NANOGLOBULES, MACROMOLECULAR MATERIALS, AND CARBON SULFIDES IN CARBONACEOUS CHONDRITES Laurence A.J. Garvie[1] and Peter R. Buseck[1,2], [1]Department of Geological Sciences, Arizona State University, Tempe, Arizona 85287-1404, lgarvie@asu.edu, [2]Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, 85287-1604, pbuseck@asu.edu.

Introduction: The CI and CM meteorites contain a diverse suite of carbonaceous materials, with the majority as insoluble, macromolecular, and kerogen-like [1-3]. This material has primarily been analyzed in bulk acid residues, and much information has been provided regarding functional groups and elemental and isotopic compositions [1,2,4,5]. Studies of carbonaceous chondrites suggest a spatial relationship of some C-rich materials with products of aqueous alteration [6,7]. Major questions remain regarding the form, composition, and location of the carbonaceous materials in primitive meteorites – issues that we address here.

Materials and Methods: We studied pieces of Alais, Orgueil, and Ivuna CIs; Tagish Lake; and Bells, Cold Bokkeveld, Mighei, Murchison, and Murray CM meteorites. Samples were prepared by gentle disaggregation followed by dispersion onto TEM grids. We also studied HF/HCl residues from Orgueil, Tagish Lake, Murchison, and Murray.

High-resolution TEM (HRTEM) images were acquired with a 002B TEM operating at 200 kV. Spectra were acquired with a GATAN 766 DigiPEELS spectrometer attached to a Philips 400-ST field emission gun TEM operated at an accelerating voltage of 100 kV. The EELS energy resolution was 0.8 eV.

Results: HRTEM imaging and EELS spectra of the residues reveal C-rich material as hollow and solid nanoglobules (fig. 1), fluffy amorphous material (fig. 1), and rare flakes of amorphous C_xS. In the disaggregated meteorites C is detected by EELS in carbonates, nanoglobules (fig. 2), clays, rims on sulfides, and rare carbides and amorphous C_xS flakes. Previous studies reported nanoglobules in Tagish Lake [8] and a range of CM chondrites [9].

Fluffy residue. The majority of the acid residues consist of an amorphous C-rich material. Our 'bulk' compositions (based on 100 C atoms for comparison) are $C_{100}S_{3.3}N_{3.7}O_{4.9}$ for Orgueil and $C_{100}S_{3.7}N_{7.2}O_{6.5}$ for the Tagish Lake. These compositions are the sum of 28 measurements from separate 20-nm sized pieces. H is excluded from the analyses since EELS cannot detect bonded H. The fluffy material is compositionally heterogeneous in N, O, and S. For example, the maximum heteroatom ratios in Tagish Lake are $C_{100}S_8$, $C_{100}N_{12.7}$, and $C_{100}O_{13.5}$. The C K-edge spectra shows an intense π^* peak confirming the high degree of aromaticity, consistent with previous studies of the macromolecular material [1,2,10].

Nanoglobules. Visually, the nanoglobules constitute up to 10% of the residues. Sparse, amorphous nanotubes occur in Murray and Tagish Lake. Nanoglobules in the residue and disaggregated meteorites occur singly and clustered. Some are solid, and others have hollow or vesicular cores. They exhibit a range of sizes, morphologies, aggregations, and are free of foreign mineral grains. The largest clusters are in Tagish Lake and Murray. Most nano-sized carbonaceous grains are amorphous, although locally ordered regions occur.

The C K-edge shapes of the nanoglobules confirm their high degree of aromaticity. The N and O K edges are similar in shape and show spectral features indicative of C=O and N=O groups. Spectral features at both the C and O K edges suggest bonded H. The shapes of the S $L_{2,3}$ and C K edges show that the S in the S-rich globules is bonded to C, rather than being elemental.

C in clays. The EELS spectra from the clays show C K edges that vary in intensity and shape. Spectral shapes range from those that are similar to those of amorphous C to spectra with a prominent peak near 290 eV. The 290 eV peak is similar in energy to C in the carbonate anion and also to C of carboxylic acid groups. HRTEM imaging of the meteorite clay failed to reveal the poorly graphitized material that constitutes the bulk of the carbonaceous residues.

Amorphous C_xS flakes. The amorphous flakes of C_xS are intriguing. They contain minor N and O, are uniformly thin, up to 800 nm across, with C:S ratios up to 10:1. They occur in disaggregated Tagish Lake and Cold Bokkeveld, and in the Tagish Lake residue. The C K-edge spectra of these flakes is similar to spectra from the S-rich areas of fluffy carbonaceous acid residue.

Discussion and Conclusions: The abundant fluffy macromolecular material of the residue is conspicuously absent in the disaggregated meteorites. We propose that the C detected with the clays is the source of this material. The acid residues show the nanometer-scale chemical heterogeneity and structural diversity of the carbonaceous materials. We confirm the intimate relationship between the meteorite organic matter and the minerals that formed as a result of aqueous alteration. These data provides important clues to early solar-system environments and processes.

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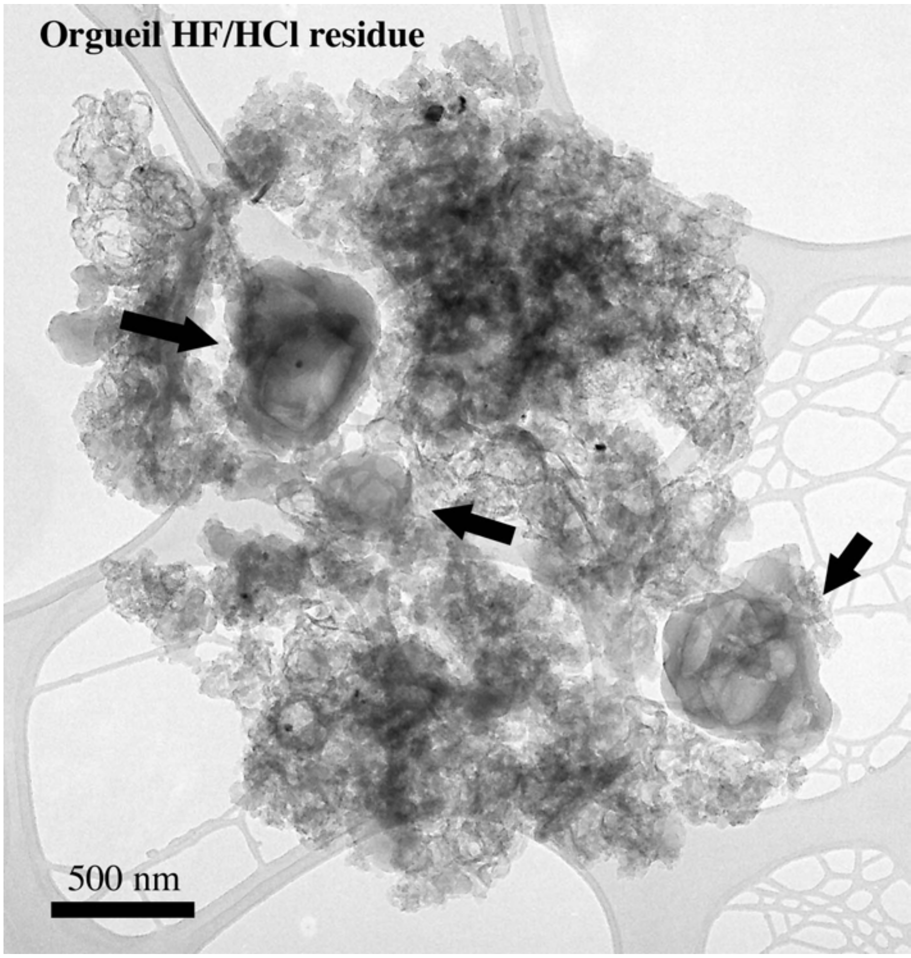

Figure 1. Transmission electron microscope image of a representative carbonaceous cluster from the Orgueil HF/HCl acid residue. The arrows point to hollow (left and right sides) and (center) solid nanoglobules. The lacy structure is the supporting film of the TEM grid.

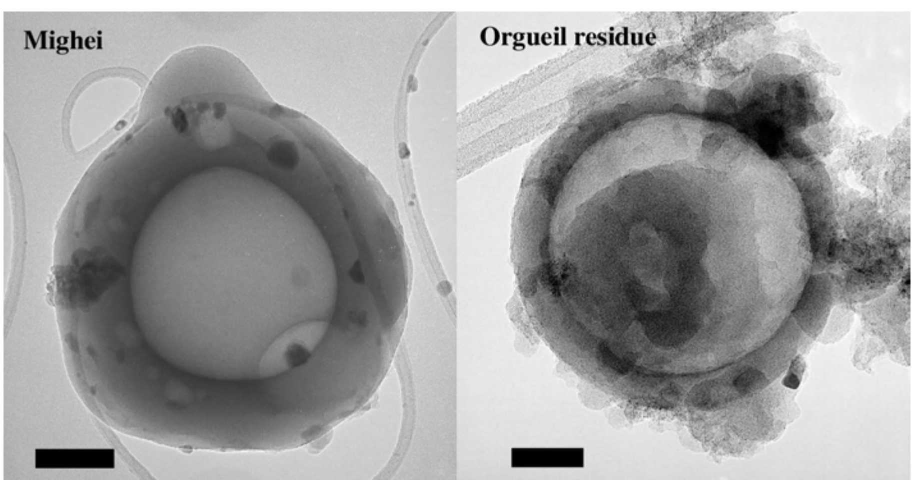

Figure 2. Transmission electron microscope images of hollow carbonaceous particles from the Mighei and Orgueil carbonaceous chondrite meteorites. The Mighei particle was disaggregated from the unprocessed meteorite. The Orgueil particle is from the HF/HCl acid residue and is surrounded with adhering kerogen-like macromolecular material. Scale bar for Mighei is 140 nm and 50 nm for Orgueil.