

Prebiotic carbon in clays from Orgueil and Ivuna (CI), and Tagish Lake (C2 ungrouped) meteorites

Laurence A. J. GARVIE^{1*} and Peter R. BUSECK^{1, 2}

¹School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287–1404, USA

²Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287–1604, USA

*Corresponding author. E-mail: lgarvie@asu.edu

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Abstract—Transmission electron microscopic (TEM) and electron energy-loss spectroscopic (EELS) study of the Ivuna and Orgueil (CI), and Tagish Lake (C2 ungrouped) carbonaceous chondrite meteorites shows two types of C-clay assemblages. The first is coarser-grained (to 1 μm) clay flakes that show an intense O K edge from the silicate together with a prominent C K edge, but without discrete C particles. Nitrogen is common in some clay flakes. Individual Orgueil and Tagish Lake meteorite clay flakes contain up to 6 and 8 at% C, respectively. The C K-edge spectra from the clays show fine structure revealing aromatic, aliphatic, carboxylic, and carbonate C. The EELS data shows that this C is intercalated with the clay flakes. The second C-clay association occurs as poorly crystalline to amorphous material occurring as nanometer aggregates of C, clay, and Fe-O-rich material. Some aggregates are dominated by carbonaceous particles that are structurally and chemically similar to the acid insoluble organic matter. The C K-edge shape from this C resembles that of amorphous C, but lacking the distinct peaks corresponding to aliphatic, carboxylic, and carbonate C groups. Nanodiamonds are locally abundant in some carbonaceous particles. The abundance of C in the clays suggest that molecular speciation in the carbonaceous chondrites is partly determined by the effects of aqueous processing on the meteorite parent bodies, and that clays played an important role. This intricate C-clay association lends credence to the proposal that minerals were important in the prebiotic chemical evolution of the early solar system.

INTRODUCTION

The carbonaceous chondrite (CC) meteorites, the most primitive known rocks, provide a unique record of prebiotic chemistry from the early solar system. These meteorites contain up to 5.81 wt% C (Grady et al. 2002) distributed as a diverse suite of organic and inorganic C-rich materials. For example, the C in the Tagish Lake meteorite is divided largely between organic C (2.49 to 2.57 wt%) and carbonates (2.69 wt%), with 1634 ppm of nanodiamonds and 8 ppm of SiC (Grady et al. 2002). Interest in the organic C stems largely from its potential to reveal information about prebiotic chemical evolution (Andersen and Haack 2005; Cody and Alexander 2005; Pizzarello 2006). Much is known regarding the identities and structures of the organic materials (Botta and Bada 2002; Cody and Alexander 2005; Garvie and Buseck 2004; Pizzarello et al. 2001; Sephton 2002). There is evidence for a relationship between organic matter and the products of aqueous alteration in the meteorites (Elsila et al. 2005; Pearson et al. 2002); however, the details of this relationship are poorly known.

The CI meteorites have been intensely altered by aqueous solutions and consist of a fine-grained, intimately mixed, C-rich matrix of phyllosilicates (henceforth called clays or clay minerals), oxides, oxy-hydroxides, carbonates, and sulfides (Bullock et al. 2005; Endress and Bischoff 1996; Morlok et al. 2006; Tomeoka and Buseck 1988). Among meteorites, the bulk compositions of the CI carbonaceous chondrites are closest to the non-volatile element abundances of the solar photosphere (Anders and Grevesse 1989), and thus they are widely accepted as the most primitive rock samples available for study. The similarity of the solar and CI element-abundance ratios are evidence that the extensive aqueous alteration experienced by these meteorites occurred in a closed system (Clayton and Mayeda 1984; Morlok et al. 2006). Mineralogical and isotopic data are consistent with aqueous alteration between 50 °C and 100 °C (Bullock et al. 2005; Leshin et al. 1997). The Tagish Lake (C2 ungrouped) meteorite also contains a C-rich matrix of clays, carbonates, and sulfides together with olivine-rich aggregates and sparse chondrules (Bland et al. 2004; Brown et al. 2000). The recent fall and brief environmental exposure of the Tagish Lake

meteorite make it a unique, pristine extraterrestrial sample (Hildebrand et al. 2006).

In contrast to Tagish Lake, the organic species in the CI meteorites, especially Orgueil, have been the subject of much controversy. In the instance of Orgueil, the concern arises because of its long residence time on Earth and the deliberate contamination of one of the stones (Anders et al. 1964), and identification of terrestrial contamination (Watson et al. 2003), although indigenous organic materials were identified (Ehrenfreund et al. 2001; Martins et al. 2006). As we show below, there are similarities in the quantity and form of the C in the clays in Tagish Lake and the CI meteorites, which supports our interpretation for an indigenous origin for much or all the C in the CI clays.

Considerable information exists regarding the identities and structures of organic materials from CC meteorites (Botta and Bada 2002; Ehrenfreund et al. 2001; Pizzarello 2006; Pizzarello et al. 2001; Sephton 2002). It can be divided into soluble and insoluble fractions (Botta and Bada 2002; Sephton 2002). Most of the organic C occurs as a macromolecular and acid insoluble organic material (IOM), which structurally consists of small aromatic units highly substituted and cross-linked by short aliphatic units (Cody and Alexander 2005; Cody et al. 2002; Gardinier et al. 2000; Sephton 2002). The soluble organic C has low molecular weight and ranges from about 1% of the total organic C in Tagish Lake (Pizzarello et al. 2001) to about 30% in CI meteorites. It may include aliphatic and aromatic hydrocarbons, amino acids, and polyols (Botta and Bada 2002; Pizzarello 2006; Sephton 2002).

Little information exists on the relationship between organic C and the products of aqueous alteration in the meteorites. In contrast, the distribution of organic matter, its form, and relationship to clays in sediments has received considerable attention. There is much evidence that an intimate association exists between clays and OM (Guggenberger and Kaiser 2003; Keil et al. 1994; Kennedy et al. 2002; Mayer 1999). The relationship ranges from monolayer adsorption of organic compounds onto clay minerals to alternation of nanometer-scale packets of OM and clay (Gonzalez and Laird 2003; Guggenberger and Kaiser 2003; Kahle et al. 2003; Keil et al. 1994; Kennedy et al. 2002; Mayer 1999; Ransom et al. 1997, 1998; Salmon et al. 2000). Such a relationship has only been indirectly shown for meteorites (Elsila et al. 2005; Pearson et al. 2002).

The clay minerals in the CC matrices are predominantly fine-grained, and therefore we used transmission electron microscopy (TEM) for their study. Quantitative chemical data and bonding information was acquired by electron energy-loss spectroscopy (EELS), and the distribution of C was determined with energy-filtered TEM (EFTEM). In combination, they provide compositional and bonding information for the same small areas. The C K edge, acquired by EELS, is a powerful probe of composition, bonding, and structure.

MATERIALS AND METHODS

EELS data were acquired with a GATAN 766 DigiPEELS spectrometer attached to a Phillips 400-ST field-emission-gun (FEG) TEM operated at an accelerating voltage of 100 kV, with the samples cooled to 77 K. The energy resolution was 1.0 eV. Spectra were acquired from electron-transparent regions of clay grains overhanging the holes in the lacey film of the TEM grid from regions <100 nm in diameter. The spectra were acquired with convergence and collection angles of 16 and 11 mrad, respectively, probe current of 1 to 2 nA, and acquisition times of 1 to 3 s per spectrum. Details on EELS processing and quantification are given in Garvie and Buseck (2006). EFTEM images were acquired with a Tecnai F20 TEM operating at 200 kV with a Gatan imaging filter (GIF).

Multiple samples were studied of Ivuna and Orgueil (CI), and Tagish Lake (C2 ungrouped) carbonaceous chondrite meteorites. Submillimeter-sized pieces of matrix were disaggregated in about 20 μ L of water, and 1 μ L of the meteorite in suspension was dried on a Cu TEM grid covered with lacey support film. The samples were in contact with water for a few minutes, which presumably affected only the very highly soluble organic C fraction, a minor component of the organic matter (Pizzarello, personal communication). Samples were also prepared by crushing and dusting dry meteorite powder onto TEM grids; the same C-bearing materials were encountered as with crushing under water. In addition, the C K-edge spectral features were identical from the clay grains, indicating that the brief contact with the water did not significantly alter either the C content nor change the C bonding with the clays.

RESULTS AND DISCUSSION

Using TEM and EELS we find C associated with clays as discrete nanoglobules, carbonates, and nanodiamonds in multiple samples of the Ivuna, Orgueil, and Tagish Lake meteorites. EFTEM imaging shows two types of C-clay assemblages (Fig. 1). Type A: coarser-grained (to 1 μ m) clays with an intense O K edge from the silicate together with a prominent C K edge (Fig. 2), but without discrete C particles. Nitrogen is common in some clay flakes, with a C:N ratio of >10:1. Type B: poorly crystalline to amorphous material occurring as submicron aggregates of C, clay, and Fe-O-rich material. Some aggregates are dominated by carbonaceous particles that are structurally and chemically similar to the IOM (Garvie and Buseck 2006). Here we focus on the C in the clays (Type A) because of the unique nature of this association.

The C content of the Tagish Lake clay flakes, expressed as O:C ratios, ranges from O_{6.9}C to O_{17.8}C, with a mean of O_{9.7}C. The range for the Orgueil clays is O_{6.7}C to O_{23.4}C, with a mean of O_{10.0}C. The similar average O:C ratios between pristine Tagish Lake and Orgueil is evidence that the C in the clays from the Orgueil samples we studied is not from

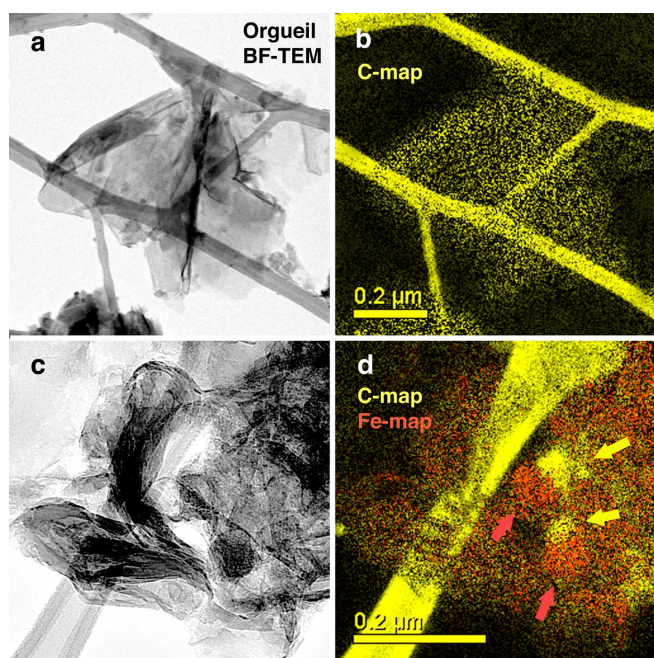


Fig. 1. Brightfield TEM (BF-TEM) and EFTEM images from the Orgueil meteorite showing the two types of C-clay assemblages. a) BF-TEM image of a thin clay flake. b) C map showing the homogenous distribution of C. c) BF-TEM image of a C-rich, poorly crystalline, submicron aggregate of clay and Fe-O-rich material. d) Superimposed Fe and C maps showing small aggregates of C (yellow arrows) and Fe-rich material (red arrows). The bright bands in (b) and (d) are from the lacey-C support film.

contamination. The O:C ratios are independent of grain thickness (Fig. 3), thus ruling out surface contamination. The constancy of the ratios for the clay flakes with respect to thickness indicates an interlayer or structural origin for the C. In contrast, the rapid decrease in C content for a nominally C-free mineral (phenakite in Fig. 3) as a function of thickness is consistent with C on the surfaces only. Thus, the C K-edge spectra of the clay minerals from the meteorites correspond to C within the structure and not a microscope contamination peak, nor from adventitious C.

The element ratios, determined using EELS, from these C-bearing clays are consistent with a trioctahedral 2:1 phyllosilicate. An example of the composition of a C-rich smectite grain from Orgueil is $C_{1.2}Mg_{2.5}Fe_{0.4}Si_{3.4}Al_{0.2}O_{12}$, determined from an area of a 1-micron clay grain 100 nm in diameter. Hydrogen is absent from the EELS data since EELS cannot detect bonded H. In general, the C content of the abundant serpentine-group minerals in Tagish Lake is below detection by EELS.

Interpretation of the C K-edge spectral features is done using the fingerprint method. This technique relies on comparing the spectral energies from an unknown material with known standard materials. There is a large database of near-edge structures from a range of organic compounds acquired by EELS and XAS, e.g., (Cody et al. 1995; Dhez

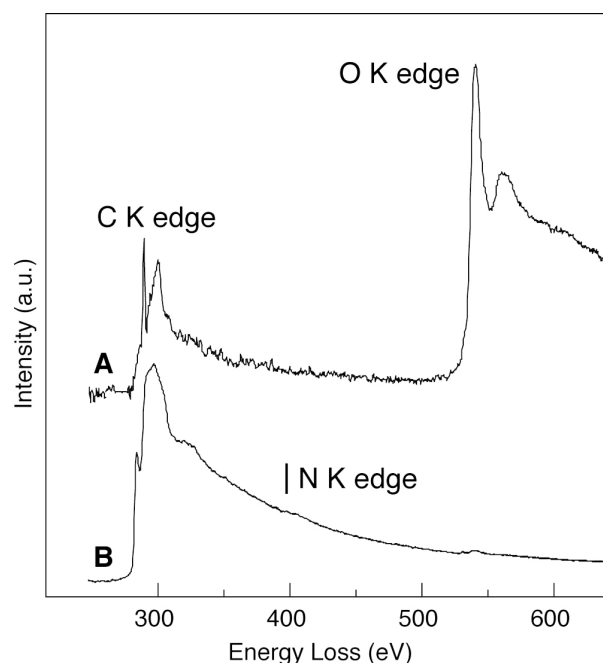


Fig. 2. Low-resolution EELS data for the C-clay assemblages. Comparison of the C, N, and O K-edge regions of the EELS spectra from a coarse-grained clay particle (a) and a poorly crystalline, fine-grained discrete C particle (b). Also visible is a weak N signal.

et al. 2003; Kikuma and Tonner 1996; Myneni 2002; Rothe et al. 2000; Scheinost et al. 2001). From these studies the energies of C in specific bonding environments and functional groups have been tabulated and used to interpret spectra from structurally complex C-rich materials such as coal, humic and fulvic acids, and natural clay organic colloids (Cody et al. 1995; Rothe et al. 2000; Scheinost et al. 2001; Schäfer et al. 2003), although not on as fine a spatial scale as we performed.

The spectra from the coarse-grained clay show multiple peaks within 10 eV of the C K-edge onset (Fig. 4). These peaks reveal the presence of a range of C functional groups (Scheinost et al. 2001; Schäfer et al. 2003). The peak near 285 eV represents transitions to unoccupied states of aromatic C. The 287.4 eV peak shows aliphatic C, and the peak at 290.4 eV inorganic or organic carbonate. Deconvolution of the C K-edge revealed a peak near 288.5 eV corresponding to carboxylic acid compounds (Scheinost et al. 2001; Schäfer et al. 2003). The intensities of the peaks in the near-edge region vary among clay grains and meteorites, confirming a range in C functional groups.

The C K-edge shape from the discrete carbonaceous particles differs from that of the coarse-grained clay (Figs. 2 and 4) and resembles that of amorphous C and the spectra from the IOM (Garvie and Buseck 2004, 2006). Spectra from the carbonaceous particles show a sharp C $1s-\pi^*$ peak near 285 eV, reflecting the high degree of aromaticity, but the distinct peaks corresponding to aliphatic C-H, COOH, and

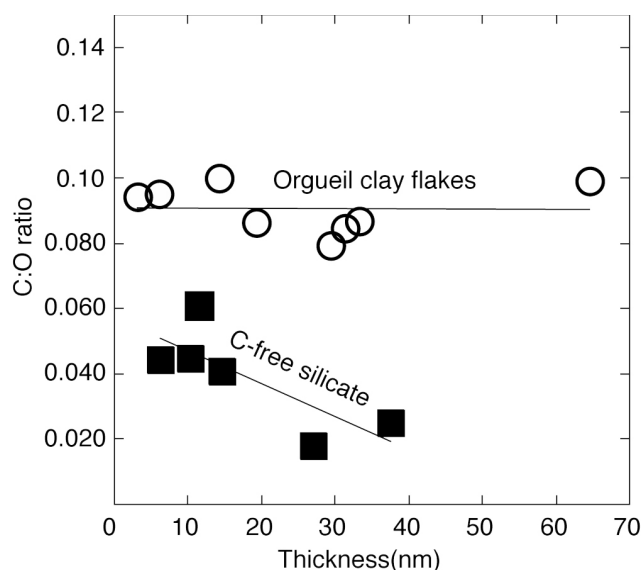


Fig. 3. Comparison of C:O ratios from separate Orgueil clay flakes (open circles) to data from phenakite (filled squares), a nominally C-free silicate.

carbonate groups are generally absent. In addition, high-spatial resolution EELS shows that nanodiamonds are locally concentrated in the carbonaceous particles.

A semiquantitative determination of the organic functional groups in the coarse-grained clays from the C K edge (Table 1) and a least-squares fit of the Ivuna spectrum (Fig. 5) shows that the organic C is dominated by aromatic (C_{arom}) and alkyl (C_{aliph}) C, with $C_{\text{arom}}/C_{\text{aliph}}$ ratios ranging from 1.5 (Orgueil) to 0.9 (Tagish Lake). The carboxylic C constitutes only a small proportion of the C in the clay flakes. The origin of the carbonate peak is puzzling. We searched for but did not find carbonate grains on the clay flakes. The carbonate may be from an organic carbonate or from absorbed CO_2 . Smectites and serpentine are the dominant minerals in the CI meteorites (Bass 1971), comprising about 64% of the meteorite, with some fragments up to about 80% clay (Bland et al. 2004). The Tagish Lake meteorite is also clay-rich, comprising about 60% interstratified saponite-serpentine (Bland et al. 2004). These mineralogies are consistent with intense aqueous processing of anhydrous silicates on the meteorite parent bodies.

Clays are well known for their ability to absorb organic molecules, forming organo-clays when the exchangeable inorganic cations are replaced by organic cations (Lagaly 1984). In vitro experiments demonstrate that smectites catalyze organic reactions under hydrothermal conditions and then protect the resulting reactants (Williams et al. 2005). For example, in the presence of smectite, methanol reacts under hydrothermal conditions to a variety of $\text{C}_7\text{-C}_{20}$ organic products, with a predominance of aromatic compounds. These compounds are retained in and protected by the clays from the surrounding environment (Williams et al. 2005).

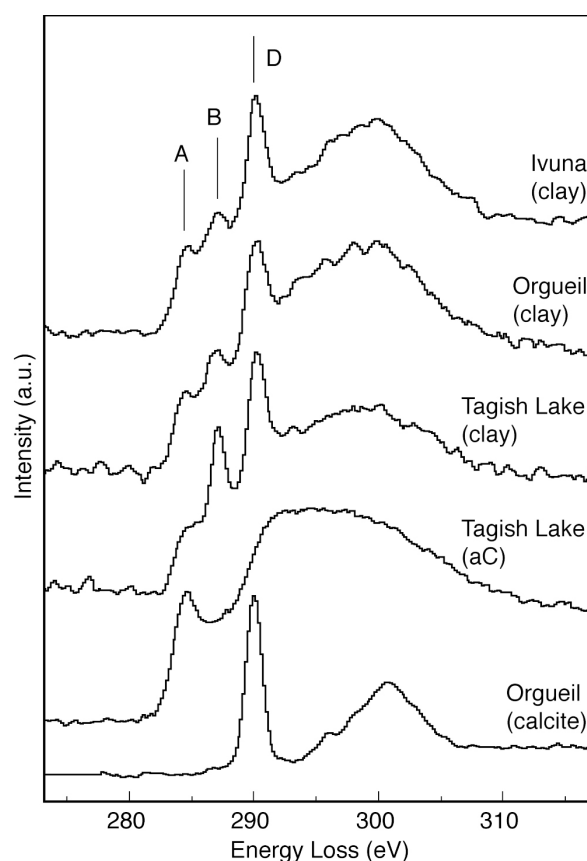


Fig. 4. High-resolution C K EELS spectra. Representative C K edges from coarse-grained clay flakes from the Ivuna, Orgueil, and Tagish Lake meteorites, compared with spectra from poorly crystalline, fine-grained discrete C (Tagish Lake, aC) and calcite (Orgueil). A background of the form $\text{AE}^{-\tau}$ was removed from beneath the edges. Three peaks are visible, and a fourth appears in the deconvolution. Peak A = $1s-\pi^*$ C=C at 284.8 eV for aromatic C. Peak B = $1s-\sigma^*$ C-H at 287.4 eV for aliphatic C. Peak D = $1s-\pi^*$ C=O at 290.4 eV for carbonate C.

Smectite also can catalyze organic reactions at temperatures as low as about 100 °C (Faure et al. 2003), suggesting similar effects in the meteorite parent bodies.

The similarity in the quantities and proportions of functional groups in Orgueil and Ivuna clays is consistent with the formation of the clays on the same or similar parent bodies, consistent with their similar mineralogies and organic chemistries (Bullock et al. 2005; Ehrenfreund et al. 2001; Morlok et al. 2006). The amino acids in the CI meteorites, which differ from those in CM2 meteorites (Botta et al. 2002), suggests a parent body that was rich in cometary components such as water, ammonia, and HCN (Ehrenfreund et al. 2001). Models of aqueous processing on the CI parent body call for multiple stages of alteration, though significant spatial mineral and element heterogeneity shows that equilibrium was not reached (Morlok et al. 2006; Tomeoka and Buseck 1988). During the aqueous processing the smectite would be available to intercalate and modify soluble organics.

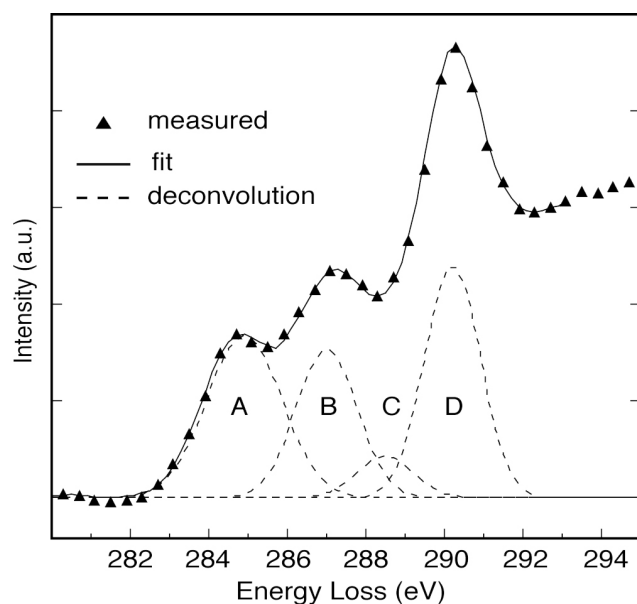


Fig. 5. Example of the deconvolution of the C K edge from Ivuna. The spectrum is fitted with four Gaussian peaks representing the main transitions, with a Peak C at 288.5 eV for the $1s\text{-}\pi^*$ COOH for carboxylic acid.

The Tagish Lake meteorite contains a low abundance of soluble organic C (Pizzarello et al. 2001). One interpretation of this low content is a parent body devoid of starting components such as ammonia and HCN (Kminek et al. 2002). Under this scenario there would have been little soluble organic C available for intercalation into the clays. Alternatively, the current low soluble organic content of Tagish Lake may represent a higher degree of chemical oxidation than experienced by the CI meteorites (Cody and Alexander 2005). Thus, the organic C intercalated into the Tagish Lake clays may have occurred during an earlier stage of chemical processing in the presence of abundant soluble organic C. This intercalated C was then protected from the later oxidizing conditions.

CONCLUSIONS

Our results show that the clays in the CI and Tagish Lake meteorites acted as sinks for organic C and may have played a catalytic role in the formation of the meteorite organic inventory. In the case of Tagish Lake, the clays may have protected the organic C from oxidizing conditions. Clays are well-known catalysts of organic polymers, and their ability to bind RNA molecules and catalyze the formation of oligomers (Ferris 2005) suggests that clays may have been important in prebiotic organic synthesis (Bernal 1949; Ferris 2005; Schulte and Shock 2004). Our results provide new insight regarding the constituents of primitive meteorites and the information they provide regarding aqueous alteration in the early solar system.

Table 1. Average relative proportions of organic functional groups in the meteorite clays.

Meteorite	Functional groups			$C_{\text{arom}}/C_{\text{aliph}}$
	Aromatic (%)	Alkyl (%)	Carboxylic (%)	
Orgueil	55	36	9	1.5
Ivuna	51	38	11	1.3
Tagish Lake	41	46	13	0.9

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REFERENCES

- Anders E., Dufresne E. R., Hayatsu R., Cavallé A., Dufresne A. and Fitch F. W. 1964. Contaminated meteorite. *Science* 146:1157–1161.
- Anders E. and Grevesse N. 1989. Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta* 53:197–214.
- Andersen A. C. and Haack H. 2005. Carbonaceous chondrites: Tracers of the prebiotic chemical evolution of the solar system. *International Journal of Astrobiology* 4:13–17.
- Bass M. N. 1971. Montmorillonite and serpentine in Orgueil meteorite. *Geochimica et Cosmochimica Acta* 35:139–148.
- Bernal J. D. 1949. The physical basis of life. *Proceedings of the Royal Society of London A* 357:537–558.
- Bland P. A., Cressey G., and Menzies O. N. 2004. Modal mineralogy of carbonaceous chondrites by X-ray diffraction and Mössbauer spectroscopy. *Meteoritics & Planetary Science* 39:3–16.
- Botta O. and Bada J. L. 2002. Extraterrestrial organic compounds in meteorites. *Surveys in Geophysics* 23:411–467.
- Botta O., Glavin D. P., Kminek G., and Bada J. L. 2002. Relative amino acid concentrations as a signature for parent body processes of carbonaceous chondrites. *Origins of Life and Evolution of the Biosphere* 32:143–163.
- Brown P. G., Hildebrand A. R., Zolensky M. E., Grady M., Clayton R. N., Mayeda T. K., Tagliaferri E., Spalding R., Macrae N. D., Hoffman E. L., Mittlefehldt D. W., Wacker J. F., Bird J. A., Campbell M. D., Carpenter R., Gingerich H., Glatiotis M., Greiner E., Mazur M. J., McCausland P. J. A., Plotkin H., and Mazur T. R. 2000. The fall, recovery, orbit, and composition of the Tagish Lake meteorite: A new type of carbonaceous chondrite. *Nature* 290:320–325.
- Bullock E. S., Gounelle M., Lauretta D. S., Grady M. M., and Russell S. S. 2005. Mineralogy and texture of Fe-Ni sulfides in CI1 chondrites: Clues to the extent of aqueous alteration on the CI1 parent body. *Geochimica et Cosmochimica Acta* 69:2687–2700.

- Clayton R. N. and Mayeda T. K. 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth and Planetary Science Letters* 67:151–161.
- Cody G. D. and Alexander C. M. O'D. 2005. NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochimica et Cosmochimica Acta* 69:1085–1097.
- Cody G. D., Alexander C. M. O'D., and Tera F. 2002. Solid-state (^1H and ^{13}C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: A self-consistent quantitative analysis. *Geochimica et Cosmochimica Acta* 66:1851–1865.
- Cody G. D., Botto R. E., Ade H., Behal S., Disko M., and Wirick S. 1995. Inner-shell spectroscopy and imaging of a subbituminous coal: In situ analysis of organic and inorganic microstructure using C(1s)-, Ca(2p)-, and Cl(2s)- NEXAFS. *Energy and Fuels* 9:525–533.
- Dhez O., Ade H., and Urquhart S. G. 2003. Calibrated NEXAFS spectra of some common polymers. *Journal of Electron Spectroscopy and Related Phenomena* 128:8–96.
- Ehrenfreund P., Glavin D. P., Botta O., Cooper G., and Bada J. L. 2001. Extraterrestrial amino acids in Orgueil and Ivuna: Tracing the parent body of CI type carbonaceous chondrites. *Proceedings of the National Academy of Sciences* 98:2138–2141.
- Elsila J. E., De Leon N. P., Buseck P. R., and Zare R. N. 2005. Alkylation of polycyclic aromatic hydrocarbons in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 69:1349–1357.
- Endress M. and Bischoff A. 1996. Carbonates in CI chondrites: Clues to parent body evolution. *Geochimica et Cosmochimica Acta* 60:489–507.
- Faure P., Schlepp L., Burkler-Vitzthum V., and Elie M. 2003. Low-temperature air oxidation of *n*-alkanes in the presence of Na-smectite. *Fuel* 82:1751–1762.
- Ferris J. P. 2005. Mineral catalysis and prebiotic synthesis: Montmorillonite-catalyzed formation of RNA. *Elements* 1:145–149.
- Gardinier A., Derenne S., Robert F., Behar F., Largeau C., and Maquet J. 2000. Solid state CP/MAS ^{13}C NMR of the insoluble organic matter of the Orgueil and Murchison meteorites: Quantitative study. *Earth and Planetary Science Letters* 184:9–21.
- Garvie L. A. J. and Buseck P. R. 2004. Nanosized carbon-rich grains in carbonaceous chondrite meteorites. *Earth and Planetary Science Letters* 224:431–439.
- Garvie L. A. J. and Buseck P. R. 2006. Carbonaceous materials in the acid residue from the Orgueil carbonaceous chondrite meteorite. *Meteoritics & Planetary Science* 41:633–642.
- Gonzalez J. M. and Laird D. A. 2003. Carbon sequestration in clay mineral fractions from C^{14} labeled plant residues. *Journal of the Soil Science Society of America* 67:1715–1720.
- Grady M. M., Verchovsky A. B., Franchi I. A., Wright I. P., and Pillinger C. T. 2002. Light element geochemistry of the Tagish Lake CI1 chondrite: Comparison with CI1 and CM2 meteorites. *Meteoritics & Planetary Science* 37:713–735.
- Guggenberger G. and Kaiser K. 2003. Dissolved organic matter in soil: Challenging the paradigm of sorptive preservation. *Geoderma* 113:293–310.
- Hildebrand A. R., McCausland P. J. A., Brown P. G., Longstaffe F. J., Russell S. D. J., Tagliaferri E., Wacker J. F., and Mazur M. J. 2006. The fall and recovery of the Tagish Lake meteorite. *Meteoritics & Planetary Science* 41:407–431.
- Kahle M., Kleber M., Torn M. S., and Jahn R. 2003. Carbon storage in coarse and fine clay fractions of illitic soils. *Journal of the Soil Science Society of America* 67:1732–1739.
- Keil R. G., Montlucon D. B., Prah F. G., and Hedges J. I. 1994. Sorptive preservation of labile organic matter in marine sediments. *Nature* 370:549–552.
- Kennedy M. J., Pevear D. R., and Hill R. J. 2002. Mineral surface control of organic carbon in black shales. *Science* 295:657–660.
- Kikuma J. and Tonner B. P. 1996. XANES spectra of a variety of widely used organic polymers at the C K edge. *Journal of Electron Spectroscopy and Related Phenomena* 82:53–60.
- Kminek G., Botta O., Glavin D. P., and Bada J. L. 2002. Amino acids in the Tagish Lake meteorite. *Meteoritics & Planetary Science* 37:697–701.
- Lagaly G. 1984. Clay-organic interactions. *Philosophical Transactions of the Royal Society of London A* 311:315–332.
- Leshin L. A., Rubin A. E., and McDeegan K. D. 1997. The oxygen isotopic composition of olivine and pyroxene from CI chondrites. *Geochimica et Cosmochimica Acta* 61:835–845.
- Martins Z., Watson J. S., Sephton M. A., Botta O., Ehrenfreund P., and Gilmour I. 2006. Free dicarboxylic and aromatic acids in the carbonaceous chondrites Murchison and Orgueil. *Meteoritics & Planetary Science* 41:1073–1080.
- Mayer L. M. 1999. Extent of coverage of mineral surfaces by organic matter in marine sediments. *Geochimica et Cosmochimica Acta* 63:207–215.
- Morlok A., Bischoff A., Stephan T., Floss C., Zinner E., and Jessberger E. K. 2006. Brecciation and chemical heterogeneities of CI chondrites. *Geochimica et Cosmochimica Acta* 70:5371–5394.
- Myneni S. C. B. 2002. Soft X-ray spectroscopy and spectromicroscopy studies of organic molecules in the environment. In *Applications of synchrotron radiation in low-temperature geochemistry and environmental science*, edited by Fenter P., Rivers M., Sturchio N., and Sutton S. Reviews in Mineralogy and Geochemistry, vol. 49, pp. 485–579.
- Pearson V. K., Sephton M. A., Kearsley A. T., Bland P. A., Franchi I. A., and Gilmour I. 2002. Clay mineral-organic matter relationships in the early solar system. *Meteoritics & Planetary Science* 37:1829–1833.
- Pizzarello S. 2006. The chemistry of life's origin: A carbonaceous meteorite perspective. *Accounts of Chemical Research* 39:231–237.
- Pizzarello S., Huang Y. S., Becker L., Poreda R. J., Nieman R. A., Cooper G., and Williams M. 2001. The organic content of the Tagish Lake meteorite. *Science* 293:2236–2239.
- Ransom B., Bennett R. H., Baerwald R., and Shea K. 1997. TEM study of in situ organic matter on continental margins: occurrence and the "monolayer" hypothesis. *Marine Geology* 138:1–9.
- Ransom B., Dongseon K., Kastner M., and Wainwright S. 1998. Organic matter preservation on continental slopes: Importance of mineralogy and surface area. *Geochimica et Cosmochimica Acta* 62:1329–1345.
- Rothe J., Denecke M. A., and Dardenne K. 2000. Soft X-ray spectromicroscopy investigation of the interaction of aquatic humic acid and clay colloids. *Journal of Colloid and Interface Science* 231:91–97.
- Salmon V., Derenne S., Lallier-Verges E., Largeau C., and Beaudoin B. 2000. Protection of organic matter by mineral matrix in a Cenomanian black shale. *Organic Geochemistry* 31:463–474.
- Scheinost A. C., Kretzschmar R., Christl I., and Jacobsen C. 2001. Carbon group chemistry of humic and fulvic acid: A comparison of C-1s NEXAFS and ^{13}C -NMR spectroscopies. In *Humic substances structures, models, and functions*, edited by Ghabbour E. A. and Davies G. Cambridge: The Royal Society of Chemistry, 387 p.
- Schulte M. D. and Shock E. L. 2004. Coupled organic synthesis and

- mineral alteration on meteorite parent bodies. *Meteoritics & Planetary Science* 39:1577–1590.
- Schäfer T., Hertkorn N., Artinger R., Claret F., and Bauer A. 2003. Functional group analysis of natural organic colloids and clay association kinetics using C(1s) spectromicroscopy. *Journal de Physique IV* 104:409–412.
- Sephton M. A. 2002. Organic compounds in carbonaceous meteorites. *Natural Products Reports* 19:292–311.
- Tomeoka K. and Buseck P. R. 1988. Matrix mineralogy of the Orgueil CI carbonaceous chondrite. *Geochimica et Cosmochimica Acta* 52:1627–1640.
- Watson J. S., Pearson V. K., Gilmour I., and Sephton M. A. 2003. Contamination by sesquiterpenoid derivatives in the Orgueil carbonaceous chondrite. *Organic Geochemistry* 34:37–47.
- Williams L. B., Canfield B., Voglesonger K. M., and Holloway J. R. 2005. Organic molecules formed in a “primordial womb.” *Geology* 33:913–916.
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