

CARBON-XANES ANALYSES OF Q-GAS RICH FRACTIONS FROM THE ALLENDE METEORITE.

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Introduction: While *Q* gases, the planetary noble gases, from different chondritic meteorites have been elementally and isotopically studied [1-3], the carrier of *Q* gases, *phase Q*, is yet to be identified despite the effort over three decades. Amari et al. (2003) [4] analyzed *Q* gases in the density-separated fractions of “*a floating fraction*” from the Allende meteorite which is similar to HCl-HF resistant residues regarding to noble gas compositions but obtained by the freeze-thaw disaggregation. They revealed that half of *Q* gases in the parent floating fraction was concentrated in the fraction with the density of $1.65 \pm 0.04 \text{ g/cm}^3$ (C1-8D). It appears that *phase Q* does not simply correspond to a whole carbonaceous residue but a specific carbon component or structure included in the carbonaceous residue. To determine the chemical structure of *phase Q*, a transmission electron microscopy (TEM) was applied to an HCl-HF resistant carbonaceous residue (*Q* rich) and its oxidized residue (*Q* lost), however, no clear difference was seen between TEM images of the two samples [5]. In this study, we apply X-ray absorption near edge structure (XANES) spectroscopy using the scanning transmission X-ray microscope (STXM) that is an appropriate technique to probe sensitively the functional groups at high spatial resolution ($< 30 \text{ nm}$), in order to focus on the quantitative molecular characterization of the fraction C1-8D, *Q*-rich carbonaceous matter from Allende.

Experimental: A floating fraction was recovered by the freeze-thaw disaggregation of the Allende CV3 meteorite and was separated into nine density fractions in a density gradient of sodium polytungstate after the colloidal separation [4]. In this study, seven of the density fractions (C1-8J, C, D, E, F, G, K), a colloidal fraction (C1-A), and an HCl-HF resistant carbonaceous residue for comparison, were used. The samples were embedded in epoxy resin and were sectioned into 100–140 nm thickness using a diamond knife and an ultramicrotome. C-XANES of these samples was conducted using STXM at Beam line 5.3.2, at the Advanced Light Source, Lawrence Berkeley National Laboratory [6].

Results and discussion: In the C-XANES spectrum of the most *Q* gas-rich fraction C1-8D, the peak intensity of aromatic carbon (Peak *a* in Fig. 1) is significantly lower than that of acid insoluble residue. The peak of $1s\text{-}\sigma^*$ exciton derived from highly conjugated sp^2 carbon (Peak *c*), i.e. graphene, is characteristic in

thermally metamorphosed chondritic organics [7], but is not seen in C1-8D. Moreover, two large peaks of carbon $1s\text{-}\sigma^*$ transitions that are derived from C-C, C-O, or C-F (Peak *d*) and C-C (Peak *e*) were originally detected in C1-8D at the energies exceeding the C $1s$ ionization threshold, ~ 292 and $\sim 295.7 \text{ eV}$. This spectral pattern was clearly distinctive from that of the acid resistant carbonaceous residue.

The C-XANES spectrum of C1-8D is also distinctive from those of graphite, fullerene, carbon nanotube, and glassy carbon all of which have the developed peaks of $1s\text{-}\sigma^*$ exciton [8]. Although the spectrum of C1-8D has a small hump that is possibly derived from diamond related carbon (Peak *b*), it is also distinctive from that of pure diamond.

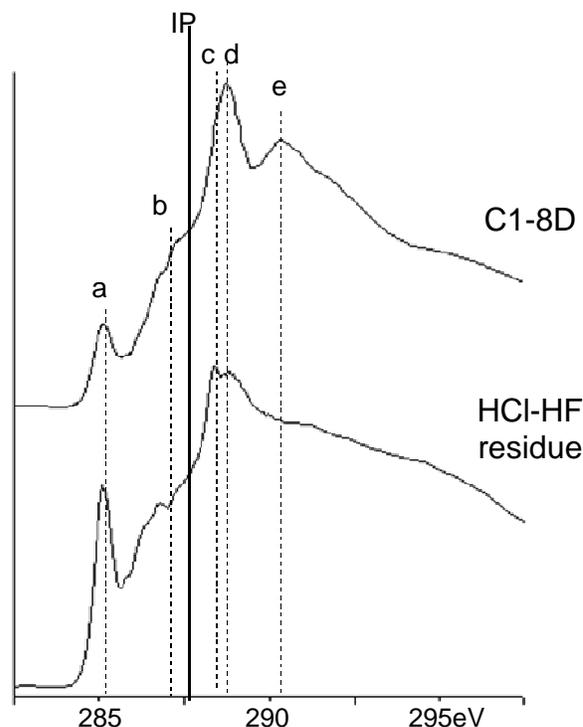


Fig. 1. C-XANES spectra of the most *Q*-rich density fraction (C1-8D) and acid insoluble residue from Allende. Peak *a* corresponds to a $1s\text{-}\pi^*$ transition of aromatic carbon; Peak *b* may be derived from diamond related carbon; Peak *c* corresponds to a $1s\text{-}\sigma^*$ exciton derived from graphene. Peak *d* corresponds to a $1s\text{-}\sigma^*$ transition of C-C, C-O, or C-F. Peak *e* corresponds to a $1s\text{-}\sigma^*$ transition of C-C.

The C-XANES spectrum of C1-8D is compared to those of the other density fractions (Figs. 2 and 3). They show similar spectra at the first glance, however, several clear differences are observed; 1) The peak intensity of aromatic carbon is the lowest in C1-8D, 2) The peak d at ~ 292 eV is shifted to 292.6 eV in C1-8D, and 3) The peak e at 295.7 eV are the most developed in C1-8D. Looking more closely, the peak energy of aromatic carbon (Peak *a*) is the lowest, 285.25 eV in C1-8D while those of the other fractions are 285.35 or 285.5 eV. A shoulder band in the range of 287-288 eV is not present only in C1-8D. Only C1-8D has Peak *b*. These results indicate that there exists the electronic structural differences between C1-8D and the other density fractions. Therefore, concentration of *Q* gas may be related to kinds or abundances of specific chemical bondings in its carrier material.

The result that only C1-8D is distinct from the other density fractions in the spectral characteristics while the others fractions are similar appears to be consistent with the micro-Raman spectroscopic behaviors of these fractions [9]. They reported that only C1-8D has the lower I_D/I_G ratios while all other fractions have similar I_D/I_G ratios. In general, the I_D/I_G ratio is proportional to the sp^2/sp^3 carbon in diamond-like carbon [10],

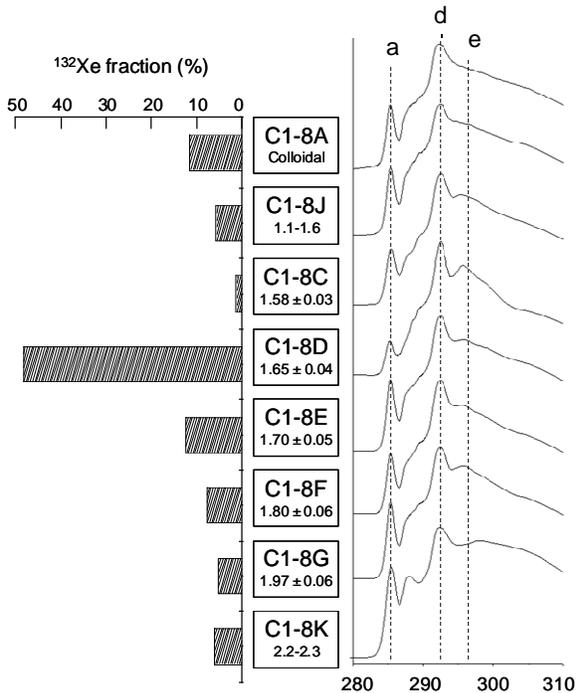


Fig. 2. C-XANES spectra of C1-8 separates from Allende. Peaks (*a*, *d*, and *e*) corresponds to those in Fig. 1. A histogram of abundances of ^{132}Xe in the C1-8 separates relative to the sum of ^{132}Xe in all separates [4] is shown together.

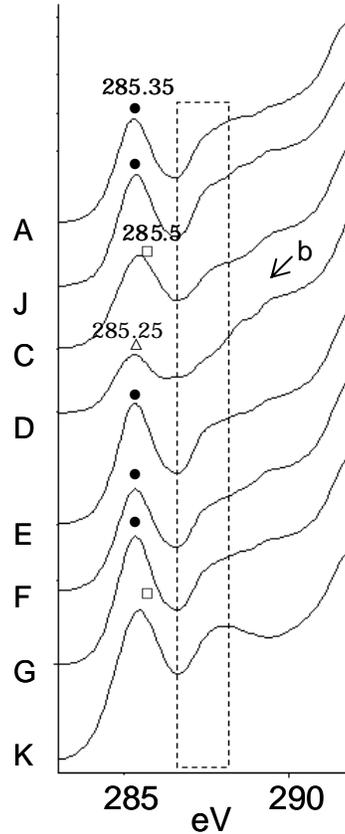


Fig. 3. Enlarged C-XANES spectra in Fig. 2. Note that the energy shifts can be observed at ~ 285 eV. C1-8D does not have a shoulder at 287-288 eV. Peak *b* is detected only in C1-8D.

and thus C1-8D may be rich in sp^3 carbon. This is consistent with this study that aromatic carbon is less abundant and carbons associated with $1s-\sigma^*$ transition are dominant in C1-8D. Consequently, *Q* gas could be concentrated in sp^3 carbon-rich material. We anticipate that application of the XANES technique to the further *Q* gas concentrated carbonaceous matter would enable the refinement of the candidate of *phase Q*.

References: [1] Wieler R. et al. (1991) *GCA*, 55, 1709-1722. [2] Huss G. R. et al. (1996) *GCA*, 60, 3311-3340. [3] Busemann H. et al. (2000) *Meteoritics & Planet. Sci.* 35, 949-973. [4] Amari S. et al. (2003) *GCA*, 67, 4665-4677. [5] Matsuda J. et al. submitted. [6] Kilcoyne et al. (2003) *J. Synchrotron Rad.* 10, 125-136. [7] Cody et al. (2008) *EPSL*, 272, 446-455. [8] Stöhr J. (1992) *NEXAFS Spectroscopy*. [9] Matsuda J. et al. (2009) *Geochem. J.* 43, 323-329. [10] Ferrari A. C. and Robertson J. (2000) *Phys. Rev. B* 61, 14095-14107.