Supporting information

Nanoscale accessible porosity as a key parameter depicting the topological evolution of organic porous networks

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This file contains 8 pages, 3 figures and 3 tables.

Organic geochemistry

The ensemble of 5 source rock samples from the Vaca Muerta (VM) formation (Neuquén basin, Argentina) was provided by Total SA. Their organic chemistry was evaluated by RockEval pyrolysis (Rock Eval 6, Vinci Technologies) and equivalent vitrinite reflectance (% R_{eq}) using standard organic petrology technique described in detail in ref. 1. As the Vaca Muerta source rock does not contain vitrinite, the bitumen reflectance was measured optically and translated into equivalent vitrinite reflectance based on the relationship established in ref. 2 and validated on our set of samples in ref. 3. The resulting vitrinite reflectance values range from 0.92 to 1.82 % R_{eq} and evidences the evolution of thermal maturity of the studied samples. The organic solid density was deduced form the relation $\rho_s = 0.342 \times R_{eq} + 0.972$, defined in ref. 4. The different peaks recorded along the pyrograms (not shown) and the total organic carbon (TOC) content were used to compute the fraction of free hydrocarbons (Free HC = S1/TOC x 100), hydrogen index (HI = S2/TOC x 100), and oxygen index (OI = S3/TOC x 100). The reader is referred to ref. 5 for the procedure of interpretation of Rock Eval pyrograms. The projection of the hydrogen indexes allows for the estimation of an "onset" hydrogen index (HI_0) of the source rock formation, which is used to compute the transformation ratio (TR_{HI}) of the organic matter, evolving here from 71.5 to 97.5 %. Our set of source rock samples therefore covers a significant range of thermal maturation experienced by the Vaca Muerta formation.

Table S1. Global information of the organic pore networks.

Tomogram #	Vitrinite reflectance	Specific Pore Volume, V_p	Porosity, φ	Mean chord length, $\langle l \rangle$	Specific surface area, S_{sp}
-	(% R_{eq})	(cm^3/g)	(vol. %)	(nm)	(m^2/g)
1	0.92	0.170	18.0	3.8	179.9
2	0.92	0.138	15.1	4.9	112.4
3	0.92	0.080	9.3	4.9	64.3
4	0.92	0.147	16.0	3.5	170.8
Mean value	*0.92*	*0.134*	*14.6*	*4.3*	*131.9*
1	1.31	0.196	21.8	3.7	211.4
2	1.31	0.200	22.1	7.6	105.2
3	1.31	0.150	17.5	4.2	142.3
4	1.31	0.223	24.0	5.4	166.1
Mean value	*1.31*	*0.192*	*21.4*	*5.2*	*156.3*
1	1.45	0.206	23.2	12.1	67.8
2	1.45	0.285	29.5	3.5	325.9
3	1.45	0.065	8.7	6.7	38.5
4	1.45	0.245	26.5	3.6	270.4
Mean value	*1.45*	*0.200*	*22.0*	*6.5*	*175.7*
1	1.65	0.263	28.8	7.8	134.3
2	1.65	0.096	12.8	4.0	96.0
3	1.65	0.187	22.4	2.2	342.5
4	1.65	0.156	19.4	3.1	200.6
Mean value	*1.65*	*0.176*	*20.9*	*4.3*	*193.4*
1	1.82	0.249	28.3	6.4	154.1
2	1.82	0.136	17.8	6.1	89.1
3	1.82	0.301	32.4	7.6	158.5
4	1.82	0.226	26.5	8.4	108.2
Mean value	*1.82*	*0.228*	*26.3*	*7.1*	*127.5*

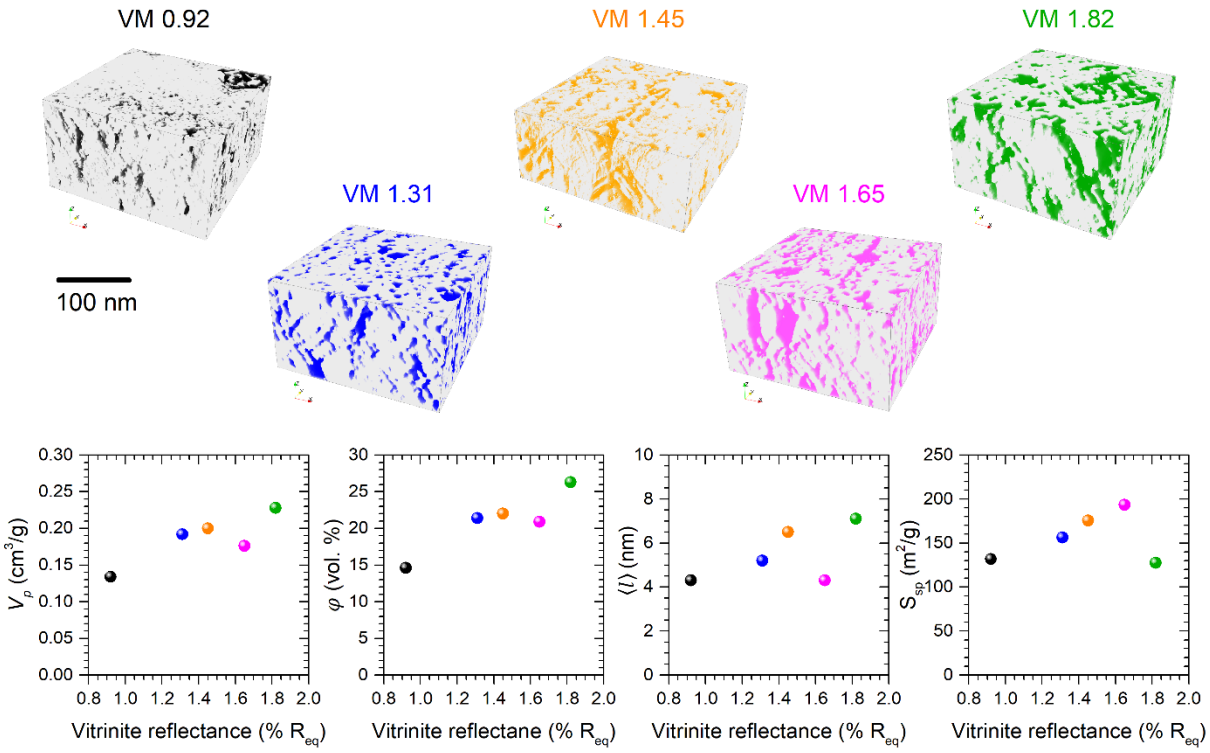

Figure S1. Examples of 3D reconstructions (top) of the organic porous networks (in color) from the Vaca Muerta samples together with the evolution of the mean dimensional information as a function of the increasing thermal maturity (bottom).

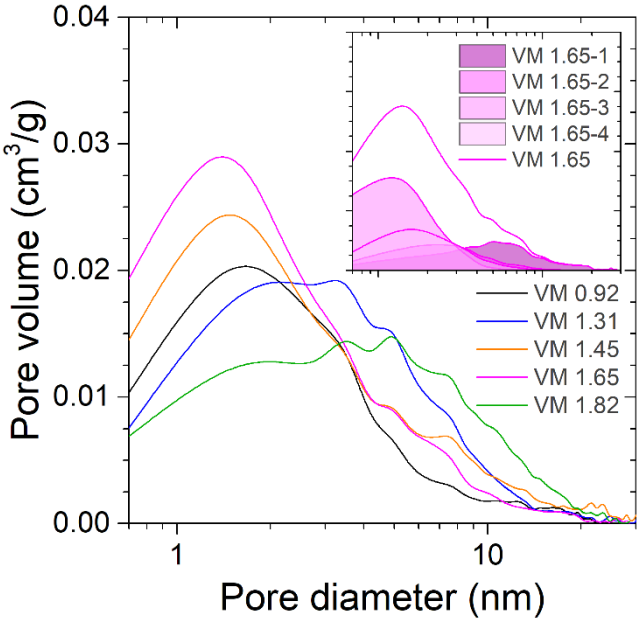

Figure S2. Pore size distributions of the VM samples from the statistical analysis of the tomograms (aperture size distribution). Inset: aperture sizes distribution of each tomograms of VM 1.65 (color filled area), the summation of these PSDs produced the general aperture size distribution (solid line).

Table S2. Morphological descriptors of the organic pore networks.

Tomogram # -	Vitrinite reflectance (% R_{eq})	Specific Mesopore volume, V_{meso} (cm^3/g)	Aperture size, h (nm)	Cavity size, H (nm)	Constriction, β -
1	0.92	0.097	3.7	11.2	0.33
2	0.92	0.098	6.8	17.0	0.40
3	0.92	0.062	5.3	12.5	0.42
4	0.92	0.076	4.9	15.4	0.32
Mean value	*0.92*	*0.083*	*5.2*	*14.0*	*0.37*
1	1.31	0.112	3.5	10.6	0.33
2	1.31	0.185	8.6	17.7	0.49
3	1.31	0.102	4.4	11.5	0.38
4	1.31	0.183	5.4	12.1	0.45
Mean value	*1.31*	*0.146*	*5.5*	*13.0*	*0.41*
1	1.45	0.199	13.9	29.1	0.48
2	1.45	0.143	3.5	13.0	0.27
3	1.45	0.055	9.0	21.1	0.43
4	1.45	0.130	3.6	12.4	0.29
Mean value	*1.45*	*0.132*	*7.5*	*18.9*	*0.37*
1	1.65	0.239	8.1	17.5	0.46
2	1.65	0.062	3.7	10.4	0.36
3	1.65	0.034	1.7	14.5	0.12
4	1.65	0.071	3.0	10.3	0.29
Mean value	*1.65*	*0.102*	*4.1*	*13.2*	*0.31*
1	1.82	0.197	6.8	16.9	0.40
2	1.82	0.113	6.4	15.1	0.42
3	1.82	0.264	7.9	18.1	0.44
4	1.82	0.206	8.6	19.4	0.44
Mean value	*1.82*	*0.195*	*7.4*	*17.4*	*0.43*

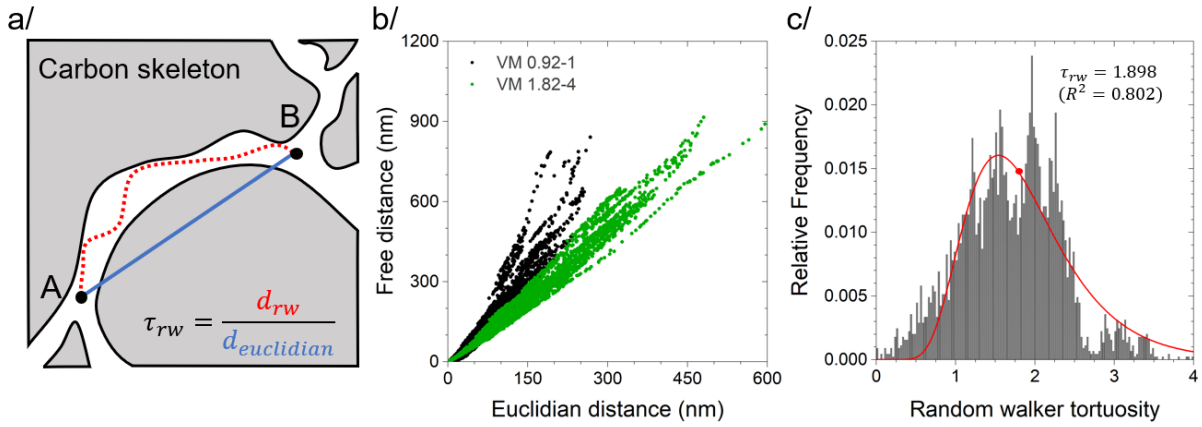

Figure S3. Random walker tortuosity τ_{rw} measurements performed on the tomograms. a/ Schematic of the free distance (red dashed line) travelled by a random walker between two points (A, B) in a pore and the corresponding Euclidian distance (blue solid line) between these two points. b/ Random walker free travel distance plotted against the corresponding Euclidian distances for VM 0.92-1 and VM 1.82-4. c/ Relative frequency histogram of the random walker tortuosities for VM 0.92-1. The median value of the lognormal fit represents the random walker tortuosities τ_{rw} reported in Table S3.

Table S3. Topological information of the organic pore networks.

Tomogram # -	Vitrinite reflectance (% R_{eq})	$\varphi_{eff}^{0.35\,nm}$ (%)	$\varphi_{eff}^{2\,nm}$ (%)	Pore connectivity, Z -	Random walker tortuosity, τ_{rw} -
1	0.92	16.5	1.5	3.25	1.90
2	0.92	5.2	4.1	3.27	1.51
3	0.92	2.4	1.1	3.22	1.69
4	0.92	9.1	1.2	3.31	1.79
Mean value	*0.92*	*8.3*	*2.0*	*3.26*	*1.72*
1	1.31	20.6	2.6	3.29	2.14
2	1.31	20.6	13.3	3.18	1.49
3	1.31	13.9	1.2	3.25	2.08
4	1.31	22.9	3.6	3.26	1.74
Mean value	*1.31*	*19.5*	*5.2*	*3.25*	*1.86*
1	1.45	20.6	19.4	3.16	1.26
2	1.45	28.7	8.8	3.37	1.87
3	1.45	1.5	0.7	3.23	1.38
4	1.45	25.6	4.6	3.38	1.84
Mean value	*1.45*	*19.1*	*8.4*	*3.29*	*1.58*
1	1.65	28.3	25.4	3.24	1.43
2	1.65	8.6	0.6	3.24	2.25
3	1.65	21.2	0.6	3.39	4.61
4	1.65	17.2	0.6	3.26	2.75
Mean value	*1.65*	*18.8*	*6.8*	*3.28*	*2.76*
1	1.82	27.3	21.5	3.34	1.34
2	1.82	14.2	4.5	3.29	1.33
3	1.82	31.7	28.4	3.33	1.36
4	1.82	25.2	22.2	3.27	1.43
Mean value	*1.82*	*24.6*	*19.2*	*3.31*	*1.37*

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