [6] Derenne et al. (2005); [7] Hayatsu et al. (1977); [8] Komiya and Shimoyama (1996); [9] Yabuta et al. (2005); [10] Hayatsu and Anders (1981); [11] Robert and Epstein (1982); [12] Kerridge et al. (1987); [13] Zinner et al. (1988); [14] Cody et al. (2002); [15] Binet et al. (2002); [16] Alexander et al. (1998); [17] Pearson et al. (2000); [18] Sephton et al. (2003).

<sup>a</sup>Value determined for Orgueil insoluble organic matter (IOM).

<sup>b</sup>Calculated by difference.

decarboxylation and decarbonylation reactions which take place upon heating (Remusat et al. 2005b). Oxygen-containing nongaseous pyrolysis products were also identified; in addition to phenol, they comprise various aromatic ketones. These products support the presence of phenolic ethers that were previously suggested based on CuO oxidation (Hayatsu et al. 1977) or hydrous pyrolysis (Sephton et al. 1998) although in the latter experiments, the oxygen atom might have originated from the reagent. However, as pyrolysis polar products are poorly detected using an apolar column in GC/MS, a specific method was developed: the pyrolysis in the presence of tetramethylammonium hydroxide (Challinor 1989).

Tetramethylammonium hydroxide is both a base and a methylating agent, cleavage of polar bonds is enhanced and pyrolysis products are methylated in situ. Using this technique, aromatic acid methyl esters were identified along with dimethyl esters of short-chain diacids, thus revealing the presence of ester linkages between aromatic moieties (Remusat et al. 2005b).

When aliphatic linkages are considered, the most precise information on oxygen groups was provided by RuO<sub>4</sub> oxidation which released hydroxy- and carboxy esters, thus showing that ether and ester functional groups occur within these linkages (Remusat et al. 2005a, 2005b).

### Sulfur Speciation

A number of sulfur-containing products are released upon pyrolysis of the Murchison IOM (Lévy et al. 1973; Komiya and Shimoyama 1996) in agreement with a substantial sulfur content in the IOM. This content largely varies in literature (Table 1). This probably reflects that, depending on the isolation procedure, elemental sulfur (S<sub>8</sub>) is more or less eliminated. In the present model, we used the organic sulfur content determined by Hayatsu and Anders (1981).

All the sulfur-containing pyrolysis products comprise thiophene rings, but these rings can either be pre-existing or formed upon pyrolysis (Remusat et al. 2005b). To investigate this question, K-edge sulfur

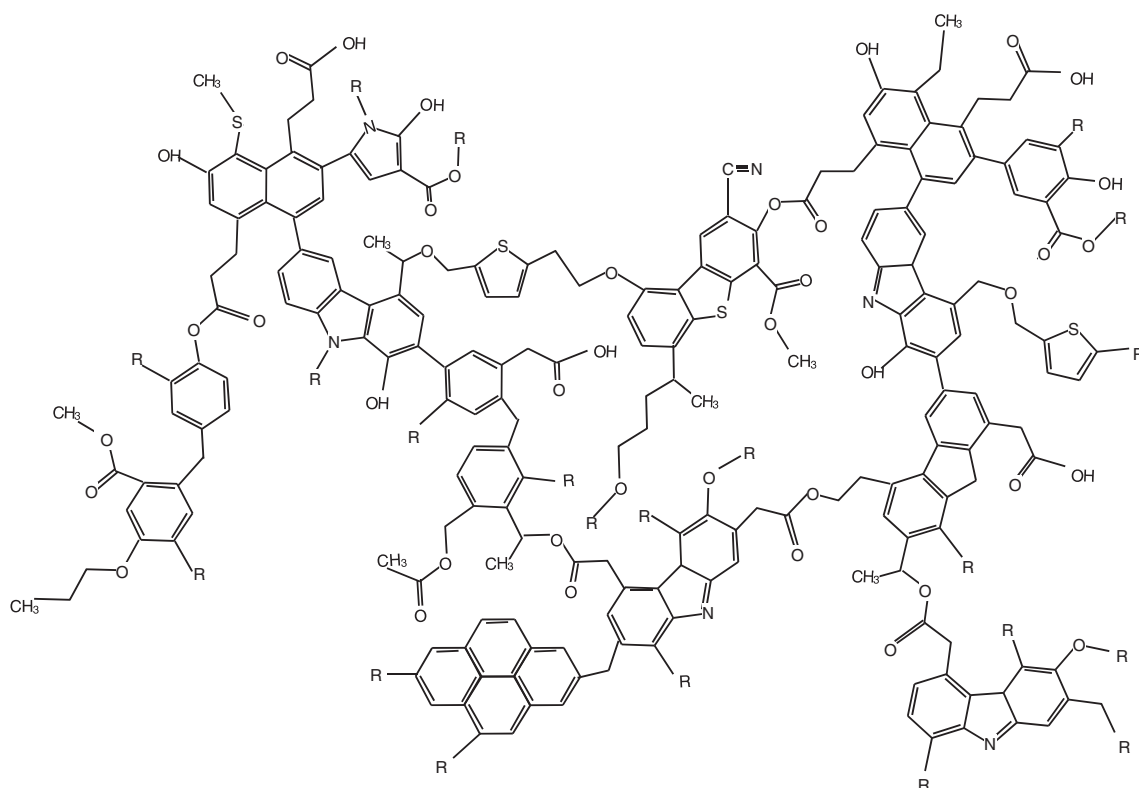


Fig. 1. Model of molecular structure of the insoluble organic matter of Murchison built from measured elemental and molecular parameters (cf. Fig. 2). R stands for an organic moiety.

XANES was performed on Murchison IOM revealing only 24% of the organic sulfur in thiophenes, the remaining 76% being in aliphatic sulfides (Derenne et al. 2002; Remusat et al. 2005b).

#### Nitrogen Speciation

Among heteroelements, nitrogen was also shown to occur in the IOM. A low amount of only one nitrogen-containing product, namely benzonitrile, could be detected in the pyrolysate from Murchison. The use of tetramethylammonium hydroxide did not improve such detection pointing to the lack (or at most very low contribution) of polar N-containing functions such as amide or amine. This was confirmed by solid-state  $^{15}\text{N}$  NMR on Orgueil IOM which revealed that nitrogen is mainly involved in heterocyclic units such as pyrroles. It must be noted that Orgueil led to the same results as Murchison when nitrogen products are considered. The lack of amide/amine functions was confirmed for Orgueil by solid-state  $^{15}\text{N}$  NMR. The conclusions derived from Orgueil on nitrogen speciation probably also holds for Murchison. The high thermal stability of these structures is in agreement with the lack of N-containing pyrolysis products and the release of  $\text{N}_2$  only at high temperatures (900 °C) (Remusat et al. 2005b). A low contribution of nitrile groups can be put

forward from the NMR spectrum of Orgueil IOM with a [Pyrrole N] to [Nitrile N] ratio being of approximately 5. No other occurrence for N (amide or amine) was detected with a detection limit of 5% relative to total N in the IOM.

#### Statistical Model of the IOM Structure

Taken together, the results derived from the different techniques described above led to a set of parameters that we used to build a model of molecular structure of the IOM. The 11 quantitative parameters that have been used are reported in Table 1. In this Table, for comparative purposes, we also report literature values of the same parameters obtained through elemental analysis and NMR on Murchison IOM samples isolated by other laboratories. The resulting structure (Fig. 1) accounts for molecular units (atoms or functional groups) whose abundance is higher than 3%. As a result, rare molecular occurrences are ignored to limit the structure around  $\approx 200$  carbon atoms. This does not affect the overall structure within the error bars assigned to each parameter. The adjustment between modeled and measured parameters is reported in Fig. 2, which shows that within  $\pm 10\%$  the model fits all available data.

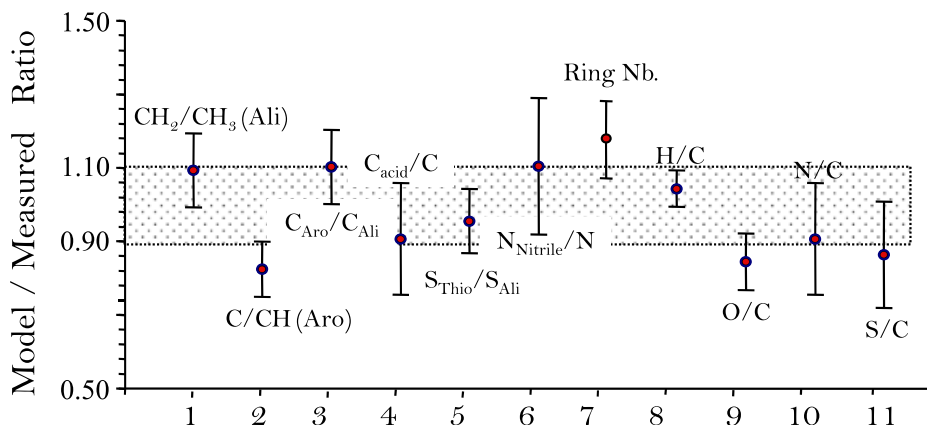


Fig. 2. Ratio of the values for the elemental and molecular parameters listed in Table 1 calculated from the modeled structure in Fig. 1 to those experimentally measured in the insoluble organic matter of Murchison.

It is worth noting that the quantitative data published in the literature on Murchison residues (Table 1) agree rather well with the presently used parameters. In particular, the fraction of aliphatic hydrogen was calculated as 0.70–0.74 by Cody and Alexander (2005) based on their <sup>1</sup>H NMR data. We have recalculated this parameter from the present model and obtain a value of 0.68 in good agreement with the aforementioned experimental value.

The present structure (Fig. 1) should be regarded as a statistical model and not as a unique solution that fits the measured parameters. Minor qualitative modifications such as position isomerism would also yield an acceptable structure. Note also that, because of its small size, this modeled structure cannot account for the large diversity of the products identified in pyrolysis and oxidation experiments.

Although the meteoritic IOM has been compared with terrestrial kerogens for a long time, it must be noted that the modeled structure is sharply different from what has been reported for kerogens and coals (Behar and Vandenbroucke 1986). Indeed, when immature terrestrial samples are considered, they contain long aliphatic chains with a low branching level in agreement with their biological origin. Such long aliphatic chains do not contribute to the IOM of meteorites. An increase in maturity in terrestrial samples induces the release of these chains hence not only an increase in aromaticity but also an increase in the size of aromatic moieties due to thermal annealing. In Orgueil, Murchison, and Tagish Lake meteorites, the size of the aromatic moieties remains small even when the aromaticity increases (Derenne et al. 2006). This is likely a consequence of the level of substitution which strongly differs between terrestrial materials and meteorites.

## COSMOCHEMICAL IMPLICATIONS

This section is based on several specific features of the IOM. They are highlighted in Fig. 3 in so-called “regions of interest” (ROI noted I–V) of the modeled chemical structure.

### Organics in Space

Organic molecules are found in a large diversity of astronomical environments (van Dishoeck and Blake 1998; Ehrenfreund and Charnley 2000). They are detected in stellar atmospheres, in dense and cool interstellar molecular clouds, and in circum-stellar disks associated with star formations. This organic matter comprises both a gaseous and a solid phase of nanometer dust particles (10–500 nm). In addition to the information derived from spectroscopy (temperature, density, and molecular species), theoretical simulations provide also a probe to the physical conditions where these molecules are formed because the rates of chemical reactions depend on time, temperature, and densities (Herbst and Millar 2008).

### From the ISM to the T-Tauri Phase of the Sun

Sun-like stars form from the collapse of cold and dense “prestellar cores” ( $n_{\text{H}} \approx 10^6 \text{ cm}^{-3}$ ,  $T \approx 10 \text{ K}$ ) that hold a complex distribution of numerous organic species and dust. The populations of dust with their icy mantles are a vast reservoir of organic species. The resulting core becomes opaque and forms a so-called YSO (young stellar object) where the warm inner envelopes are heated by the central protostar ( $n_{\text{H}} \approx 10^{7-8} \text{ cm}^{-3}$ ,  $T \approx 100 \text{ K}$ ) and where a complex organic chemistry is sometimes also observed (Ceccarelli and Dominik 2005). Much of this matter is blown away

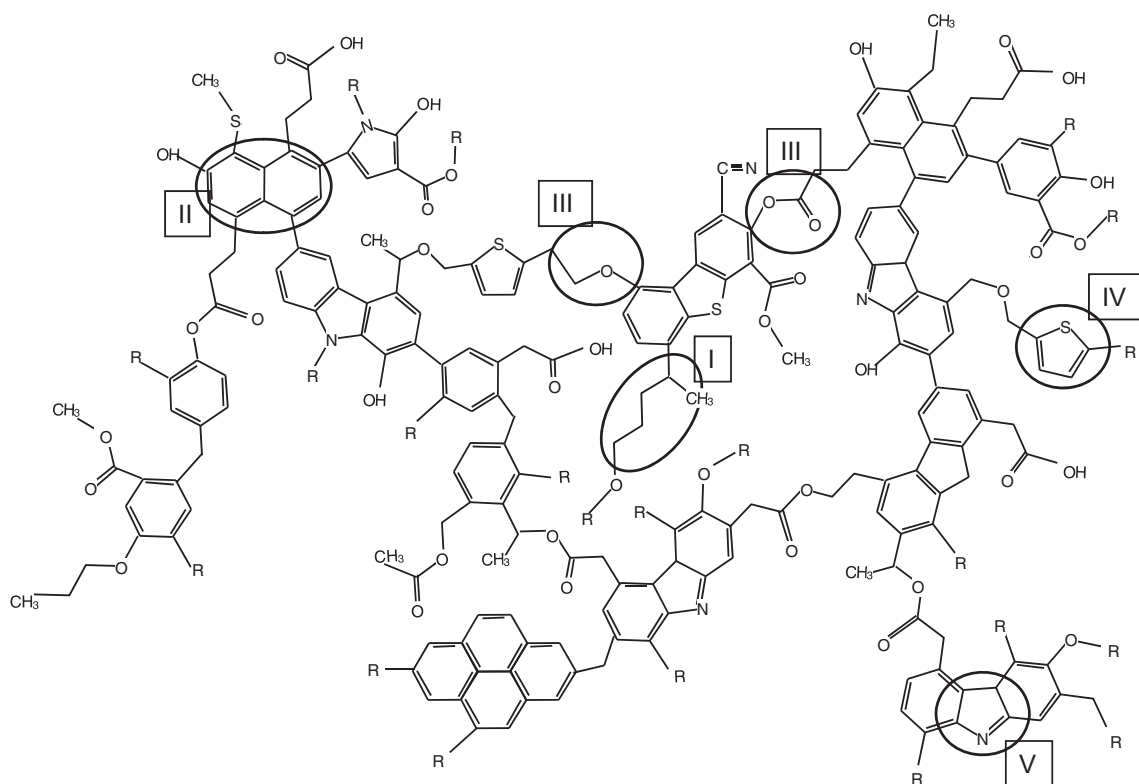


Fig. 3. Model of molecular structure of the insoluble organic matter of Murchison highlighting the region of interest discussed in the Cosmochemical Implications section. ROI I shows the aliphatic linkages, ROI II the aromatic moieties, ROI III the oxygenated functions, ROI IV the S-containing functions, and ROI V the N-containing ones.

and the newly born star starts its life as a T-Tauri star encircled by a dense protoplanetary disk. The average disk temperature is around 100 K, whereas the central regions, close to the star, where the telluric planets and the chondritic planetesimals formed, reach the vaporization temperature of refractory silicates and oxides (up to 2000 K) (Dullemond et al. 2002; Siebenmorgen and Krugel 2010).

As is obvious from this brief description, a profound evolution of the organic species can take place at each of the different stages of the formation of our own solar system (Herbst and van Dishoeck 2009). In this respect, the challenge of organic cosmochemistry is to provide a link between astronomical and chondritic observations.

In prestellar cores, the gas-phase chemistry is triggered by the presence of  $H_2$ . If the temperature exceeds the sublimation temperature of  $CH_4$  or CO condensed on grains, chains of ion-molecule reactions starting with  $H_3^+$  formed via  $H_2 + H_2^+ \rightarrow H_3^+ + H$ , lead to a variety of complex organic molecular ions (Woodall et al. 2008). As a result of the processes involved in this type of ionic chemistry, organic molecules produced in the gas phase are mainly hydrogen-poor (Herbst and Millar 2008) and can form long carbon chains. The situation is different on grains.

On grains, solid CO can be hydrogenated via reactions involving atomic hydrogen and producing  $CH_3CO$ ,  $CH_3CHO$ ,  $C_2H_5OH$  among others (Charnley 2001). These molecules are released in the gas phase when the temperature allows the sublimation of grains, i.e., during the formation of YSOs.

Little is known about the gaseous organic fraction in the T-Tauri disks because of the observational difficulties linked to these small astronomical objects (the radius of these disks is commensurable with the present-day solar system dimensions). Most of our knowledge about this fraction comes from the study of the volatile organic molecules outgassed from comets (Bockelée-Morvan et al. 2004). They are the parent species evaporated from the icy core of the comets. A robust correlation in the relative abundances is found between these cometary species and interstellar molecules, demonstrating that the volatile fraction observed in the parent cores of T-Tauri disk is incorporated into the solar system bodies that were formed at temperatures down to 30 K.

#### *Polycyclic Aromatic Hydrocarbons*

Because their small sizes allow them to be heated to high temperatures, the polycyclic aromatic hydrocarbons

(PAHs) were first proposed as the carriers of the aromatic IR bands observed in the diffuse interstellar medium (ISM). Based on the IR features of these PAHs, their carriers were attributed to a compound comprising at least hundreds of carbon atoms. Although most models conclude that astronomical PAH consist of 50 carbon atoms on average, i.e.,  $\approx 20$  aromatic rings (Pendleton and Allamandola 2002; Visser et al. 2007; Tielens 2008), the size of aromatic moieties in interstellar space remains an open issue (Kwok 2004). For example, quenched carbonaceous composites were produced by heating  $\text{CH}_4$  up to 3000 K followed by a rapid expansion into a vacuum chamber and condensation at room temperature (Sakata et al. 1987). The mass spectrometry of the resultant material suggests that most of their aromatic components have only one to two rings, i.e., 10 carbon atoms. Although it is not yet certain what material gives the best approximation for the interstellar carbonaceous dust (Kwok 2004), it is clear that it includes both aromatic and aliphatic components.

In T-Tauri disks, the IR emission feature is attributed to the presence of 100 C-atom PAHs having a 1/1 mixture of neutral and ionized molecules. The variations in the relative abundances of the PAHs are due to their photodissociation caused by the intense ultraviolet (UV) radiation field caused to the central star (Ehrenfreund et al. 2006; Visser et al. 2007). The lack of detection of these PAHs in different disks is attributed to the low efficiency of visible photons exciting PAHs but not to their absence in the disk. The organic composition of the solar T-Tauri disk is now better known from the analyses of the samples returned from The Stardust space mission (Sandford et al. 2006). In Stardust samples, many organic species are PAHs with typical size much smaller than those from the interstellar space, i.e., a few aromatic rings.

The PAHs observed in disks are not attributed to an in situ formation process after the collapse and main infall phases; they are considered interstellar products. Indeed, the formation and growth of PAHs in a disk would require (1) high temperatures (approximately 1000 K), (2) high density, (3) high abundance in the aromatic ring precursors—presumably acetylene? (Frenklach and Feigelson 1989; Cherchneff and Barker 1992) and (4) for the smallest PAHs, a low UV radiation field to prevent their rapid photodissociation. However, experimental simulations have shown that (Nuth et al. 2008), at temperatures between 500 and 900 K, a carbonaceous coating is formed on grain surfaces via Fischer-Tropsch type reactions by self-perpetuating catalytic reactions. The macromolecular structures of this coating resemble those found in the presently modeled chondritic IOM, suggesting in turn that T-

Tauri disks are able to produce fairly large quantities of the precursors of the IOM.

In most T-Tauri disk models, these conditions correspond to regions close to the central star ( $< 0.1$  AU) and it is unlikely that this in situ production of PAHs affects the interstellar PAH population observed at larger radii in the disk (Visser et al. 2007). This conclusion has been reached by a detailed study of the destruction rates of PAHs by UV photons, in T-Tauri disks (Siebenmorgen and Krugel 2010).

## Comparison With the ISM

### *The “Universal IR Spectrum” Around $3.3 \mu\text{m}$*

The structure reported in Fig. 1 yields the spectrum observed around  $3.3 \mu\text{m}$  in the diffuse ISM (galactic and extra-galactic; Pendleton and Allamandola 2002). Such a spectrum is peculiar in the sense that the  $-\text{CH}_2/-\text{CH}_3$  ratio in aliphatics is close to 2 (Ehrenfreund et al. 1991, 1992). In Murchison, this ratio measured through NMR is 2 (Gardinier et al. 2000). These values are much lower than those found in terrestrial kerogens where long chains—with  $[\text{CH}_2/\text{CH}_3] > 10$ —occur within the macromolecule. As highlighted as ROI I in Fig. 3, this ratio results from the combination of two features: aliphatic chains are short and highly branched. The low value of this ratio results from the statistical combination of C and H in short aliphatic chains exhibiting all its possible isomers. For example, a single chain of five carbons attached to a unit has a  $\text{CH}_2/\text{CH}_3$  ratio of 4/1, whereas the same chain with five carbons exhibiting all the possible isomers has a  $\text{CH}_2/\text{CH}_3$  ratio of 3/2. Such a tendency for the  $\text{CH}_2/\text{CH}_3$  ratio to decrease through isomerization is a general rule. It can thus be stated that the low  $-\text{CH}_2/-\text{CH}_3$  ratio of the extraterrestrial organic matter is a direct consequence of the random distribution of C and H in aliphatic chains. This distribution is a signature for the absence of biochemical activity governing the chain elongation mechanism. This statement applies to both the solar and the interstellar organosynthesis.

### *Aromatic–Aliphatic Relationship*

Spectroscopic and microscopic data on IOM revealed that aromatic moieties comprise a relatively low proportion of protonated carbons thus suggesting that they are highly substituted. It can be reasonably assumed that aromatic moieties in such materials are derived from cyclization and aromatization of linear chains. As a result, the more branched the linear chains, the more substituted the aromatic rings. The high branching level in the aliphatic units is therefore fully consistent with the low level of protonation of the

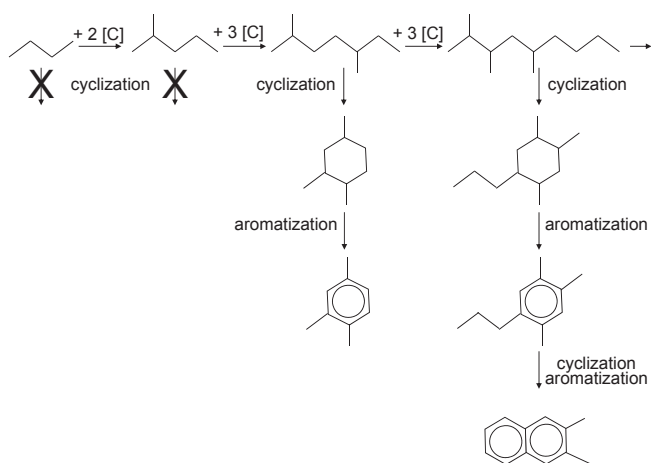


Fig. 4. Illustration of a possible formation pathway of aromatic moieties in the gas phase. The starting drawing accounts for an ion or radical with four carbon atoms. H atoms are not indicated for the sake of clarity. Such a scheme does not take into account heteroelements.

aromatic moieties. These specificities give a basis for a model of organic synthesis in space: the insoluble matter would result from a statistical combination of all possible bonds involving  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  radicals in the gas phase, producing both aliphatic and aromatic moieties. Such free organic radicals would be the result of energetic radiations such as cosmic rays or UVs. In such a model, the organic synthesis would take place by successive addition of single-carbon units as previously suggested by Herbst (2001) through two potential mechanisms (insertion of carbon or radiative association). Such an elongation process would end by a spontaneous cyclization when the chain length exceeds about seven carbons. This process can be illustrated by the following schematic reaction:



When the principal chain of the aliphatic radical has more than seven carbons, the cyclization spontaneously takes place followed by aromatization. This cyclization is made especially possible in the gas phase. Such a cyclization/aromatization process is commonly observed, for example, upon thermal treatment of aliphatic polymers (Madorsky 1964). Fused rings are then formed through the classical mechanism of annealing. A schematic example is given in Fig. 4. As a result, (1) no long linear chains contribute to the macromolecular network and (2) aromatics are highly substituted because of the highly branched nature of the aliphatics.

Another mechanism might be a priori considered: it involves the addition of aliphatic chains onto pre-existing aromatic moieties. This would be favored by

the presence of aromatic radicals which would capture aliphatic radicals. A recent observation tends to rule out this mechanism. NanoSIMS examination of Murchison shows that the organic matter that exhibits high D enrichments (interpreted as related to organic free radicals) is heterogeneously distributed both in bulk IOM and in bulk rock (Rémusat et al. 2009). In other terms, organic radicals seem not to be the nucleus of the polymerization of the whole IOM.

Unfortunately, because of the present lack of experimental simulation, it is not possible to specify (1) the nature of the reactants (ions, radicals, and neutral species), (2) an involvement of a possible catalyst in the condensation reactions (grain surfaces?), and (3) the physicochemical conditions (T, redox, etc.) that prevailed at the time of the IOM formation. Because of its high D/H ratio, this IOM was often regarded in the literature as formed at low temperature ( $T < 200$  K) (Robert 2006). However, for the Orgueil meteorite, it has been shown recently that the deuterium was added to the IOM after its formation (Remusat et al., 2006). Therefore, the temperature at which the above mechanism can take place can be as high as 650 K, i.e., the temperature above which the aliphatic chains start to become unstable.

Note that the rings are far from being saturated in H. If the chain elongation involves ion chemistry, the neutralization process produces fragments that tend to have at least one H atom less than the parent ion; this is illustrated by the following dissociation recombination reaction:  $\text{C}_n\text{H}_2^+ + e \rightarrow \text{C}_n\text{H} + \text{H}$  (Herbst and van Dishoeck 2009). As in the T-Tauri disk half of PAHs are ionized (Tielens 2008), the fact that rings are unsaturated in the IOM reinforces the idea that the matter present in meteorites was condensed in a highly ionized medium.

#### The Size of the Aromatic Units

The aromatic (ROI II in Fig. 3) units that occur in the macromolecular structure of the IOM are clearly much smaller than those postulated for interstellar PAHs (Allamandola et al. 1999; Galvez et al. 2002; Kwok 2004). The size of interstellar PAHs has been extensively discussed in the astronomical literature to account for the features of the IR spectra as well as in the models of their formation, evolution, and destruction (see, for example, the reviews by Tielens 2008 and Herbst and van Dishoeck 2009). Akin to the molecular model proposed here for the chondritic IOM, several two-dimensional molecular models have been published for interstellar PAHs. They all involved moieties having  $\text{C}_{50}\text{--}\text{C}_{100}$  in size. A similar situation exists when comparing the PAHs from the comet Wild 2 analyzed in the samples returned to Earth by the



Stardust mission: PAHs in Wild 2 are also much smaller than their interstellar counterpart. Such dissimilarity must be considered as a serious problem as far as the origin of the organic matter in the solar system is concerned.

There are two ways out of this problem:

1. The chondritic IOM results from the fragmentation of larger interstellar PAHs by photodissociation (Derenne et al. 2005). Based on the recent observations made by the Spitzer Space Observatory, a reappraisal of this interpretation was made by several authors (Geers et al. 2006; Visser et al. 2007; Siebenmorgen and Krugel 2010). They have shown that virtually all PAHs must be destroyed at disk distances where the telluric planets and the parent body meteorites formed. As PAHs are nevertheless observed in T-Tauri disks and as the formation of PAHs in the opaque zones of the disks—i.e., inaccessible to optical observation—is supposed to be too slow to compete with their destruction, they suggest that the turbulent vertical replenishes the surface of the disk.
2. The chondritic IOM is formed in the hottest part of the solar T-Tauri disk (Nuth et al. 2008) and redistributed over large distances by turbulence (Bockelée-Morvan et al. 2002).

Although the first interpretation cannot be dismissed, the second one seems more in accordance with the isotopic compositions of the IOM.

### Parent Body Alteration Signatures

It must be emphasized here that as the D/H ratio is higher in organics than in clays, an organosynthesis taking place in circulating fluids of the parent body can be ruled out. Consequently, this organic matter has been synthesized in another environment than the parent body and then has been mixed with the precursors of the mineral matrix. However, once in the rock, the circulation of the water may have altered the molecular structure and the chemical/isotopic compositions. This process of alteration is discussed in this section.

### Oxygen and Sulfur Speciation

The molecular speciation of oxygen and sulfur in chains can be regarded as the consequence of the alteration of the parent body. The main evidence for such a conclusion was derived from the comparison between the Murchison and the Orgueil meteorites.

The oxygen-containing functions are probably related to the aqueous alteration experienced by primitive carbonaceous chondrites. Indeed, warm water circulation could have resulted in an oxidation of IOM

leading to the formation of ether or ester functional groups. Upon pyrolysis (Remusat et al. 2005b), a higher amount of phenols and substituted homologs are released from Orgueil than from Murchison in agreement with the higher oxygen content obtained from the elemental analyses of Orgueil (16.6 wt%) compared with Murchison (14.5 wt%). In addition, the pyrolysis and ruthenium tetroxide oxidation results suggest that in Orgueil, oxygen is preferentially connected to aromatic carbons as in phenols, whereas in Murchison, oxygen is more often located within the aliphatic linkages as ester or ether functional groups as shown by ROI III in Fig. 3.

When Orgueil and Murchison are compared, a much higher content of total sulfur is noted in Murchison according to elemental analysis. X-ray diffraction and K-edge sulfur XANES revealed that 29% of the sulfur in Murchison occurs as minerals (17% of sulfide such as pentlandite and 12% of sulfate), whereas all sulfur was considered to be organic in Orgueil. However, the resulting organic sulfur is still three times more abundant (with respect to carbon) in Murchison than in Orgueil. In addition to this major quantitative difference, the nature of the organic sulfur also differs between the two meteorites. If in both cases, the organic sulfur mainly occurs as aliphatic sulfides and thiophenes (see ROI IV in Fig. 3), the sulfides to thiophenes ratio is 1.3 in Orgueil and 3.1 in Murchison (Derenne et al. 2002; Remusat et al. 2005b). This higher relative contribution of thiophenes with respect to aliphatic sulfides in Orgueil points to a higher hydrothermal event in this meteorite, as it is known that aliphatic sulfides are converted into thiophenes under thermal stress (Riboulleau et al. 2000).

### Relationship Between Soluble and Insoluble Organic Fractions

Thanks to solid-state  $^{15}\text{N}$  NMR, it was shown that nitrogen is mainly contained within pyrrole functions (see ROI V in Fig. 3). The virtual lack of amide groups in the IOM a priori prevents this macromolecule from being the source of the amino acids that occur in the soluble fraction of the carbonaceous chondrites. Moreover, as discussed in Remusat et al. (2005b), the comparison of the D/H,  $^{15}\text{N}/^{14}\text{N}$  and  $^{13}\text{C}/^{12}\text{C}$  isotopic ratios points also against a common origin for IOM and soluble amino acids. Conversely, amino acids would therefore be derived from another reservoir of nitrogen. For instance, UV irradiation of HCN-rich interstellar ices (in the presence of aldehydes and/or ketones) can yield amino acids (Lerner 1997; Muñoz Caro et al. 2002).

By contrast, other moieties of the IOM are supposed to share a common origin with their soluble counterparts. They comprise the aromatic hydrocarbons

as reported by Pering and Ponnampuruma (1971). Moreover, Huang et al. (2007) have shown that the soluble aliphatic acids are related to the aliphatic linkages of the IOM (based on their  $^{13}\text{C}/^{12}\text{C}$  and D/H ratios).

Therefore, the soluble fraction seems to be a mixture of products derived from different processes—hydrothermal degradation of the IOM, reactions in ice mediated by UV light, terrestrial contamination, etc. This is at variance with what is commonly expected, i.e., a continuum from small soluble molecules to large insoluble ones. Another explanation might be that soluble compounds are derived from a precursor which has now be totally converted into the products, the IOM being the leftover part of an initially more composite material.

### **IOM Features Reveal an Organosynthesis in the Solar T-Tauri Disk?**

As pointed out by Alexander et al. (2007) and experimentally shown by Nuth et al. (2008), efficient synthesis of PAHs from simple linear hydrocarbons in solar gas requires high temperatures (1100–900 K) and pressures ( $10^{-7}$ – $10^{-6}$  bars). Alexander et al. (2007) therefore estimated that the IOM production is unlikely to take place in the solar nebula. However, several features of the IOM chemical structure point to a formation in the Solar T-Tauri disk as discussed below. As already mentioned above, our interpretation of the small size of the aromatic moieties is one of them. Additional indices are provided by the nature of the free radicals (as studied using EPR), D/H distribution at the molecular level and the location of noble gases in the so-called organic-rich Q-phase. These points are successively addressed below.

Electron paramagnetic resonance revealed the presence of a significant amount of organic free radicals in the IOM from Murchison. These free radicals are organized as clusters with high local concentrations compared to the bulk IOM (Binet et al. 2002). Such a heterogeneity seems to be unique among the natural organic macromolecules and therefore can be regarded as a specificity for extraterrestrial organic matter (in addition to Orgueil and Murchison, it was also observed in Tagish Lake, Binet et al. 2004a). Moreover, it must be noted that as in terrestrial samples, these free radicals survive the drastic acid treatments used to isolate the IOM (Binet et al. 2002).

Moreover, diradicaloid structures were found in the same IOMs (Binet et al. 2004a, 2004b). Such structures are highly reactive thus suggesting that they are protected within microdomains. The formation mechanism of these radicals is still unknown but based

on their chemical structure, one can assume that they indicate two possible origins: (1) a condensation of small aromatic moieties in a highly irradiated medium (UVs, cosmic rays, and stellar winds) and (2) a quench condensation of hot aromatic radicals in a cold gas, thus preventing the pending bonds to capture H $\cdot$ . Interestingly, these two environments can be reproduced in the laboratory. Preliminary experiments point to the formation of diradicaloids during the quench condensation of rings from a gas phase. However, their organization in clusters remains puzzling. Because the physicochemical conditions of their synthesis are, at the present time, largely unknown, producing these diradicaloids in laboratory experiments represents a challenge that would yield new constraints on the conditions of the formation of the IOM. Anyhow, their formation during the hydrothermal event appears highly unlikely as water tends to erase the radicals.

Two additional observations are also in favor of an organosynthesis in the T-Tauri disk, although they were so far only reported in Orgueil IOM.

Recent studies combining NanoSIMS and pulsed EPR data have demonstrated that the organic radicals are the carriers of an exceptional deuterium enrichment (Gourier et al. 2007), probably acquired after the formation of the macromolecular network. Such a secondary deuteration process is difficult to reconcile with the low density of the interstellar medium. At the present time, the simplest explanation is to admit that this isotope exchange had taken place in the UV-irradiated regions of the T-Tauri solar disk.

Xenon and likely the other noble gases, which are mass dependently fractionated relative to the solar composition, are mechanically trapped (i.e., not adsorbed or embedded inside the carbon rings) between the lattices of the macromolecular layers of the IOM (Marrocchi et al. 2005). Such a location is also difficult to reconcile with a direct condensation in the ISM where the low xenon density prevents such an addition by simple trapping ( $[\text{H}] < 10^3 \text{ cm}^{-3}$  corresponding to  $[\text{Xe}] < 10^{-13} \text{ cm}^{-3}$ ).

*Acknowledgment*—Pascale Ehrenfreund is warmly thanked for helpful comments on a previous version of the manuscript.

*Editorial Handling*—Dr. A. J. Timothy Jull

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## APPENDIX

Insoluble organic matter (IOM) was isolated from Murchison bulk rock as the insoluble residue remaining after water and solvent extractions and base and acid hydrolyses as previously described (Gardinier et al. 2000).

The structure and microstructure of the IOM were studied by high-resolution transmission electron microscopy (HRTEM) using Philips CM20 operating at 200 kV as described in Derenne et al. (2005). HRTEM images were analyzed using the procedure developed by Rouzaud and Clinard (2002) so as to derive semiquantitative data.

Free radicals were studied by electron paramagnetic resonance (EPR) from room temperature to 4 K with a

Bruker ESP300e spectrometer operating at 9.4 GHz (X-band) as described in Binet et al. (2002, 2004b).

The main functional groups of the chemical structure of the IOM were identified through Fourier transform infrared (FTIR) spectroscopy on KBr pellets using a Digilab FTS 40 spectrometer and solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) at 100.62 MHz using a Bruker MSL 400 spectrometer as described in Gardinier et al. (2000).

Nitrogen speciation was analyzed through solid-state  $^{15}\text{N}$  NMR using a Bruker DMX 400 operating at 40.55 MHz with a CP/MAS sequence (Remusat et al. 2005b).

Sulfur speciation was studied through X-ray absorption near-edge spectroscopy (XANES) at the K-edge of the sulfur. The X-ray absorption measurements

were performed using synchrotron radiation from the SA 32 line of the LURE (Orsay, France) running in the storage ring mode at 1.1 GeV with a germanium crystal monochromator was used (2000–6820 eV). The samples as a pentane suspension were deposited onto a copper plate and then allowed to dry prior to introduction into the high vacuum chamber ( $10^{-5}$  atm). S-XANES spectra were recorded in the total electron yield.

Molecular insight into the chemical structure of the IOM was achieved through chemical and thermal

degradations followed by gas chromatography/mass spectrometry (GC/MS) analyses using an Agilent 6890N gas chromatograph and an Agilent 5973 mass spectrometer. Detailed conditions for GC/MS analyses are reported in Remusat et al. (2005a, 2005b). RuO<sub>4</sub> oxidations and Curie point pyrolyses (in the presence or not of tetramethylammonium hydroxide) are performed as described in Remusat et al. (2005a, 2005b, respectively).

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