SPECIFIC SURFACE AREA AND PORE-SIZE DISTRIBUTION IN CARBONACEOUS CHONDRITES

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Introduction: Clay-rich rocks can have complex pore structures controlled by the microstructure and aggregation of the clays. The multiscale clay aggregate structures give rise to porosity with different dimensions and scales [1]. Similarly, many carbonaceous chondrites (CC) of petrologic type 1 and 2 are argillaceous rocks and dominated by phyllosilicates and other clays-sized minerals [2-5]. Bulk powder XRD shows that the clays are dominated by serpentines and smectites [2-5]. While the bulk porosity of meteorites has received considerable attention [6,7], the submicron porosity is less well understood. The porosity and pore-size distribution are important properties in argillaceous rocks affecting their mechanical behaviors, and the movement and flow of fluids. However, the fine-scale porosity in CCs has received relatively little attention. Here, we use an N_2-adsorption technique to study the surface area and micro- and mesoporosity of CC meteorites. We apply the Brunauer, Emmett and Teller (BET) method of adsorption of N_2 and the Barrett, Joyner, and Halenda (BJH) method is applied to create pore volume and surface area distributions based on adsorption-desorption isotherms.

Samples and analysis: Adsorption/desorption isotherms were measured under N_2 at 77 K on a Micromeritics® TriStar II Plus surface area and porosity analyzer. The meteorites were characterized by applying the BET N_2 sorption method. Data was analyzed using the t-Plot method assuming a Harkins and Jura thickness equation and BJH analyses with Halsey-Faas correction to derive the pore data. Measurements were made on Tarda (C2-ung), Orgueil (CI1), Aguas Zarcas (CM2), Allende (CV), and for comparison the ordinary chondrite Leedey (L6). Samples were run as mm-sized fragments (f) and some as powders (p). Samples were outgassed in vacuum at 100 °C for 24 h before analysis. One sample – $Tarda^{nh}$ (nh-not heated) was run directly from a dry N_2 cabinet without 100 °C heating.

Results and discussion: The isotherms for the clay-rich CCs show pronounced hysteresis (**Panels a,b**), consistent with the presence of mesopores. The absence of a plateau at high p/p0 indicates the presence of macropores. The desorption branch shows a marked hysteresis at p/p0 ~ 0.35–0.45, which indicates the presence of <4 nm pores [1]. The isotherms for Allende (**Panel c**) and Leedey show an almost reversible shape indicating the presence of macropores with minimal micro-macropores. The degree of uptake for p/p0 ~1 is proportional to the total porosity up to ~ 200 nm, whereas degree of uptake for p/p0 <0.01 is proportional to the total micropore volume.

The specific surface areas for the clay-rich meteorites range from 15.21 to 66.97 m^2/g (**Table**), and significantly lower for those without clays (**Table**). Powdering has little effect on the surface area measurement, i.e., compare $Tarda^f$ and $Tarda^p$. However, degassing the sample significantly increased the surface area – compare $Tarda^{nh}$ with $Tarda^f$ (**Table**), suggesting a significant proportion of terrestrially bound water. The specific surface areas of the clay-rich meteorites are within the range of terrestrial argillaceous rock and clays [1]. The BET value for Orgueil is half that previously measured [8]. This difference may be the result of the varied curatorial histories of samples since its fall in 1864, however, the value measured here is still within the range for smectite-rich argillaceous rocks. The Allende and Leedey data are consistent with a low volume of micro- and mesopores, typical of igneous rocks (e.g., Table 4-3 in [9]), though these meteorites possess significant bulk porosity of 21.9 and 9.1%, respectively [6,7].

The meteorites show significant differences in their <200 nm pore-size distributions (**Panel d**). Tarda has significant micro– and mesoporosity, with a mesopore maximum near 3 nm. The mineralogically similar Orgueil has a bimodal pore-size distribution with a major peak near 40 nm and a minor peak around 3 nm. The profile for Aguas Zarcas shows a less-pronounced 3-nm peak and broader maximum that straddles the meso- macropore boundary. The two samples without clays -Allende and Leedey, lack the 3-nm peak and have broad maxima around 100 nm.

The 3-nm-pore peak in the pore-size distribution from smectite-rich rocks is attributed to "intra-tachoid" porosity [1]. Tachoids are 2- to 50-nm sized aggregates with turbostratic stacking of the phyllosilicate TOT plates. Tarda is smectite-rich, and the 3-nm-pore peak is consistent with intra-tachoid porosity. However, the rapid decrease in dV/dlog(w) with increase in pore size (**Panel f**) suggests relatively low density of pores in the 50- to 100-nm size range between the tachoids, whereas Orgueil and Aguas Zarcas possess significant intertachoid and intra-aggregate porosity.

Conclusions: The CCs studied here show significant differences in their surface areas, pore volumes, and pore-size distributions. The CC data are also of interest because similar materials are present on samples returned from asteroid Ryugu and thought to be present on asteroid 101955 Bennu. Thus, the detailed study of the CCs provides the framework and basic knowledge with which to study the samples returned from hydrated, clay-rich asteroids.

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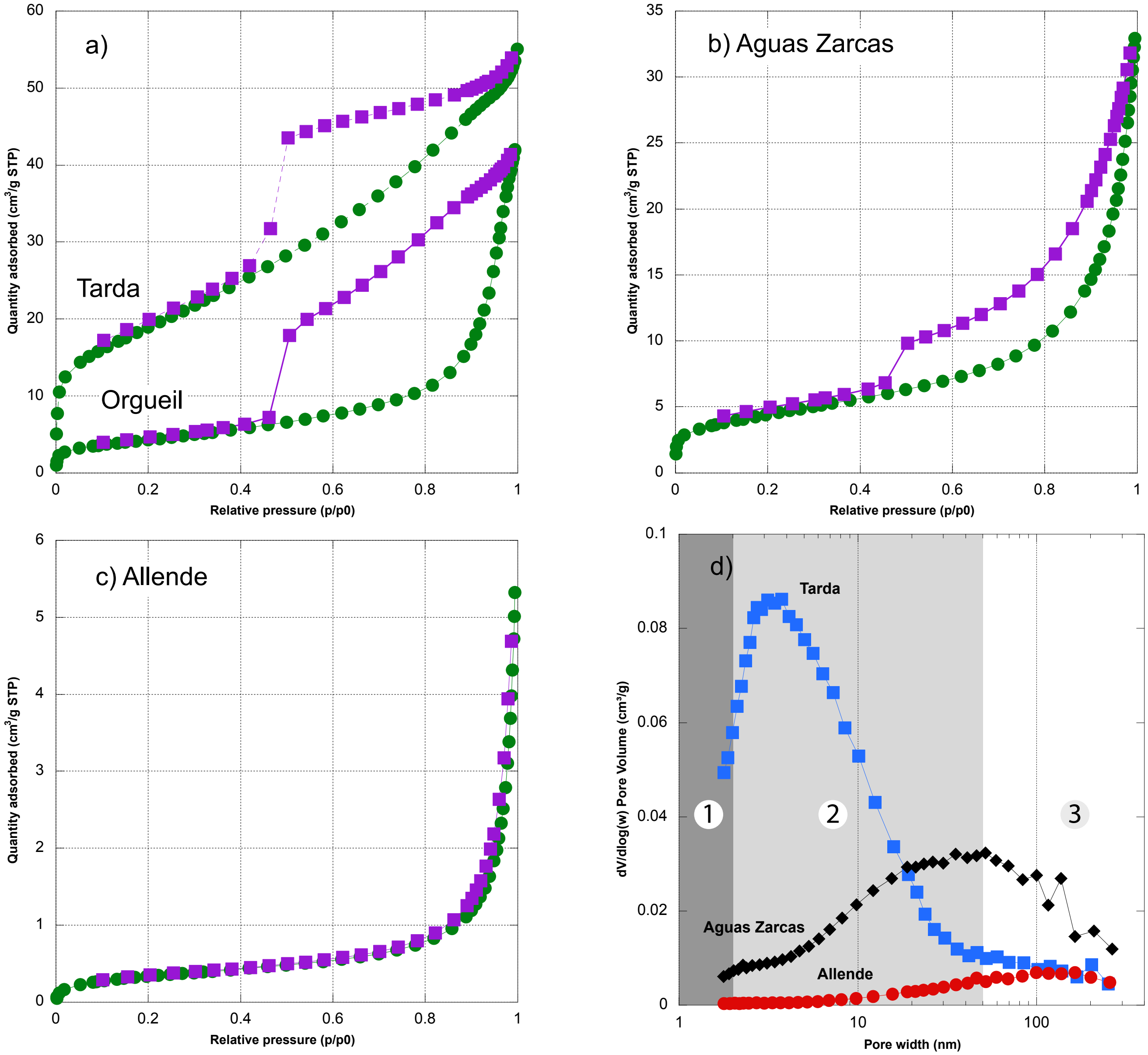

Figure. Panels **a** to **c**) Volume of gas (at STP) sorbed during N_2 adsorption and desorption at 77 K plotted vs. relative pressure p/p0. Adsorption (green circles) and desorption (purple squares) isotherms for Tarda, Orgueil, Aguas Zarcas, and Allende. Panel **d**) BJH Adsorption dV/dlog(w) pore volume determined using the Halsey Faas correction. The separate pore width regions are 1 - micropores, 2 - mesopores, and 3 - macropores.

Table. BET surface area, Langmuir surface area, pore volume and pore size for selected meteorites.

Meteorite (mass g)	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Pore volume[1] (cm^3/g)	Pore size[2] (nm)
Tarda[f] (0.4928)	66.97±0.35	88.11±2.54	0.079	4.91
Tarda[p] (0.5605)	64.97±0.38	77.15±2.56	0.088	5.56
Tarda[nh] (0.3068)	33.67±0.25	38.79±1.47	0.053	5.64
Orgueil[f] (0.7148)	15.21±0.09	18.50±0.60	0.064	15.11
Aguas Zarcas[f] (0.41)	15.53±0.09	17.60±0.50	0.049	12.87
Aguas Zarcas[p] (0.5518)	15.76±0.09	19.49±0.60	0.056	14.04
Allende[f] (0.7860)	1.21±0.01	1.49±0.05	0.008	28.01
Leedey[f] (1.0260)	0.85±0.06	0.90±0.01	0.003	35.03

f – fragments, **p** – powder, **nh** – sample not outgassed at 100°C for 24 hr. **1** - BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width. **2** - BJH Adsorption average pore width (4V/A).