

STRUCTURE AND BONDING OF CARBON IN CLAYS FROM CI CARBONACEOUS CHONDRITES

Laurence A.J. Garvie¹ and Peter R. Buseck^{1,2}, ¹Department of Geological Sciences, Arizona State University, Tempe, Arizona 85287-1404, lgarvie@asu.edu, ²Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, 85287

Introduction: Carbonaceous chondrites (CC) contain a diverse suite of C-rich materials. Acid dissolution of these meteorites leaves a C-rich residue with chemical and structural affinities to kerogen [1-3]. This material has primarily been analyzed in bulk, and much information has been provided regarding functional groups and elemental and isotopic compositions [1,2,4,5]. However, comparatively little work has been done on C in unprocessed meteorites. Studies of CCs suggest a spatial relationship of some C-rich materials with products of aqueous alteration [6,7]. Recent studies revealed discrete submicron-sized, C-rich particles in Tagish Lake and a range of CM2 meteorites [8,9]. A challenge is to correlate the findings from the bulk acid-residue studies with those of high-spatial resolution-mineralogical and spectroscopic observations of unprocessed meteorites. Hence, the relationship between the C-rich materials in the acid residues and its form and locations in the unprocessed meteorite remains unclear. Here we provide information on the structure and bonding of C associated with clays in CI carbonaceous chondrites.

Materials and Methods: We studied pieces of the Alais, Ivuna, and Orgueil (CI) meteorites. Submillimeter-sized pieces of matrix free of visible mineral inclusions were gently disaggregated and dispersed onto lacey transmission electron microscope (TEM) grids. Images were acquired with a Topcon 002B TEM operating at 200 kV. Electron energy-loss spectroscopy (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 0.8 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.

Results: The TEM-EELS combination shows C associated with clays, as discrete nanoglobules, carbonates, and nanodiamonds. The C is most commonly seen with the clays, which are the focus of this study.

There are two types of C-clay assemblages. Type A: C-rich, poorly-crystalline to amorphous material occurring as sub-micron-sized aggregates of clay, Fe-O-rich material, and C. Some aggregates are dominated by amorphous C. These aggregates commonly have a mottled appearance in the TEM. Type B: coarser-grained phyllosilicates with a prominent C K edge, but without discrete C particles.

These two phyllosilicate types correspond to the “fine phyllosilicate” and “coarse phyllosilicate” fractions described from Orgueil [10]. The C K edge from Type A is similar in shape to that from amorphous C (fig. 1), whereas the type B grains show spectral shapes characterized by up to three peaks (fig. 1).

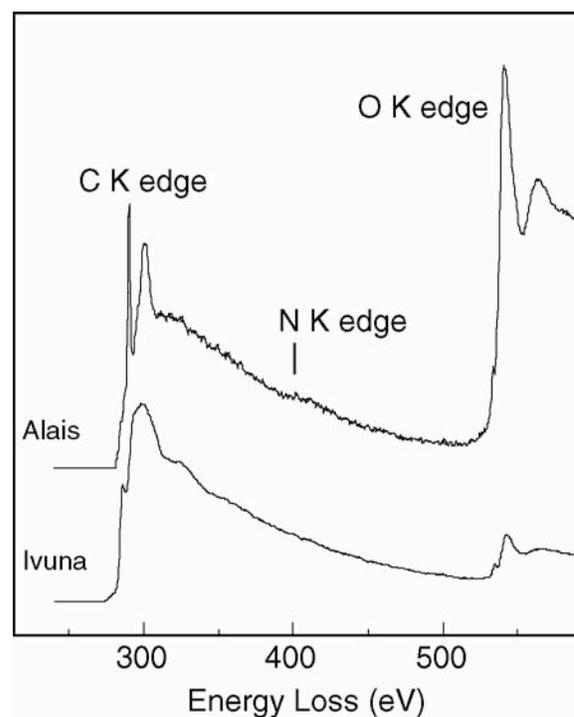


Fig 1. Comparison of the C and O K edge region of the EELS spectra from a coarse-grained phyllosilicate grain (Alais) and poorly-crystalline aggregate of clay and C (Ivuna). Also visible is a weak N signal.

The shapes of the C K edges reflect the nature of the bonding of the C. The spectra from the clay flakes (type B) show energy features at 285, 287, and 290 eV (fig. 2). The peak at 285 eV corresponds to sp^2 -hybridized C in aromatic C (C_{AR}). The intensity of this peak varies among clay grains, confirming a variation in aromatic C content. The 287-eV peak is similar in energy to $C_{AR}-OH$ (phenol)[11]. The 290-eV peak corresponds to C that is three-fold coordinated with O such as in inorganic [12,13] and organic carbonates [14,15].

The C:O ratio of the coarse phyllosilicate grains, free of visible (in the TEM) mottling of carbonaceous

material is typically below 0.08. For example, the C:O ratio oscillates around 0.087 for different clay grains from the Orgueil meteorite, regardless of thickness, and we find similar constant ratios for other clay grains that contain C.

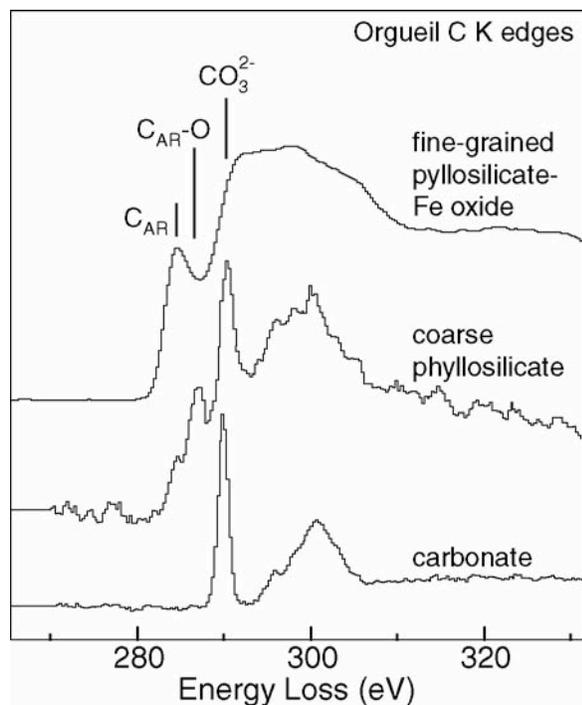


Fig. 2. C K edges from three C-rich grains in the Orgueil meteorite. C_{AR} - Aromatic C.

Discussion: The constant C:O ratios with respect to thickness from the coarse phyllosilicates points to an interlayer or structural location for the C, in contrast to a surface layer of C that would show a decrease in C:O as sample thickness increases. A structural location for the C would require the presence of available C during crystal growth, whereas interlayer C could be absorbed after mineral formation from aqueous solutions.

The EELS data show three primary types of C bonding, with the coarse phyllosilicates. Most prominent is a C K spectrum resembling that from the carbonate anion. Next in intensity is a spectrum similar in shape to that of amorphous C, which shows a component with aromatic character. The sharp but distinct peak near 287 eV is assigned to aromatic C bonded to O as in phenol or aryl ether. The compositional and bonding information provided by EELS shows a complex C material that is likely sited in the interlayer space of the coarse phyllosilicates.

The C K edge from the fine-grained C-clay aggregates displays the high degree of aromaticity of the C. The carbonate anion peak visible from the

coarse phyllosilicates is rarely observed in the fine clays, and the C_{AR} -OH peak is of low intensity. These fine clays are believed to have formed from the alteration of the coarse phyllosilicates during aqueous processing [10]. As such, the C present in the coarse phyllosilicates would be released and further processed, forming, in part, the highly aromatic amorphous C of the fine-grained C-clay aggregates.

Our data show the nanometer-scale chemical heterogeneity and structural diversity of the carbonaceous materials associated with clays. We confirm the intimate relationship between the meteorite organic matter and the minerals that formed as a result of aqueous alteration.

We propose that the C detected with the fine-grained clays is a significant source of the macromolecular material isolated in acid residues. In addition, we have found C with clays in CC meteorites such as Tagish Lake (ungrouped), Cold Bokkeveld and Murray (CM2), and GRA95229 (CR2). These data provide clues to early solar-system environments and processes and suggest an important role for clays in C chemical processing.

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