

On the limits of CO₂ capture capacity of carbons

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Abstract

This study shows that standard techniques used for carbons characterization, such as physical adsorption of CO₂ at 273 K and N₂ at 77 K, can be used to assess, with a good accuracy, the maximum capacity of carbons to capture CO₂ under post- and pre-combustion conditions. The analysis of the corresponding adsorption isotherms, within the general theoretical framework of Dubinin's theory, leads to the values of the micropore volume, W_0 , and the characteristic energy, E_0 , of the carbons, which provide direct information on the equilibrium CO₂ uptake of the carbons at different pressures and temperatures.

Although in special cases slightly higher values can be obtained, an overall assessment of the textural parameters for a large variety of activated carbons, indicates that a CO₂ uptake upper-bound around 10-11 wt % seems to be realistic for standard activated carbons under post-combustion conditions. In the case of pre-combustion conditions, this limit would not exceed 60-70 wt %.

Keywords: CO₂ capture, adsorption, activated carbon

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1. Introduction

Current trends in energy supply and use are economically, environmentally and socially unsustainable. Without decisive action, energy-related CO₂ emissions will more than double by 2050. In this context, low-carbon energy technologies will have a crucial role to play. Energy efficiency, many types of renewable energy, carbon capture and storage (CCS), nuclear power and new transport technologies will all require widespread deployment.

The International Energy Agency (IEA) is developing a series of roadmaps for some of the most important technologies. The roadmap on CCS ascertains that CO₂ capture technology is commercially available today, but the associated costs need to be lowered and the technology still needs to be demonstrated at commercial scale. Additional research and development is also needed, particularly to address different CO₂ streams from industrial sources and to test biomass and hydrogen production with CCS [1]. Thus, it is patently clear that reduction of carbon dioxide emissions on an industrial scale requires the development of low-cost capture methods.

A number of different carbon capture processes for post and pre-combustion applications have been tested and deployed at various scales, but it is too early to tell if any particular technology will emerge as the preference for CO₂ capture. Adsorption is considered a promising technology for CO₂ capture applications since adsorbents present high adsorption capacity, great selectivity, good mechanical properties and they remain stable over repeated adsorption-desorption cycles [2,3]. Selective adsorption of CO₂ on inorganic and organic adsorbents like zeolite, silica gel, alumina and activated carbon is used commercially for separation of bulk CO₂ from gas mixtures and removal of trace CO₂ from a contaminated gas [4]. The varied morphology and surface chemistry of these adsorbents give rise to different characteristics for adsorption of CO₂ as a pure gas or as a component of a gas mixture.

Activated carbons are suitable candidates for CO₂ capture, their adsorption performance being dependent on the pore structure and the properties of the surface chemistry [5,6]. Although capture capacities of activated carbons are, in general, lower than those of zeolites and molecular sieves under low pressure and ambient conditions, they present a series of

advantages as CO₂ adsorbents such as larger capacities at higher pressures, ease of regeneration, potential low-cost and less sensitiveness to moisture. Other types of carbonaceous sorbents, such as charcoal and coal, have been studied in a different CO₂ context [7,8] and only recently have been proposed for carbon capture from flue gas [9].

Efforts have been made to improve the CO₂ adsorption capacity of carbon-based adsorbents modifying the chemical structure of the carbon by means of impregnation with amines [10-12], heat treatment in the presence of ammonia gas [13] or functionalization with amino groups by electrophilic aromatic substitution [14]; other strategies were based on the introduction of nitrogen-rich carbon precursors as carbon matrix [15].

Most of the literature on carbons applied to CO₂ capture is based on maximum adsorption capacities determined from CO₂ adsorption isotherms or on equilibrium CO₂ uptakes at the desired temperature. Thus, comparison of the results is not always straightforward and inconsistencies between authors are often found depending on the conditions tested. Besides, little work has been published on the influence of both textural and surface chemistry factors on the CO₂ adsorption capacity. Therefore, the search for an optimized carbon for CO₂ capture becomes highly empirical.

The present contribution, based on the systematic study of series of phenolic resin-derived activated carbons, provides more detailed understanding of CO₂ capture by carbons. It shows that the equilibrium CO₂ uptake capacity under post- and pre-combustion conditions can be evaluated within the general theoretical framework of Dubinin's theory for the volume filling of micropores. The advantage of this approach lies, firstly, in the fact that the textural parameters determining the CO₂ capture capacity of carbons are identified. Secondly, it illustrates that tools widely used for the structural characterization of carbons, such as the physical adsorption of CO₂ at 273 K and N₂ at 77 K, also allow the assessment of the potential of carbons for CO₂ retention under post- and pre-combustion conditions.

2. Theoretical background

The physical adsorption of vapours by microporous carbons is well described by the equation of Dubinin and Radushkevich (D-R) [16]

$$N_a = N_{a0} \exp[-(A/\beta E_0)^2] \quad (1)$$

where $A = RT \ln(p_s/p)$. The quantity N_a , is the amount adsorbed at relative pressure p/p_s , and N_{a0} is the limiting amount as p tends towards p_s . The latter is related to the total micropore volume $W_0 = N_{a0} V_m$, accessible to the molecular probe, V_m being the molar volume in the adsorbed state at a given temperature. β is a scaling factor depending on the adsorbate. The quantity E_0 , usually given in kJ mol^{-1} , is called the characteristic energy of the solid. It has been shown that it is related to the average micropore width, L_0 , of the slit-shaped micropores by [17]

$$L_0 \text{ (nm)} = 10.8/(E_0 \text{ (kJ mol}^{-1}) - 11.4) \quad (2)$$

As shown in detail elsewhere [18,19], adsorption of CO_2 by carbons simply follows the Dubinin's theory and, therefore, leads to a common characteristic curve with other small adsorbates, e.g. CH_4 [20], NH_3 [21], C_6H_6 [22]. This means that reliable predictions for CO_2 adsorption/capture at any pressure and temperature can be made by using the D-R eq. with $\beta(\text{CO}_2) = 0.36$ [19, 22] and the corresponding molar volume $V_m(\text{CO}_2)$

3. Experimental

3.1. Carbons

This study is based on five series of activated carbons derived from phenolic resins. M series were produced by Mast Carbon International Ltd. using a Novolak-type phenolic resin as raw precursor. The control of the CO_2 activation conditions as well as the addition of a solvent pore former (ethylene glycol) prior to the resin curing step result in highly porous carbons

with a wide variety of porous textures. Details on the preparation process can be found elsewhere [23-25].

The other series include carbons produced in our laboratory from Resol (PFN-) and Novolak (CLC-, E-, PE-) phenol-formaldehyde resins. In the case of E- and PE-carbons, ethylene glycol and polyethylene glycol (1-10 wt %) were added, respectively, as pore formers. The production process involved a carbonization under inert atmosphere of nitrogen at 700-800 °C and a subsequent activation with carbon dioxide at 750-900 °C to different burn-off degrees.

3.2. Characterization of the textural properties of the carbons

The solids were well characterized by standard adsorption techniques, N₂ at 77 K (Micromeritics ASAP 2010) and CO₂ at 273 K (Micromeritics TriStar 3000). In agreement with Lozano-Castelló et al. [26], the combination of both adsorptives provided valuable information to explain the performance of microporous carbons in CO₂ capture.

The analysis of the adsorption isotherms by means of the D-R equation (1) led to the corresponding micropore volume, W_o, and the characteristic energy, E_o, as perceived by the corresponding molecular probe.

The average micropore width, L_o, has been obtained by applying eq. (2). And, consequently, the surface area of the slit-shaped micropores has been estimated by the geometrical relation [16]:

$$S_{mi} \text{ (m}^2 \text{ g}^{-1}\text{)} = 2000 W_o \text{ (cm}^3 \text{ g}^{-1}\text{)} / L_o \text{ (nm)} \quad (3)$$

On the other hand, the reliable technique based on the comparison of the N₂ adsorption isotherm with a reference isotherm (*Vulcan 3G*) led to the surface area, S_e, found in wider pores or on the surface of the solid [27]. The combination of both approaches allowed the estimation of the total surface area of carbons, S_{total} = S_{mi} + S_e.

The mesopore size distributions (diameters D_{KJS}) have been obtained by applying the Kruk-

Jaroniec-Sayari (KJS) method to the N₂-adsorption isotherm branch [28].

The main textural properties of the studied carbons are summarized in Table 1.

3.3. CO₂ capture capacities

CO₂ capture capacities at both atmospheric (1 bar) and high pressure (20 bar) were determined at 298 K. Samples were dried at 373 K for one hour prior to any experiment. For the CO₂ capture tests at atmospheric pressure, a thermogravimetric analyser (Setaram) was used whereas for the high-pressure capture tests a magnetic suspension balance (Rubotherm-VTI) was employed. In both cases equilibrium capture capacities were evaluated by the maximum mass increase of the sample when exposed to a pure CO₂ atmosphere. Thus, the adsorption capacity was reported in terms of mass of CO₂ per mass of dry adsorbent, g CO₂/100 g carbon (wt %).

The D-R equation (1) with $V_m(\text{CO}_2, 298 \text{ K}) = 45.7 \text{ cm}^3 \text{ mol}^{-1}$ (Ozawa's equation [29]) allowed the calculation of the theoretical equilibrium CO₂ uptakes by using E_0 and W_0 obtained from the standard approach for the characterization of carbons (Table 1).

4. Results and Discussion

A suitable basis for a systematic study is provided by the carbons selected in this work. As reported in Table 1, they display total surface areas ranging from 231 to 1349 m² g⁻¹ and cover a wide range of micro- and mesoporosity features. Some materials may be regarded as exclusively microporous with average pore-widths $L_0(\text{N}_2)$ between 0.66 and 1.46 nm. Other samples also display contributions from larger pores with relatively narrow uni- and bi-modal mesopore size distributions with maxima between 2.5 and 54 nm. There are also carbons with a broad porosity above 10 nm [30].

The good agreement existing between the experimental CO₂ uptakes under post- and pre-combustion conditions, and the values predicted by Dubinin's theory for 23 activated carbons with a large variety of porous characteristics, confirms that CO₂ capture by carbons responds to a pore volume-filling process and adsorption is not limited to the surface.

Fig. 1 displays the excellent correlation between the experimental CO₂ retention by carbons at 1 bar and 298 K (C1 exp) and the values calculated (C1 calc) from Eq. (1) using the textural parameters derived from standard CO₂ isotherms at 273 K (micropore volume, W_0 [CO₂, 273K] and characteristic energy, E_0 [CO₂, 273K]). This is not surprising since, as a consequence of the relatively high saturation pressure of CO₂, the process of CO₂ capture at low pressures corresponds to a small degree of pore filling which involves, exclusively, the narrower micropores in the carbons. On the other hand, standard CO₂ isotherm, typically performed up to relative pressure $p/p_s \sim 0.03$ at 273 K, provides information on the so-called ultramicroporosity contribution (< 1 nm) and does not take into account larger micropores [26].

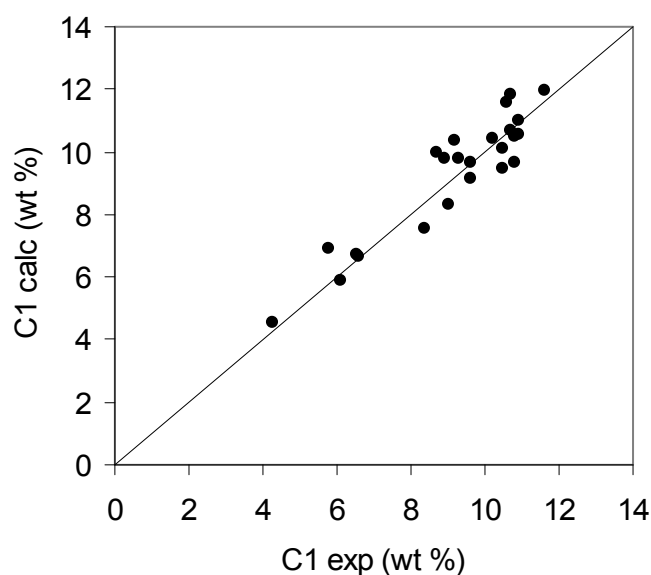


Figure 1. Correlation between calculated and experimental CO₂ uptake at 1 bar and 298 K for carbons in Table 1, using Eq. (1).

As a first step, this approach shows that maxima CO₂ retention capacities under post-combustion conditions can only be found for carbons with high micropore volumes coming from micropores below 0.6 nm ($E_0 > 29$ kJ/mol). This information provides a pathway to the design of optimized carbons for this application.

Secondly, D-R equation offers the possibility to predict with reasonable accuracy the limits for CO₂ capture by carbons under post-combustion conditions. Fig. 2 illustrates the variation of the characteristic energy, E_o [CO₂, 273 K], with the micropore volume, W_o [CO₂, 273 K] for a variety of porous carbons obtained from different precursors and methods [13, 18, 31-36]. For typical activated carbons, W_o [CO₂, 273K] is in the range of 0.2 - 0.3 cm³ g⁻¹, whereas E_o [CO₂, 273K] generally varies from 28 to 30 kJ mol⁻¹ ($L_o \sim 0.60$ nm). Although in special cases both parameters can reach slightly higher values, an upper-bound around 10-11 wt % CO₂ uptake seems to be realistic for standard activated carbons under post-combustion capture conditions. This limit is also confirmed by data quoted in the literature [2,5].

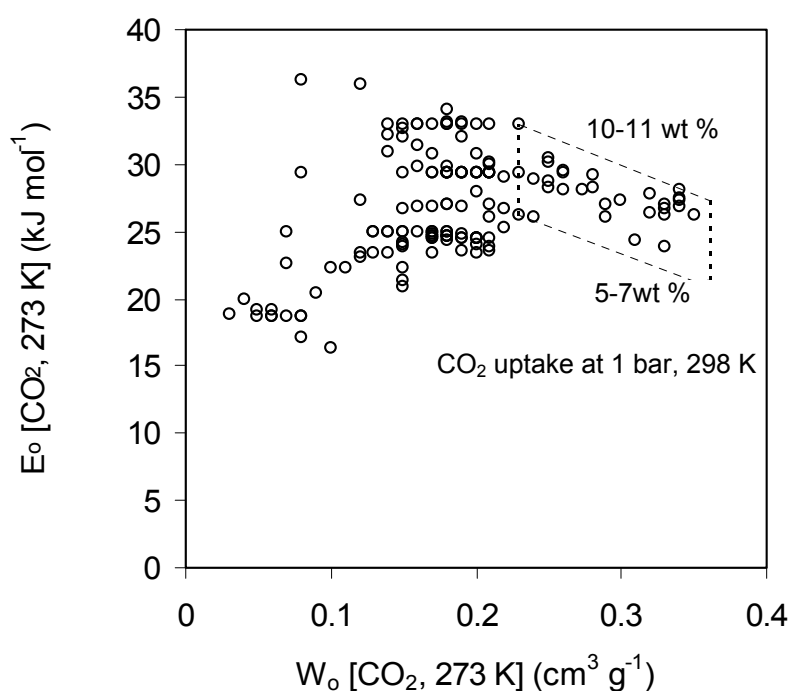


Figure 2. Variation of the characteristic energy, E_o [CO₂, 273 K], with the micropore volume, W_o [CO₂, 273 K], for a variety of porous carbons obtained from different precursors and methods [13, 18, 31-36].

In the case of pre-combustion conditions, the experimental results do not follow the previous pattern and a different approach must be found to accurately describe CO₂ capture at high pressure. It was observed that CO₂ uptake by carbons at 20 bar (C20 exp) is directly related

to the micropore volume and the characteristic energy obtained from the D-R equation applied to adsorption isotherms of N_2 at 77 K.

The good agreement revealed by Fig. 3 between C20 exp and the theoretical values (C20 calc) derived from W_o [N_2 , 77K] and E_o [N_2 , 77 K] according to Eq. (1) indicates that the retention of CO_2 under pre-combustion conditions occurs by filling of the entire microporosity. This is not accidental, because under such experimental conditions (298 K and 20 bar), CO_2 adsorption is close to saturation.

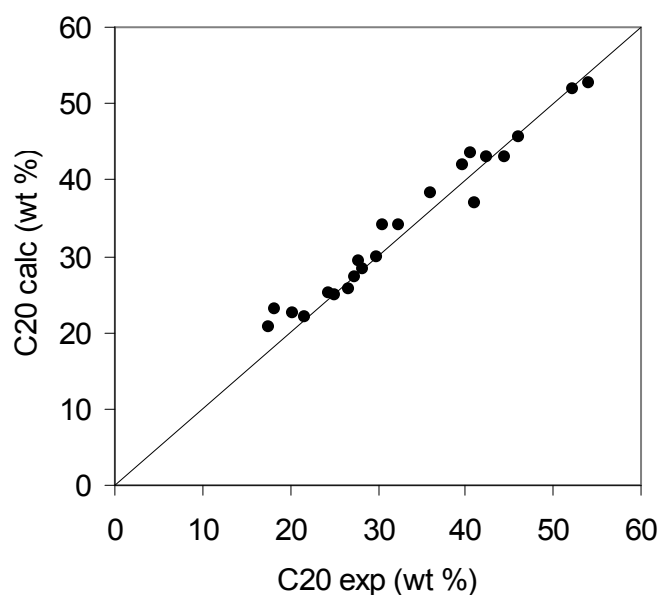


Figure 3. Correlation between calculated and experimental CO_2 uptake at 20 bar and 298 K for carbons in Table 1, using Eq. (1).

As discussed elsewhere [6], the micropore size tends to increase with the micropore volume of carbons, as the activation progresses. Such evolution, reflected by Fig. 4 for a variety of activated carbons [37-41], indicates that maxima CO_2 uptakes of around 60-70 wt % would be achieved at 20 bar by standard materials with micropore volumes ranging from 0.6 to 0.8 cm^3g^{-1} , and average micropore size, L_o (N_2 , 77 K), between 0.9 and 1.6 nm (E_o of around 24-18 $kJ mol^{-1}$). Higher CO_2 capture capacities of up to 98-100 wt % could only be reached for highly activated carbons with micropore sizes centered in the supermicropore range (1.5 - 2 nm). This is the case for PX-21, a KOH-superactivated carbon with a total micropore

volume of $1.2 \text{ cm}^3 \text{ g}^{-1}$ and an average micropore size around 2.0 nm (E_o around 17 kJ mol^{-1}).

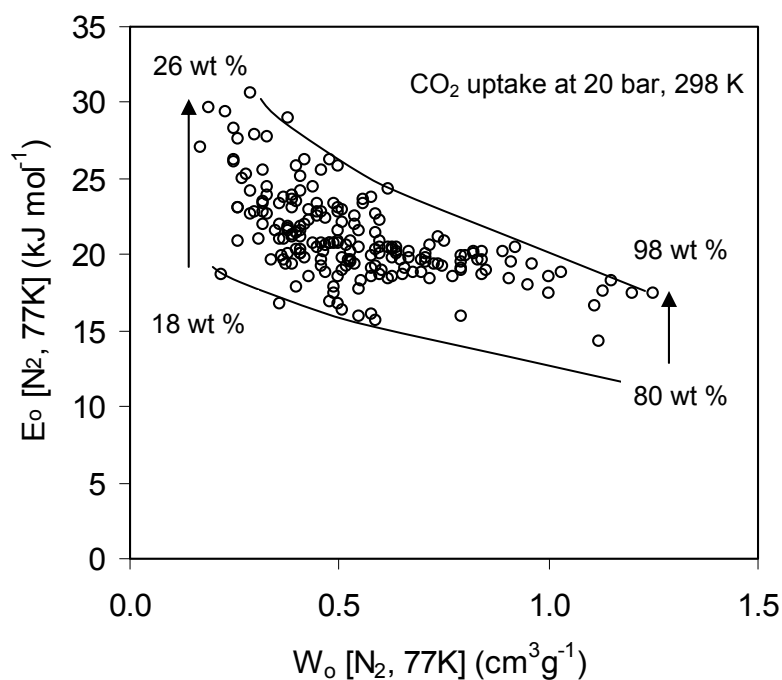


Figure 4. Variation of the characteristic energy, E_o [N_2 , 77 K], with the micropore volume W_o [N_2 , 77 K], for a variety of porous carbons obtained from different precursors and activation methods [37-41].

The comparison between carbons in Table 1, with similar micropore sizes but widely different mesoporosity contribution, suggests that the participation of the wider pores on CO_2 capture appears to be small. Clearly, capture capacity results from the micropore volume and not from the total pore volume. Nevertheless, the presence of larger pores may enhance the kinetics of the CO_2 capture process by providing wider transport paths into the smaller pores. Further evidences on this point will be provided by studies under dynamic conditions.

The experimental data presented in this work correspond to CO_2 capture tests under static conditions. Obviously, there may be numerical changes in the light of data obtained under dynamic performance, but it appears that there are clear limits for the removal of CO_2 by activated carbons under post- and pre-combustions conditions.

5. Conclusions

The systematic analysis of series of activated carbons in the general theoretical framework of Dubinin's theory confirms that the CO₂ capture capacity of carbons essentially responds to a micropore volume-filling process and not to adsorption limited to the surface. It is shown that both micropore volume, W_o , and average micropore width, L_o , are the only factors controlling the equilibrium CO₂ capture performance of carbons. In view of the diversity of experimental conditions, the design of carbon materials with optimized capture performance should be conducted differently depending on their application under post- or pre-combustion conditions.

The Dubinin-Radushkevich equation has proved to be a useful tool to estimate the suitability of a carbon to be applied as adsorbent for CO₂ capture. It provides a good prediction of the CO₂ uptake under post- and pre-combustion conditions, on the basis of the micropore volume, W_o , and the characteristic energy, E_o , estimated by the analysis of standard CO₂ adsorption isotherms at 273 K.

The present work leads to the following particular conclusions:

(a) The process of CO₂ capture under post-combustion conditions (1 bar and 298 K) involves exclusively the smaller micropores of carbons. Maxima CO₂ retention capacities under post-combustion conditions can only be found for carbons with high micropore volume coming from pores below 0.6 nm ($E_o > 29 \text{ kJ mol}^{-1}$).

(b) The CO₂ uptake of carbons under pre-combustion conditions (20 bar and 298 K) occurs by filling of the entire microporosity. CO₂ capture capacities up to 98-100 wt % could only be reached for highly activated carbons with pore sizes centered in the supermicroporosity range (1.5-2 nm).

(c) Although in special cases slightly higher values can be obtained, an overall assessment of the textural parameters, combining the data from CO₂ (273 K) and N₂ (77 K) adsorption on a large variety of activated carbons, indicates that a CO₂ uptake upper-bound around 10-11 wt % seems to be realistic for standard activated carbons under post-combustion conditions. In the case of pre-combustion conditions, this limit would not exceed 60-70 wt %.

Acknowledgements

Thanks are due to Mast Carbon International Ltd. for supplying phenolic-resin-derived activated carbons. Work carried out with financial support from Spanish MICINN (Project ENE2008-05087). C.F.M. acknowledges a JAE-predocctoral grant from Spanish CSIC, co-financed by the European Social Fund.

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Table 1. Textural parameters of the phenolic-resin-derived activated carbons

Carbon	N ₂ (77 K) - adsorption								CO ₂ (273 K) - adsorption			
	V _{tot} (N ₂) (cm ³ g ⁻¹)	W ₀ (N ₂) (cm ³ g ⁻¹)	E ₀ (N ₂) (kJ mol ⁻¹)	L ₀ (N ₂) (nm)	S _{mi} (N ₂) (m ² g ⁻¹)	S _e (N ₂) (m ² g ⁻¹)	S _{total} (N ₂) (m ² g ⁻¹)	D _{KJS} (N ₂) (nm)	W ₀ (CO ₂) (cm ³ g ⁻¹)	E ₀ (CO ₂) (kJ mol ⁻¹)	L ₀ (CO ₂) (nm)	S _{mi} (CO ₂) (m ² g ⁻¹)
M1	0.35	0.33	27.7	0.66	1000	10	710	-	0.34	28.0	0.65	1046
M2	0.55	0.51	22.9	0.94	1085	11	1105	-	0.34	27.3	0.68	1000
M3	0.60	0.54	22.0	1.02	1059	8	1200	-	0.34	26.8	0.70	971
M4	0.58	0.50	21.5	1.07	935	13	1190	-	0.29	27.0	0.69	840
M5	0.85	0.71	20.1	1.25	1136	6	1467	-	0.35	26.2	0.73	959
M6	1.50	0.36	21.0	1.12	643	269	909	5.2-54.0	0.26	29.5	0.59	881
M6b	0.80	0.32	22.75	0.95	674	326	771	4.6-22.0	0.25	30.1	0.58	862
M7	0.55	0.29	24.2	0.84	690	187	648	24.4	0.28	29.2	0.61	918
M8	0.71	0.45	22.8	0.95	947	140	961	26.5	0.34	27.5	0.67	1015
M9	0.85	0.64	20.2	1.23	1041	116	1472	29.7	0.32	26.3	0.72	889
M10	1.36	0.63	20.4	1.20	1050	299	1488	31.5	0.48	23.5	0.89	1079
M11	0.27	0.25	26.5	0.71	704	81	550	Broad PSD>10	0.25	30.5	0.57	877
M12	0.59	0.51	22.1	1.01	1010	110	1140	Broad PSD>10	0.33	26.7	0.71	930
GPFNA-20	0.30	0.29	24.3	0.84	690	2	755	-	0.30	27.3	0.68	882
CLC8A9-20	0.26	0.24	22.6	0.96	500	5	626	-	0.22	26.6	0.71	620
CLC8A9-40	0.61	0.51	18.8	1.45	703	6	1381	-	0.29	26.0	0.74	784
E1C7A75-16	0.31	0.31	24.1	0.85	729	2	781	-	0.32	27.8	0.66	970
E1C7A8-24	0.34	0.33	23.4	0.90	733	9	841	-	0.33	27.0	0.69	957
E1C7A8-41	0.56	0.51	20.8	1.15	887	15	1269	-	0.33	26.2	0.73	904
E10C8A9-46	0.52	0.40	19.2	1.38	580	19	1103	-	0.33	23.8	0.87	759
PE1C8A9-20	0.17	0.12	21.5	1.07	224	7	306	2.5-7.1	0.15	26.6	0.71	423
PE1C8A9-27	0.29	0.22	21.0	1.12	393	15	553	7.6	0.22	25.2	0.78	564
PE1C8A9-36	0.52	0.38	18.8	1.46	520	32	1005	-	0.24	26.0	0.74	648