

REFINEMENT OF PHASE Q CARBON CHEMISTRY THROUGH COMPARISON STUDY OF Q-GAS RICH AND DEPLETED FRACTIONS FROM THE ALLENDE METEORITE.

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Introduction: Since when Lewis et al. (1975) [1] found that a large part of the planetary heavy noble gases were preserved in an acid resistant carbonaceous residue from the Allende CV3 meteorite, subsequent studies have proposed that meteoritic carbonaceous matter is most likely a candidate for the carrier of the nobles gases “*phase Q*” [2]. *Q* gases from different chondritic meteorites have been elementally and isotopically studied [3-5], however, *phase Q* itself is yet to be identified despite the effort over three decades.

Matsuda et al. (2010) [6] has revealed that transmission electron microscopy (TEM) observations did not show any clear difference between an acid resistant carbonaceous residue (*Q* rich) and its oxidized residue (*Q* depleted), while the differences in Raman spectroscopic parameters between the two residues were observed. They concluded that release of *Q* gases during oxidation is not accompanied by mass loss and that the release of *Q* gases simply resulted from rearrangement of carbon structure during oxidation.

Our previous X-ray absorption near edge structure (XANES) spectroscopic study [7] has reported that the physically separated *Q*-rich fraction with the density of $\sim 1.65 \text{ g/cm}^3$ (C1-8D) may be rich in diamond-related sp^3 carbon, which appears to be consistent with Raman features [8]. Thus, the release of *Q* gases and/or *phase Q* itself could be related to carbon functional group chemistry rather than carbonaceous morphology. This study focuses on XANES analyses of the acid resistant carbonaceous residue and its oxidized residue from Allende, in order to refine carbon chemistry that is likely associated to the release of *Q* gases. In addition, *Q*-rich fractions obtained through the two different methods, suspension [6] and physical separation [9] from Allende, are analyzed for comparison.

Experimental: An Allende meteorite fragment (4.9154 g) was treated with 10M HF-1M HCl for preparing an acid resistant carbonaceous residue [4]. During the removal of elemental sulfur from the acid resistant residue with CS_2 , One-seventh of the total fraction of the residue suspended in the supernatant was recovered (AMD3) [4]. The rest (six-seventh) of the fraction (AMD1), which is rich in *Q* gases, was further treated with $0.5\text{N Na}_2\text{Cr}_2\text{O}_7 - 2\text{N H}_2\text{SO}_4$ to remove *Q* gases, yielding the oxidized residue, AMD2 [4]. Apart from AMD samples, “a floating fraction (G1)”, *Q* rich frac-

tion, was obtained by the freeze-thaw disaggregation of Allende meteorite in stainless beaker [9]. All the samples (AMD1, AMD2, AMD3, and G1) were embedded in sulfur and were sectioned into about 130 nm thickness using a diamond knife with an ultramicrotome. C-XANES of these samples was conducted using a scanning transmission X ray microscope (STXM) at Beam line 5.3.2, at the Advanced Light Source, Lawrence Berkeley National Laboratory [10].

Results and discussion:

Comparison between AMD1 and AMD2

The C-XANES spectra of AMD1 (*Q* rich) and AMD2 (*Q* depleted) are compared in Fig. 1. The intensities of Peaks A and B, which correspond to aromatic C=C and aliphatic C-H, respectively, are much lower in AMD2 than those in AMD1. The intensity of Peak C, carbonyl C=O, are slightly higher in AMD2 than that in AMD1. On the other hand, the peak intensities of $1s-\sigma^*$ exciton derived from highly conjugated sp^2 carbon (D), i.e. graphene, are not changed between AMD1 and AMD2. The differences in molecular features between AMD1 and 2 may not be directly reflected by *phase Q*.

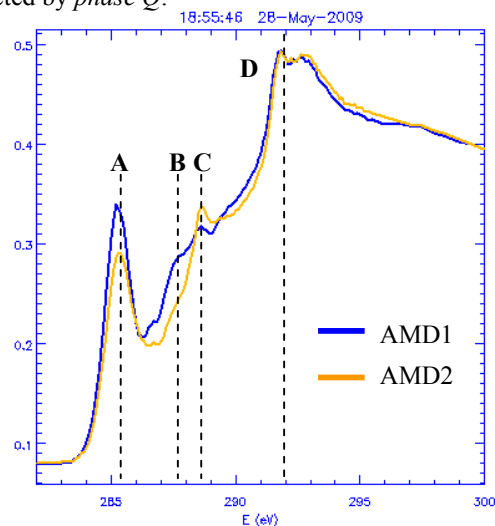


Fig. 1. Carbon-XANES spectra of AMD1 (blue, *Q*-rich) and AMD2 (orange, *Q*-depleted) from Allende. Peak A ($\sim 285 \text{ eV}$) corresponds to a $1s-\pi^*$ transition of aromatic C=C; Peak B ($287.3 - 288 \text{ eV}$) corresponds to $1s-3p/\sigma^*$ transition of aliphatic C-H; Peak C ($\sim 288.5 \text{ eV}$) corresponds to a $1s-\pi^*$ transition of carbonyl carbon; Peak D (291.6 eV) corresponds to a $1s-\sigma^*$ exciton derived from graphene.

Rather, they more likely indicate the changes in major organic macromolecule as seen in Peaks **A**, **B**, and **C** by oxidation. Nonetheless, the depletion of aliphatic (and partial decrease of aromatic) and production of carbonyls probably influence the amorphization and structural rearrangement related with the release of *Q*-gases, as discussed in [6]. No quantitative change Peak **D** before and after oxidation indicates that *phase Q* is unlikely related to graphene sheets, which is consistent with the TEM observation [6].

Comparison between AMD1 and AMD3

The C-XANES spectra of AMD1 and AMD3, suspended fraction, are compared in Fig. 2. Only one clear difference between the two fractions is a peak at 287.43 eV in AMD 3 (**B'**) is remarkably developed compared to AMD1. In general, a peak around at this energy range is generally assigned to sp^3 aliphatic C-H carbon. However, such clear appearance of aliphatic carbon is rare in chondritic organic carbon (even in terrestrial kerogen). As an alternative possibility, detection of a peak derived from another sp^3 carbon, such as -C-CF of fluorinated diamond, at this energy range is also reported [11]. Although Peak **B'** is not exactly identified at present, it may have an important relation to *Q*-richness, since noble gas concentrations in AMD3 are 2-4 times higher than those of AMD1 [6]. Except for the Peak **B'**, other spectral features are very similar.

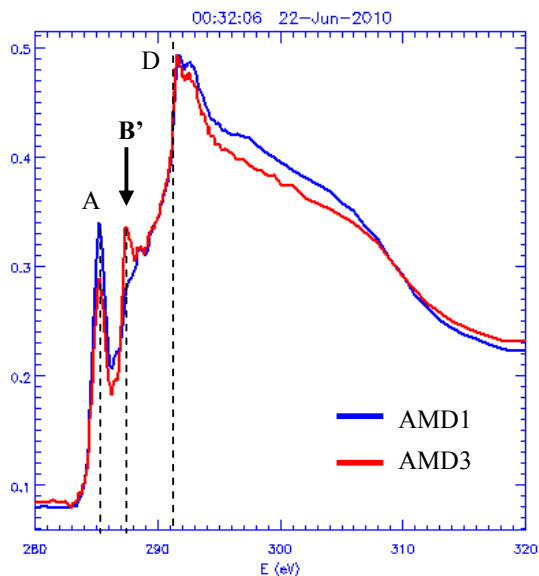


Fig. 2. Overlaid Carbon-XANES spectra of AMD1 (blue) and the suspended fraction (red, *Q*-rich, AMD3) from Allende. Peak assignments of **A** and **D** corresponds follows Fig. 1. Peak **B'** at 287.43 eV, unidentified peak at present.

C-XANES spectrum of G1 (bulk floating fraction)

G1 showed a quite different C-XANES spectrum from those of AMD1 and AMD3 (Fig. 3). While aro-

matic carbon (Peak **A**) is low compared to Figs 1 and 2, unidentified Peaks **E** and **F** are detected at 288.46 and 289.5 eV. Peak **F** is possibly derived from diamonds [12] or their related compounds. Such spectral features are very similar to the density fraction C1-8D that concentrates half of the *Q* gases [9]. In addition, C-XANES measurements of different regions of G1 showed heterogenous spectra: a new peak appears at 286.6 eV. These spectra are not exactly the same as those of individual density fractions in our previous study [7]. It may be because the individual density fractions show more detailed spectral features that were covered in bulk fractions, or might have been partially contaminated with Teflon from Teflon beaker used for the past freeze-thaw disaggregation.

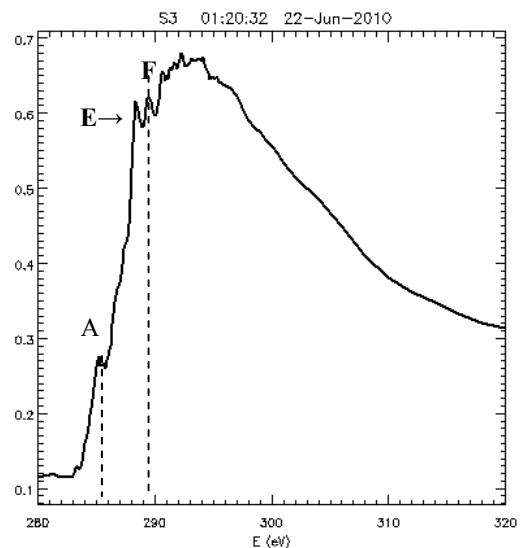


Fig. 3. Carbon-XANES spectrum of physically separated *Q* rich fraction, G1, from Allende. Peak assignment of **A** follows Fig. 1. Peaks **E** and **F** are unidentified.

To summarize, it is further suggested that some sp^3 carbon may be related to the release of *Q* gases and/or *phase Q*. In future studies, examination of more *Q* gas concentrated carbonaceous matter and spectral comparison of several standards will be necessary.

References: [1] Lewis R. S. et al. (1975) *Science*, 190, 1251-1262. [2] Ott U. et al. (1981) *GCA*, 45, 1751-1788. [3] Wieler R. et al. (1991) *GCA*, 55, 1709-1722. [4] Huss G. R. et al. (1996) *GCA*, 60, 3311-3340. [5] Busemann H. et al. (2000) *Meteoritics & Planet. Sci.* 35, 949-973. [6] Matsuda J. et al. (2010) *GCA*, 74, 5398-5409. [7] Yabuta et al. (2010) *LPS XXXI*, Abstract #1202. [8] Matsuda J. et al. (2009) *Geochem. J.* 43, 323-329. [9] Amari S. et al. (2003) *GCA*, 67, 4665-4677. [10] Kilcoyne et al. (2003) *J. Synchrotron Rad.* 10, 125-136. [11] Yu et al. (2003) *Appl. Surface Sci.*, 219, 228-237. [12] Stöhr J. (1992) *NEXAFS Spectroscopy*.