EFFECT OF TUBE-BASED X-RAY MICROTOMOGRAPHY IMAGING ON THE AMINO ACID AND AMINE CONTENT OF THE MURCHISON CM2 CHONDRITE. D. P. Glavin[1], J. M. Friedrich[2,3], J. C. Aponte[1,4], J. P. Dworkin[1], D. S. Ebel[2], J. E. Elsila[1], M. Hill[2], H. L. McLain[1,4], and W. H. Towbin[2,5]. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, e-mail: daniel.p.glavin@nasa.gov. [2]American Museum of Natural History, New York, NY 10024. [3]Fordham University, Bronx, NY 10458. [4]Catholic University of America, Washington DC 20064. [5] Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York 10964.

Introduction: X-ray and synchrotron X-ray microcomputed tomography (μCT) are increasingly being used for three dimensional reconnaissance imaging of chondrites and returned extraterrestrial material prior to detailed chemical and mineralogical analyses [1,2]. Although μCT imaging is generally considered to be a non-destructive technique since silicate and metallic minerals in chondrites are not affected by X-ray exposures at the intensities and wavelengths typically used, there are concerns that the use of μCT could be detrimental to the organics in carbonaceous chondrites. We recently conducted a synchrotron μCT experiment on a powdered sample of the Murchison CM2 carbonaceous chondrite exposed to a monochromatic high energy (~48 keV) total X-ray radiation dose of ~1 kilogray (kGy) using the Advanced Photon Source beamline 13-BMD at Argonne National Laboratory and found that there were no detectable changes in the amino acid abundances or enantiomeric compositions in the chondrite after exposure relative to a Murchison control sample that was not exposed [3].

However, lower energy bremsstrahlung X-rays could interact more with amino acids and other lower molecular weight amines in meteorites. To test for this possibility, three separate μCT imaging experiments of the Murchison meteorite using the GE Phoenix v|tome|x s 240 kV microfocus high resolution tungsten target X-ray tube instrument at the American Museum of Natural History (AMNH) were conducted and the amino acid abundances and enantiomeric compositions were determined. We also investigated the abundances of the C1-C5 amines in Murchison which were not analyzed in the first study [3].

Materials and Methods: A single 10 g fragment of the Murchison meteorite ("Grade A", Chicago Field Museum) was crushed to a powder and homogenized by mixing using a ceramic mortar and pestle inside a positive pressure HEPA filtered laminar flow hood at NASA's Goddard Space Flight Center (GSFC). All glassware, ceramics and sample handling tools were pyrolyzed at 500 ºC in air overnight. Four separate aliquots (~0.5 g each) of the meteorite powder were transferred to individual borosilicate glass screw capped vials and sealed in air for the X-ray tube based imaging experiment. The vials were sent to the AMNH and three were exposed to X-rays. The X-ray 1 and 2 samples were irradiated for a duration (~42 min) needed for a typical imaging experiment. The samples were rotated during X-ray exposure to simulate a typical CT acquisition. The X-ray source is a tungsten target and the spectrum produced is a superposition of both tungsten characteristic X-ray peaks and bremsstrahlung peaks. We also changed the experimental conditions to study the effects of adding a Cu filter (X-ray 2) and substantially increasing the exposure duration (X-ray 3) to the maximum typically used for an X-ray microtomography imaging scan (Table 1). The Cu filter sits between the X-ray tube and the sample and reduces sample exposure to the lower energy X-ray radiation. One vial was not exposed and served as the experimental control for the three irradiated samples.

Table 1. Experimental details of the X-ray irradiation of the Murchison meteorite samples.

	Control	X-ray 1	X-ray 2	X-ray 3
Murchison mass (g)	0.5313	0.5048	0.5181	0.5152
X-ray tube potential (keV)	n/a	180	180	180
X-ray tube current (μA)	n/a	120	120	120
Copper filter (0.3 mm)	n/a	no	yes	no
Exposure duration (min)	0	42.2	42.7	459
Total Dose (Gy)	0	~270	~10	~2950

Following the X-ray experiments at AMNH, the vials were returned to GSFC and a portion of each sample (~250 mg) was flame sealed in a glass tube in 1 mL Millipore ultrapure water and heated to 100ºC for 24 h. After hot-water extraction, half of the water extract was desalted by cation exchange chromatography and the NH_4OH eluate derivatized by *o*-phthaldialdehyde/N-acetyl-L-cysteine (OPA/NAC) and analyzed for amino acids by ultrahigh performance liquid chromatography with UV fluorescence detection and time of flight mass spectrometry (LC-FD/ToF-MS) [4].

The other half of the water supernatant was acidified with 100 μl 6M HCl, concentrated by drying under vacuum and then analyzed by OPA/NAC derivatization and LC-FD/ToF-MS. The amino acid and amine abundances were determined by comparison of the UV fluorescence and ToF-MS mass peak areas to the corresponding areas of standards run under the same chromatographic conditions on the same day. The free amino acid and amine concentrations in the extracts were then determined from the average of three separate

measurements. The abundances and amino acid enantiomeric ratios of the irradiated meteorite extracts were compared to the non-irradiated control.

Results and Discussion:

Amino acid data. The abundances of D,L-aspartic and glutamic acids, D,L-serine, D,L-threonine, glycine, D,L-alanine, β-alanine, D,L-α-, D,L-β-, and γ-amino-*n*-butyric acid, α-aminoisobutyric acid, D,L-valine, D,L-isovaline, and ε-amino-*n*-caproic acid in the hot-water extracts were determined and the total amino acid abundances in the X-ray irradiated samples relative to the control are shown in Figure 1. We observed no change in the total amino acid concentrations (Fig. 1) or D/L ratios (Table 2) in the Murchison extracts after X-ray irradiation within analytical errors. These results are consistent with our previous study [3].

Table 2. Amino acid enantiomeric ratios (D/L) measured in the hot-water extracts of the control and X-ray exposed Murchison meteorite samples.

Amino Acid	Control (D/L)	X-ray 1 (D/L)	X-ray 2 (D/L)	X-ray 3 (D/L)
Asp	0.56 ± 0.15	0.56 ± 0.09	0.54 ± 0.11	0.60 ± 0.15
Glu	0.69 ± 0.17	0.69 ± 0.15	0.61 ± 0.10	0.75 ± 0.08
Ala	1.03 ± 0.11	1.02 ± 0.13	0.99 ± 0.06	1.07 ± 0.08
Iva	0.85 ± 0.06	0.86 ± 0.07	0.85 ± 0.05	0.93 ± 0.07

Amine data. The C1-C5 amine abundances of methylamine, ethylamine, propylamine, isopropylamine, isobutylamine, *sec*-butylamine, *tert*-pentylamine, *sec*-pentylamine, 3-aminopentane, 2-amino-3-methylbutane, 2-methylbutylamine, and isopentylamine in the hot-water extracts were determined and the total amine abundances in the X-ray irradiated samples relative to the control were determined (Fig. 1). Although there may be some evidence for amine decomposition in the X-ray 1 sample, the most surprising result is the two-fold increase in total amine abundances in the X-ray 2 and X-ray 3 samples relative to the control indicating significant amine (or amine precursor) production as a result of the X-ray irradiation. Since the amino acid and amine analyses were carried out on the same water extract, sample heterogeneity cannot explain the differences observed. In addition, there is no evidence of amino acid decomposition into amines during these irradiation experiments, therefore it is possible that the addition of the Cu filter and extended irradiation exposure time in the X-ray 2 and X-ray 3 experiments, respectively, contributed to an increase in degradation of the large insoluble macromolecular organic component (IOM) known to be present in Murchison [5]. Release of free amides in Murchison during irradiation that later formed amines by partial hydrolysis during hot water extraction is also possible. Additional testing will be required to determine if the breakdown of IOM in Murchison is contributing to the production of amines or their precursors during X-ray irradiation exposure under these conditions.

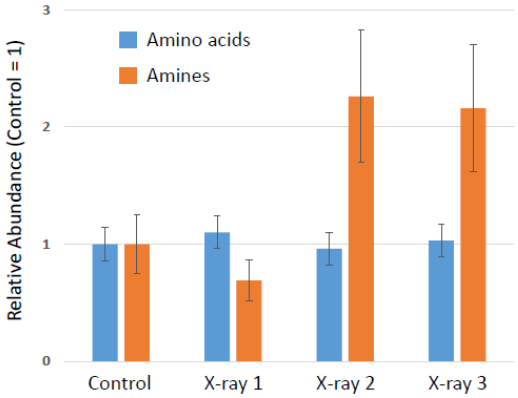

Fig. 1. Comparison of the relative abundances of free amino acids and amines in the hot-water extracts of powdered samples of the Murchison meteorite exposed to X-rays using the microfocus high resolution X-ray tube CT instrument at AMNH under different conditions compared to a control sample that was not irradiated. Instrument conditions for the samples are shown in Table 1.

Conclusions: We conclude that tube-based X-ray microtomography imaging tested under a variety of experimental conditions had no measurable effect on the amino acid content of the CM2 carbonaceous chondrite Murchison. However, a significant enhancement of the total amine abundance outside of experimental uncertainty was observed after X-ray irradiation exposure using a Cu filter (10 Gy dose), and for long exposure times without a Cu filter (2950 Gy), but not for short exposure without a filter (270 Gy). These data provide confidence in the use of μCT and similar non-invasive methods for amino acid analyses of carbonaceous chondrites and returned asteroid samples from OSIRIS-REx and Hayabusa2. However, depending on the μCT experimental conditions, significant changes to the amine content during irradiation are possible.

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