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

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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 (Gugenberger 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 Philips 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 μL of water, and 1 μL 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 μm) 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_{9.5}C to O_{17.8}C, with a mean of O_{9.7}C. The range for the Orgueil clays is O_{6.5}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
Prebiotic carbon in clays from Orgueil, Ivuna, and Tagish Lake 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 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 $\text{C}_1\text{.}_2\text{Mg}_{2.5}\text{Fe}_{0.4}\text{Si}_{3.4}\text{Al}_{0.2}\text{O}_{12}$, 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.

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), although not on as fine a spatial scale as we performed.

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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. 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.

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.
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 ($C_{\text{arom}}$) and alkyl ($C_{\text{aliph}}$) 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 $C_7$-$C_{20}$ 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).

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.
Prebiotic carbon in clays from Orgueil, Ivuna, and Tagish Lake

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.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Aromatic (%)</th>
<th>Alkyl (%)</th>
<th>Carboxylic (%)</th>
<th>C arom/C alph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orgueil</td>
<td>55</td>
<td>36</td>
<td>9</td>
<td>1.5</td>
</tr>
<tr>
<td>Ivuna</td>
<td>51</td>
<td>38</td>
<td>11</td>
<td>1.3</td>
</tr>
<tr>
<td>Tagish Lake</td>
<td>41</td>
<td>46</td>
<td>13</td>
<td>0.9</td>
</tr>
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