**3D SUBMICRON POROSITY STRUCTURE OF A MM-SIZED CARBONACEOUS CHONDRITE.**

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**Introduction:** Recently, two sample return missions to carbonaceous asteroids (162173) Ryugu and (101955) Bennu, by JAXA's Hayabusa2 and NASA's OSIRIS-REx missions, respectively, have revealed that the asteroids are significantly more microporous than expected [1,2] and preliminary analysis of samples from Ryugu confirm that they are more highly microporous than their analog CI meteorites [3]. The origin of this unexpectedly high porosity is not known. It could represent porosity created from a secondary process such as meteoroid bombardment or cracking due to diurnal thermal stress [2]. However, it is also hypothesized that it may be the original, primary porosity of the carbonaceous chondrite material that accreted to the asteroid [1,2].

The porosity of analog carbonaceous chondrites to Bennu and Ryugu have previously been measured in the lab using both bulk (He pycnometry) and direct imaging (scanning or transmission electron imaging (SEM/TEM); X-ray computed tomography (XCT)) methods [e.g., 4-7]. The bulk microporosity of the Ryugu samples was estimated as 46% using the measured density and an assumption of CI chondrite grain density [3]. While bulk porosity measurements are likely to be accurate, they lack detail on the type (intragranular, intergranular, fracture, etc.), morphology, or location of the porosity that is critical for determination of its origin and evolution. Direct imaging of the pores provides this detail, but 2D imaging such as SEM or TEM requires destructive preparation (sectioning) of the sample and examines only a limited area (for TEM, on the order of ~100 $\mu m^2$).

XCT is able to examine porosity within intact samples while preserving 3D spatial context [e.g., 8]. A few studies have used XCT to examine porosity within chondrites but have been limited by the scale of observation due to measuring only discrete pores [6,9,10]. Typically, a discrete feature (such as a pore) can be accurately measured only when it has a diameter of at least a few (~3) voxels [8]. Therefore, XCT imaging the nanometer-sized porosity within CCs requires either very small (<200 µm) particles [6,10] or is not able to detect a significant porosity fraction within larger, more representative samples [9].

XCT imaging utilizing a heavy noble gas such Xe, which is highly attenuating to X-rays, has allowed inspection of extremely fine-scale porosity in terrestrial samples [11-13]. The sample is imaged twice, once infiltrated by air and once infiltrated by Xe gas, and by carefully aligning, cross-calibrating, and subtracting these data volumes one obtains a 3D map of where the gas has infiltrated, and thus the porosity. In such maps, each voxel value corresponds to partial porosity, or the fraction of the voxel that contains pore space, and therefore allows examination of 3D porosity even when it is below the spatial resolution of the data.

We have applied this XCT noble gas imaging method for the first time to an extraterrestrial sample, CM Murchison (an analog meteorite for carbonaceous asteroids), to demonstrate and refine the technique for application to current and future sample return missions to these highly microporous and complex targets.

**Methods:** We imaged a 50 mg chip (~3 mm in diameter; ~12 $mm^3$ total volume) of CM Murchison with XCT twice - once in the presence of pressurized xenon gas (400 PSI) and once in atmospheric air. The sample was scanned in a 12.7 mm PEEK rod that was bored out to a 3 mm inner diameter. PEEK is a thermoplastic rated for high pressure work that also has a relatively low X-ray attenuation. All connections used SwageLok™ connectors rated for high pressure work and were tested for leaks using $N_2$. XCT scans were done at the University of Texas High-Resolution X-ray Computed Tomography Facility (UTCT) on a Zeiss Versa 620 XRM at 90 kV and 12 W with the 0.4X detector, 1601 views, and 2 frames per view, and either a 15s (Xe gas) or 10s (air) per-frame acquisition time. After loading the sample into the chamber, we first pumped the system to low vacuum and then filled the chamber with Xe gas at 400 PSI. After the first scan we gradually released the pressured Xe (to prevent fracturing), let the system equilibrate with ambient air for 30 minutes, and then rescanned the sample.

A beam hardening correction was applied to both scans using the Zeiss reconstruction software and were reconstructed with a voxel size of 3.01 µm/voxel and exported as series of 32 bit TIFF images. We next manually aligned the two subvolumes and linearly rescaled the Air scan volume so non-porous phases had a similar CT value to that of the Xe scan. This is necessary because the polychromatic X-rays are filtered by the Xe gas surrounding the sample, changing the effective X-ray spectrum compared to the Air scan. Further, different beam hardening corrections were used for each scan, also affecting their relative scaling. After rescaling, the Air scan volume was subtracted from the Xe scan volume to derive the final CT data volume of Xe gas penetration.

We next scaled the Xe gas penetration CT volume, which was comprised of unitless CT data values representing effective relative attenuation, into porosity space. We scaled an interior portion of CT data volume (to avoid beam hardening and edge effects) such that the bulk porosity of the volume matched that of Murchison measured with He pycnometry. Because the small size of the chip precluded measurement of its bulk porosity directly with He pycnometry, we used the average bulk porosity (21.9 ± 2.2 %) among 14 Murchison samples previously measured by [4].

**Results:** A significant amount of xenon infiltrated the sample interior indicating a high degree of interconnected porosity that is below the spatial scale of the CT data. We find that the matrix in CM Murchison has a significantly higher porosity (22-34%) compared to chondrules and chondrule fragments (< 17%) (Fig. 2). In addition, some portions of fine-grained rims (FGRs) have even higher porosity (up to 38%) than the matrix (Fig. 2; bottom left plot). Two-dimensional views of the data suggest that these high porosity FGR areas represent layers of higher porosity (Fig. 1), such as have been found in CM Paris [7]. However, when viewed in 3D, we discover that these high porosity areas have a complex 3D geometry (Fig. 2) that suggest formation of the FGRs via dust aggregates or variable secondary processing around the rim after accretion.

**Future Work:** We are continuing to refine our technique to be applied to returned samples including building more sample chambers, using Kr instead of Xe as the heavy noble gas, and scanning in $N_2$ instead of ambient air. We are also assessing possible Kr or Xe contamination by measuring Kr/Xe isotopes of samples before and after exposure to the gas during scanning.

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**References:** [1] Okada et al. (2020) *Nature* 579, 518-522 [2] Rozitis et al. (2020) *Science Adv.* 6, eabc3699 [3] Yada et al. (2021) *Nature Astro.* [4] Macke et al. (2011) *MAPS* 46, 1842-1862 [5] Daly et al. (2018) LPSC, abstr. #1499 [6] Dionnet et al. (2020) *MAPS* 55, 1645-1664 [7] Zanetta et al. (2021) *Geochim. Cosmoch. Acta* 295, 135-154 [8] Hanna & Ketcham (2017) *Chemie der Erde – Geochem.* 77, 547-572 [9] Friedrich & Rivers (2013) *Geochim. Cosmoch. Acta* 116, 63-70 [10] Tsuchiyama et al. (2104) *MAPS* 49, 172-187 [11] Lu et al. (2014) *AIChE Journal* 40, 1246-1253 [12] Vega et al. (2014) *Transport in Porous Media* 101, 81-97 [13] Mayo et al. (2015) *Fuel* 154, 167-173.

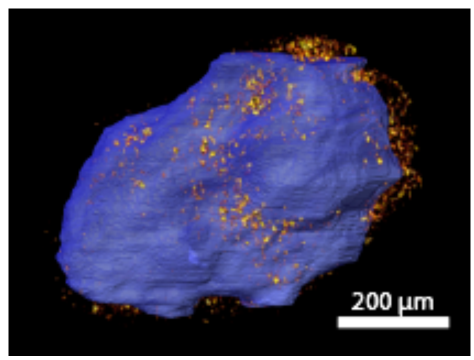


**Fig. 2 (above):** 3D rendering of chondrule surface (transparent blue) and areas of highest porosity (> 35%) (orange to yellow; same color scale as in Fig. 1). Highest porosity within FGR is localized on the 'right' side of the chondrule, and mostly on the 'top'.

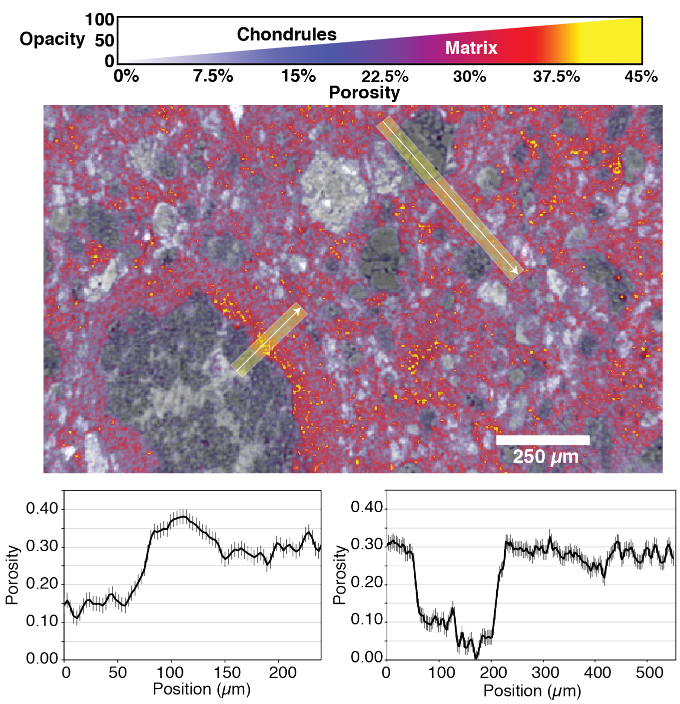


**Fig. 1 (left)**: XCT slice 706. Porosity data (colorized with variable opacity) overlain on XCT data of Air scan (greyscale). Porosity value indicated is that corresponding to an individual voxel. White lines with yellow shaded regions show location of line profiles plots below. (Below) Line profile plots of porosity using 15-pixel wide average (yellow regions on lines) with vertical bars representing the standard error of the mean (2.1%). The matrix has a relatively higher porosity (22-34%) compared to the chondrules (< 17%), and some FGR areas have even higher porosity (up to 38%).