XANES analyses of the hydrous pyrolysis residues of the IOM from the Murchison carbonaceous chondrite.

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Introduction:

The major fraction of chondritic carbon is now known as IOM (Insoluble Organic Matter). It is characterized by condensed aromatic moieties cross-linked by aliphatic and ether linkages, with various functionality external to the aromatic structure [1]. IOM can be further subdivided into two types: thermally labile and refractory components [2, 3]. During hydrous activity on the meteorite parent bodies, the labile part could be removed and yield some solvent-extractable organic compounds such as mono- and dicarboxylic acids [4, 5]. The δD-$\delta^{13}C_{Bulk}$ plot of the Murchison IOM including its hydrous pyrolysis residues shows an isotopic sequence. The IOMs from several Antarctic chondrites lie on or near that sequence depending on the degree of hydrous and/or thermal alteration [6]. XANES and IR analyses are useful tools to evaluate the thermal history of the parent bodies [7, 8, 9]. In this investigation, we examined the structure of the Murchison IOM and its hydrous pyrolysis residues together with IOMs from two Antarctic chondrites using XANES and IR techniques, to clarify the processes involved in aqueous alteration.

Samples and methods:

Three IOMs from the Murchison, A881458, B7904 CM2 chondrites and three hydrous pyrolysis residues of the Murchison IOM were analyzed. The procedure of IOM preparation was described in Oba and Naraoka [6]. Hydrous pyrolyses of the Murchison IOM have been performed at 270, 300, or 330°C for 72h. [6]. Each sample was pressed onto a copper plate. And Carbon, nitrogen, oxygen *K*-edge XANES spectra were measured on BL12 at the Kyushu Synchrotron Light Research Center. IR spectra of the IOMs were obtained using the spectrometer, Perkin-Elmer Spectrum One.

Results and Discussion:

Figs.1 show C-XANES spectra of the IOM from Murchison and its hydrous pyrolysis residues. The spectrum of the original Murchison IOM (Fig.1a) shows fine structures in the region ranging from 280 to 290 eV, suggesting aromatic/olefinic (~285.2eV), nitrile (~286.7eV), aliphatic (~287.4eV), alcohol/ether (~289.0eV). The spectra of the hydrous pyrolysis residues (Figs.1b-1d) show well-developed absorption near 286.2eV suggesting keto-structure, and the original fine structure has become unclear. Peculiar O incorporation into IOM was reported during the hydrous pyrolysis at 270 and 300°C [6]. This process was interpreted as the original carboxyl groups were lost by decarboxylation and new O-containing groups such as hydroxyl and ketone were produced [6]. The suggested keto-structure by the C-XANES spectra is consistent with that hypothesis.

Figs.2 show the IR spectra of the original Murchison IOM and its residue at 300°C. The original IOM shows carbonyl stretching band at a frequency of 1716cm^{-1}, while the 300°C residue shows the slightly weak band, and its position shifted to slightly lower frequency of 1699cm^{-1}. This frequency shift and the decrease of intensity suggest decarboxylation during hydrous pyrolysis [6, 9]. By $\delta^{13}C$ analysis, oxidation of methylene carbon during the process is also suggested [6]. Chondrites metamorphosed with higher H_2O and O_2 activities show the C=O stretching bands at lower frequencies in the 1660-1690cm^{-1} range, plausibly leading the formation of unsaturated ketones via oxidation of aromatic side groups and possible oxygen addition to dienes [9]. Although the observed peak shift between the original Murchison IOM and its 300°C residue is small, it may also indicate the formation of keto-structure suggested by C-XANES analysis.

The C-XANES spectrum of the 330°C residue is quite similar to the spectrum of B7904 (Fig.3) that suffered intensive thermal metamorphism, being consistent with the similar O/C value of the Murchison 330°C residue. B7904 also shows well-developed aryl/vinyl-keto absorption at 286.2eV. However, the aromatic absorption at ~285.2eV is not clear, being observed only as a shoulder at the main 286.2eV absorption, unlike crystalline graphite. And the C-XANES spectra of 330°C residue and B7904 are not largely different from those of the 270 and 300°C residues. This suggests that not only simple heating metamorphism but oxidation may play an important role in the evolutionary processes of chondritic IOM.

References:

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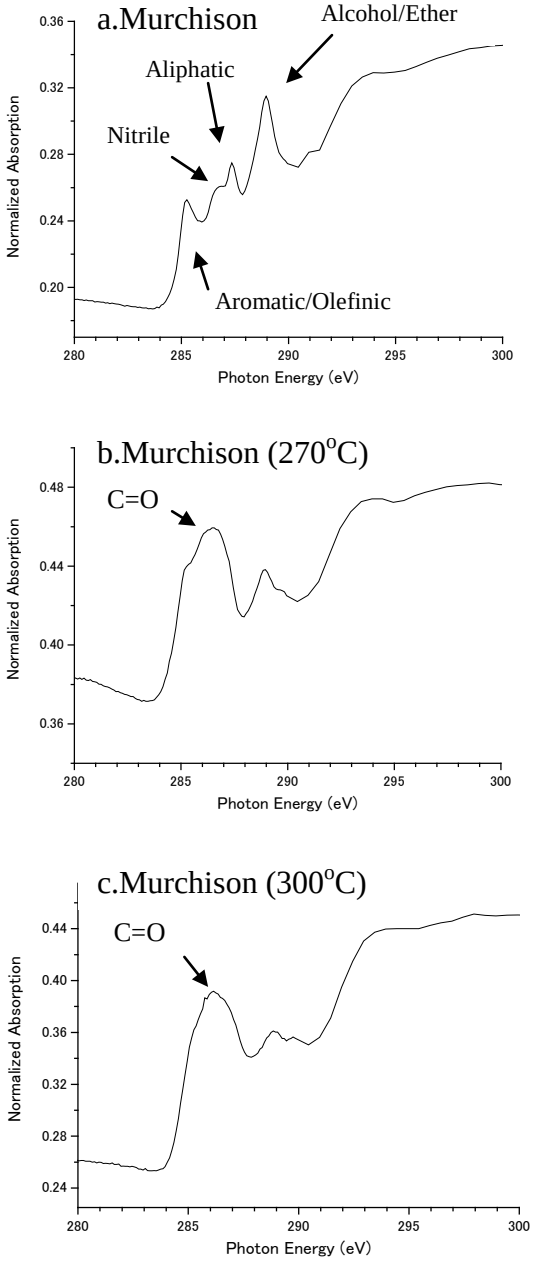
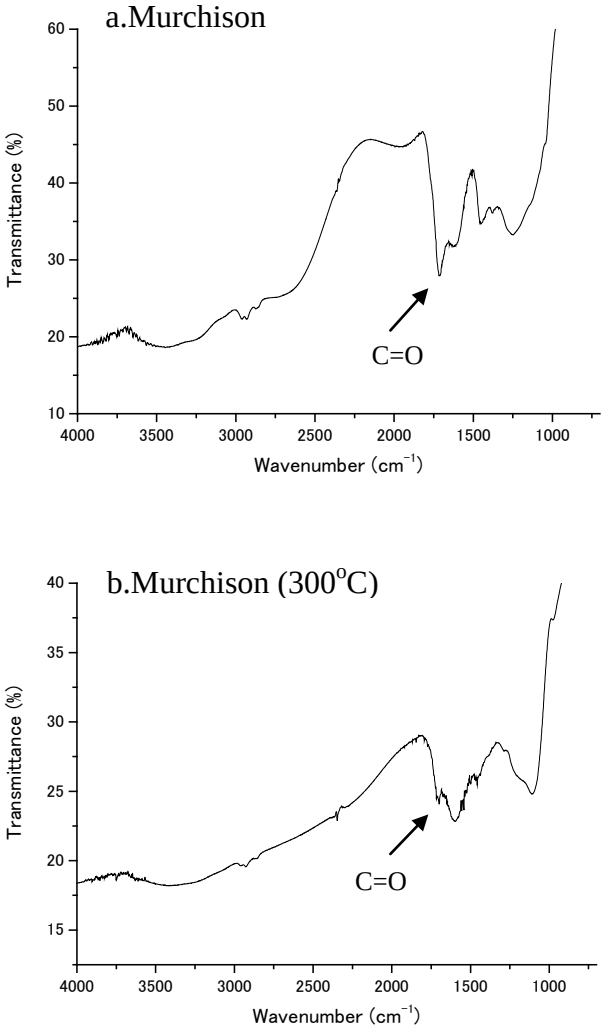


Figs.1 C-XANES spectra of the IOM from the Murchison chondrite and its hydrous pyrolysis residues.



Figs 2. IR spectra of the IOM from the Murchison chondrite and its hydrous pyrolysis residue at 300°C.

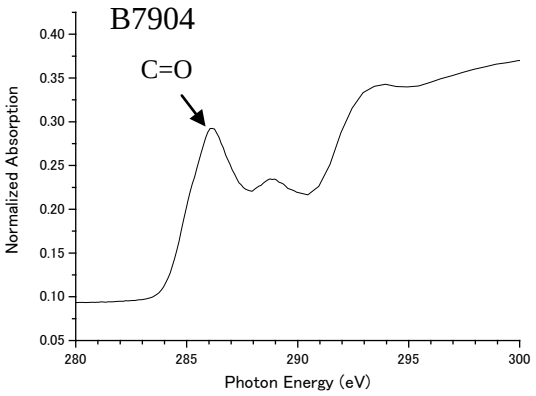


Fig.3 C-XANES spectrum of the IOM from B7904.