Supporting Information for

New Perspectives on Supercritical Methane Adsorption in Shales and Associated Thermodynamics

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Section 1 provides both fitting and extrapolating results of adsorption isotherms, methane density (gaseous/adsorbed phase) as a function of pressure and temperature in four different shales, and associated isosteric enthalpy and entropy shown in Figures S1 to S16.

Section 2 provides fitting parameter of 3-parameter Langmuir and SDR models for measured methane adsorption isotherms in four different shales shown in Table S1.

Section 1 Fitting and extrapolating results of adsorption isotherms, methane density (gaseous/adsorbed phase) as a function of pressure and temperature in four different shales and associated isosteric enthalpy and entropy.

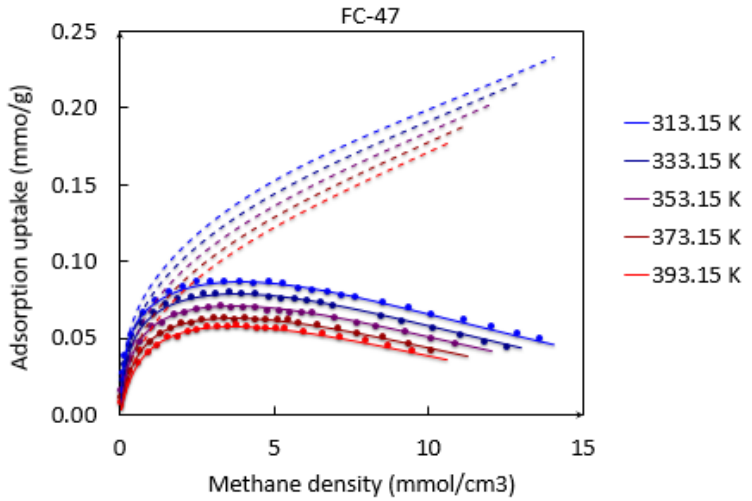

Figure S-1 Fitting and modelling results for supercritical methane in F-47 shale: dotted points represent measured data, solid lines represent fitting curve, and dotted lines represent extrapolated absolute uptake

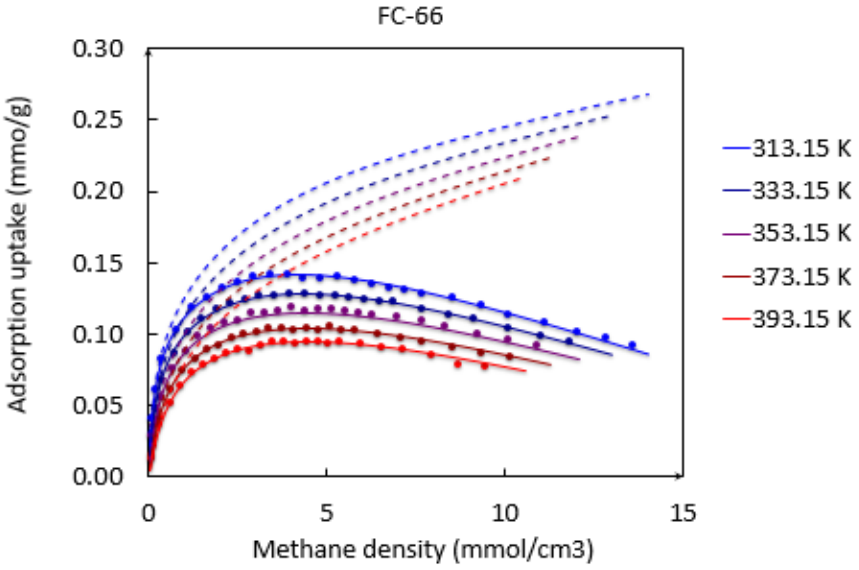

Figure S-2 Fitting and modelling results for supercritical methane in FC-66 shale: dotted points represent measured data, solid lines represent fitting curve, and dotted lines represent extrapolated absolute uptake

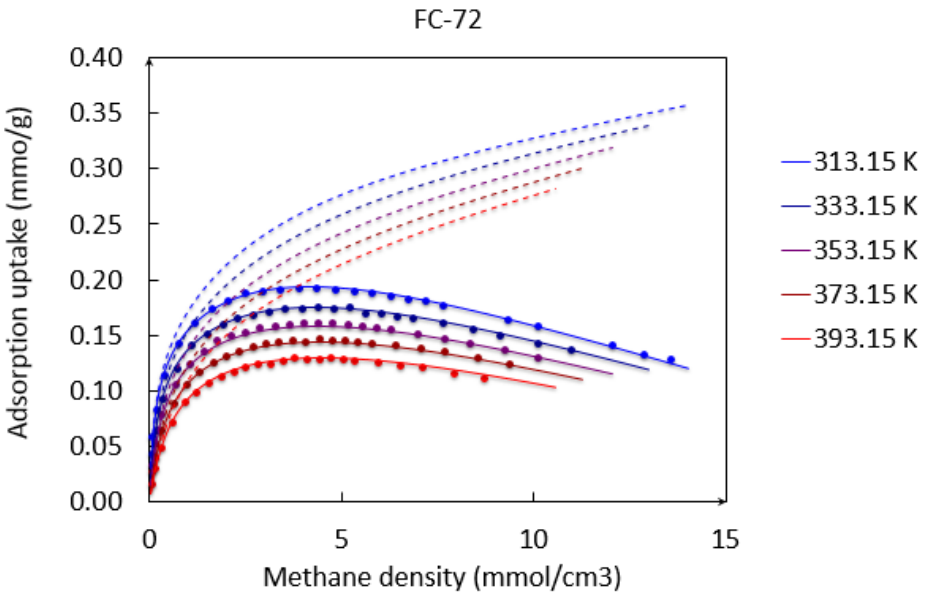

Figure S-3 Fitting and modelling results for supercritical methane in FC-72 shale: dotted points represent measured data, solid lines represent fitting curve, and dotted lines represent extrapolated absolute uptake

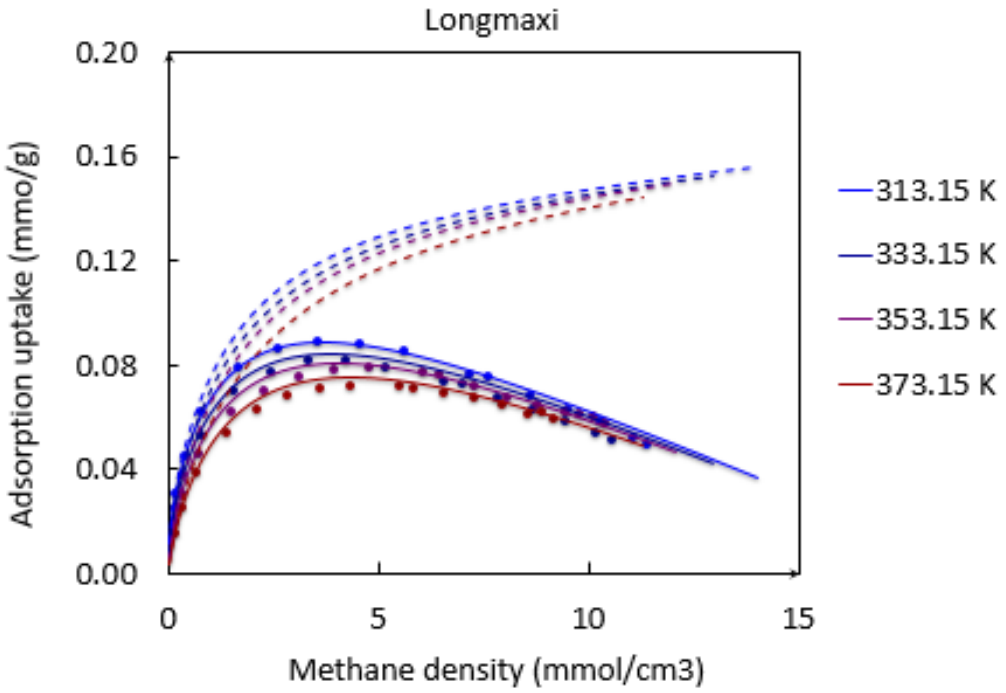

Figure S-4 Fitting and modelling results for supercritical methane in Longmaxi shale: dotted points represent measured data, solid lines represent fitting curve, and dotted lines represent extrapolated absolute uptake

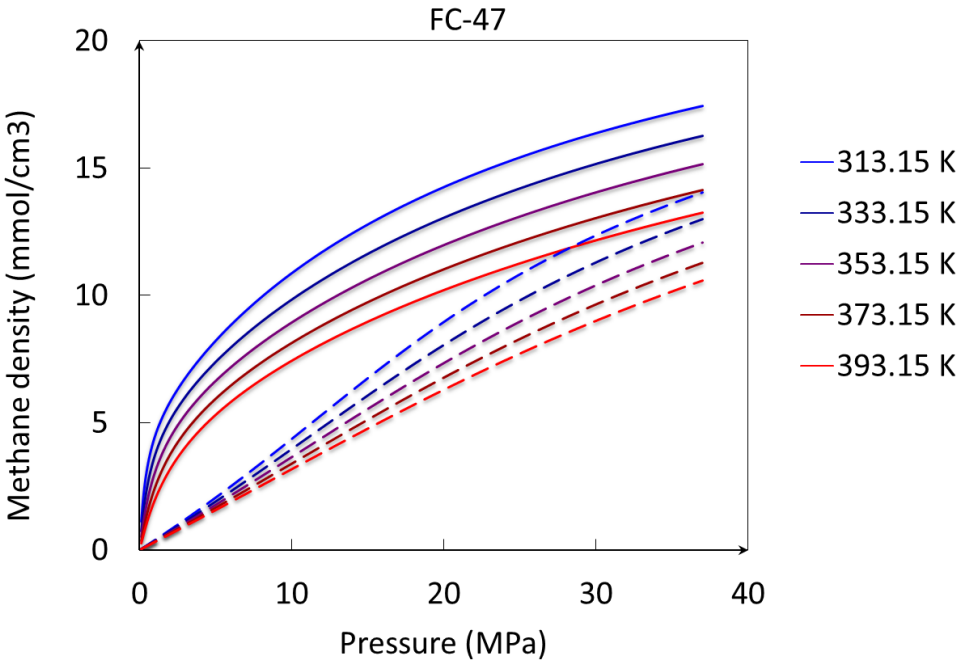

Figure S-5 Methane density (gaseous/adsorbed phase) as a function of pressure and temperature in FC-47 shales: dotted lines represent gaseous methane density, solid lines represent adsorbed methane density

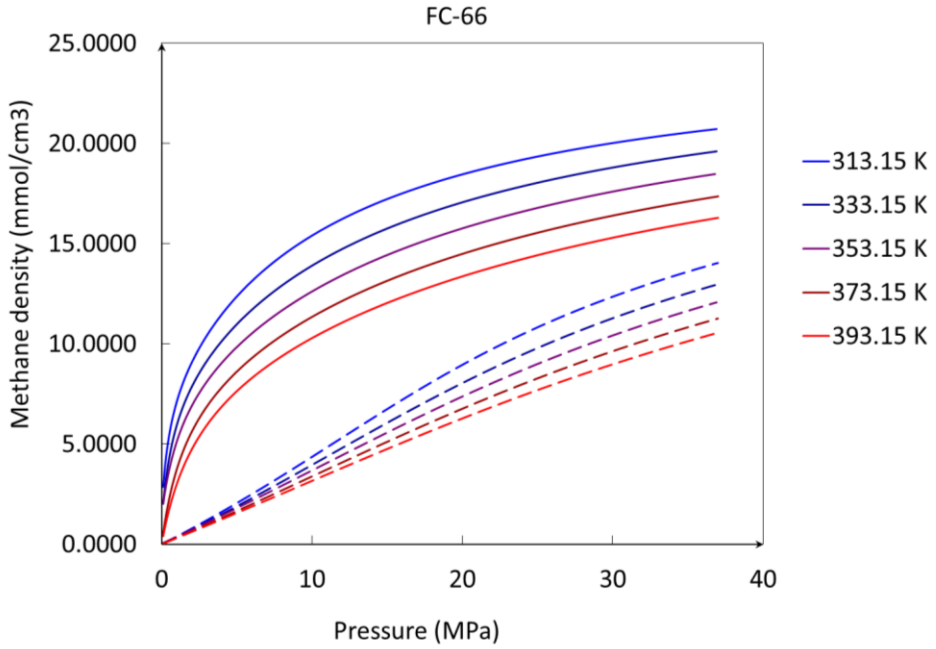

Figure S-6 Methane density (gaseous/adsorbed phase) as a function of pressure and temperature in FC-66 shales: dotted lines represent gaseous methane density, solid lines represent adsorbed methane density

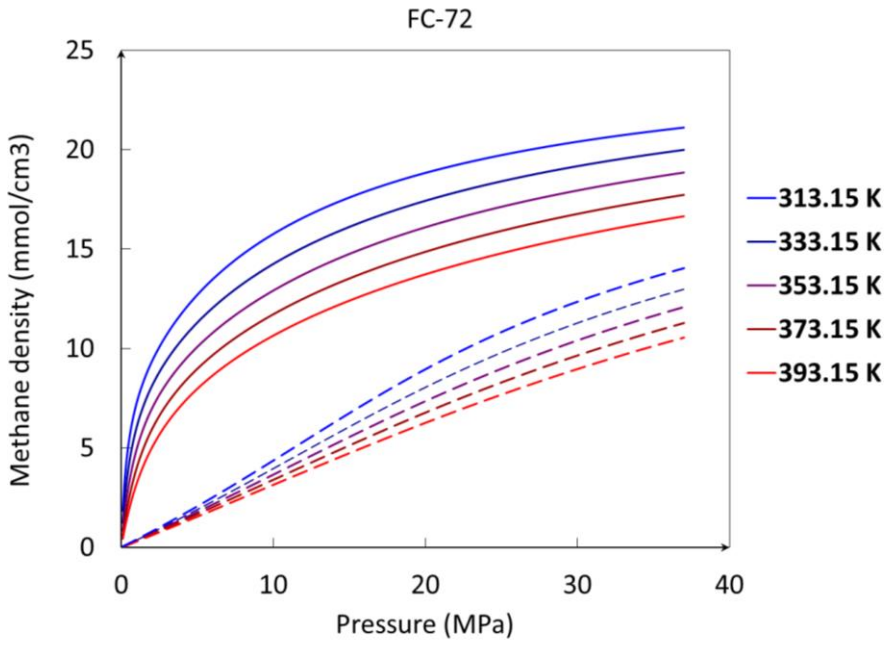

Figure S-7 Methane density (gaseous/adsorbed phase) as a function of pressure and temperature in FC-72 shales: dotted lines represent gaseous methane density, solid lines represent adsorbed methane density

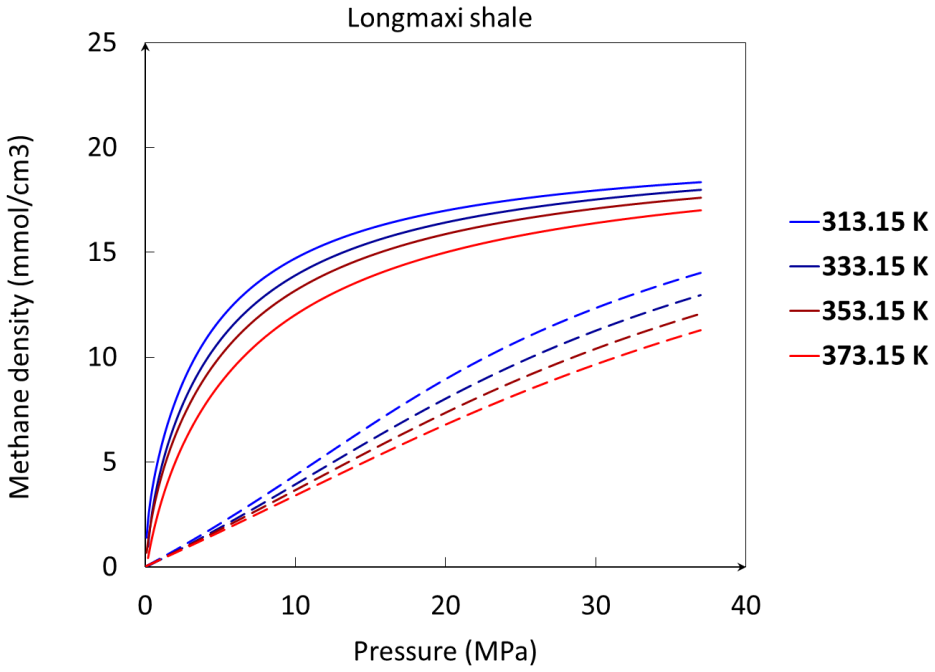

Figure S-8 Methane density (gaseous/adsorbed phase) as a function of pressure and temperature in Longmaxi shales: dotted lines represent gaseous methane density, solid lines represent adsorbed methane density

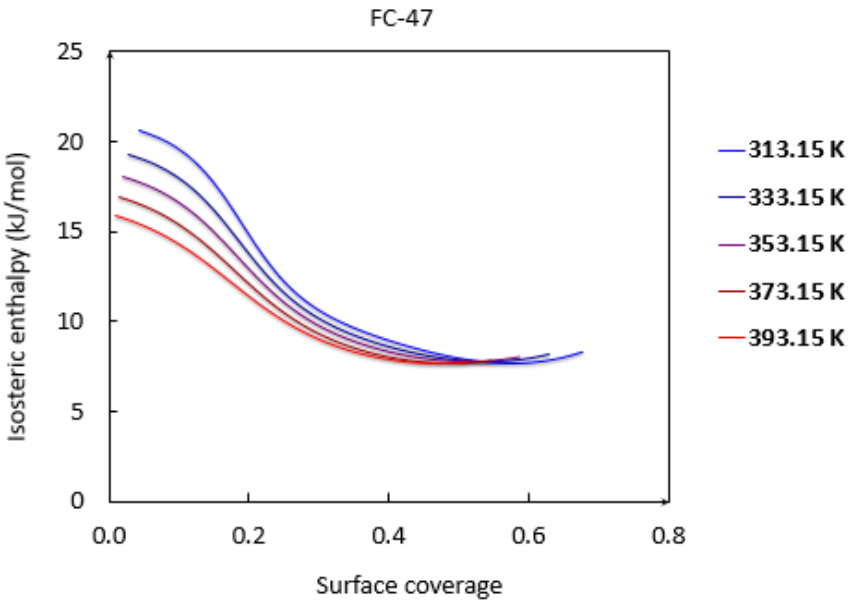

Figure S-9 Isosteric enthalpy as a function of surface coverage and temperature in FC-47 shales

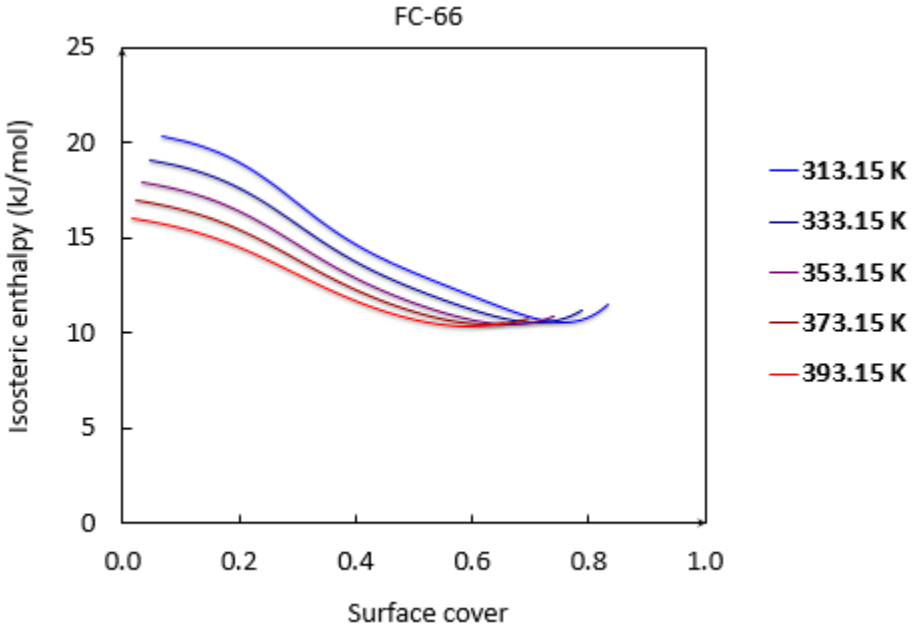

Figure S-10 Isosteric enthalpy as a function of surface coverage and temperature in FC-66 shales

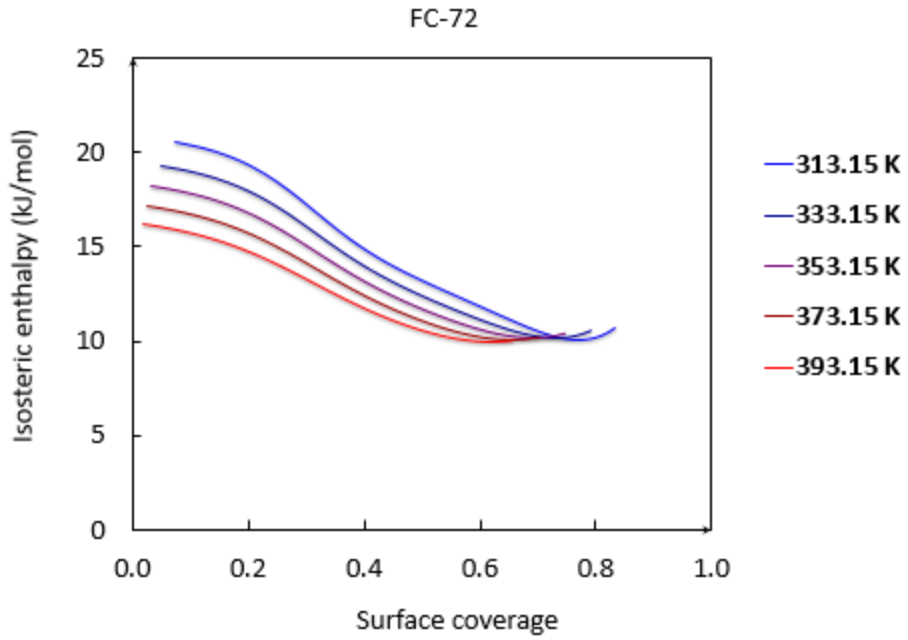

Figure S-11 Isosteric enthalpy as a function of surface coverage and temperature in FC-72 shales

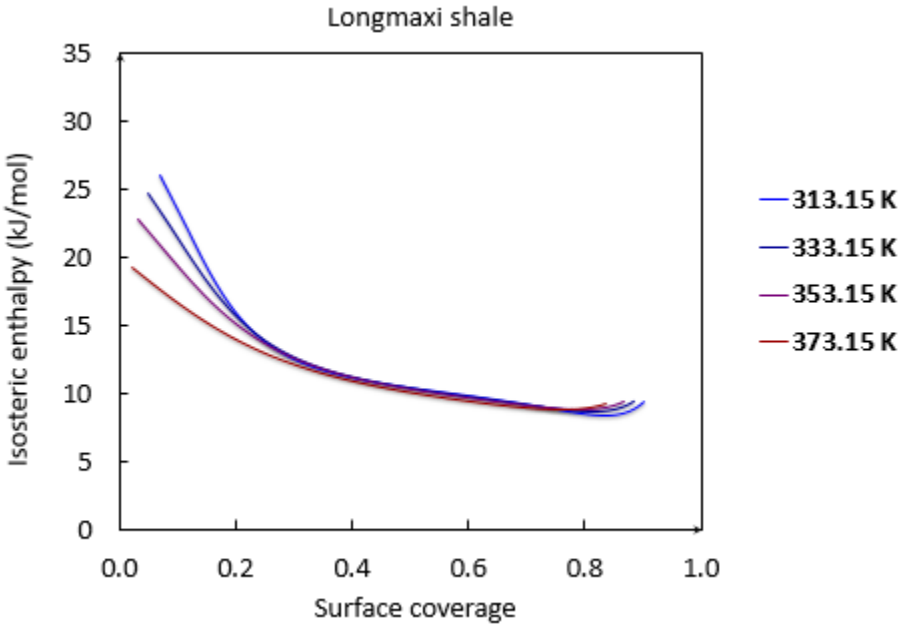

Figure S-12 Isosteric enthalpy as a function of surface coverage and temperature in Longmaxi shales

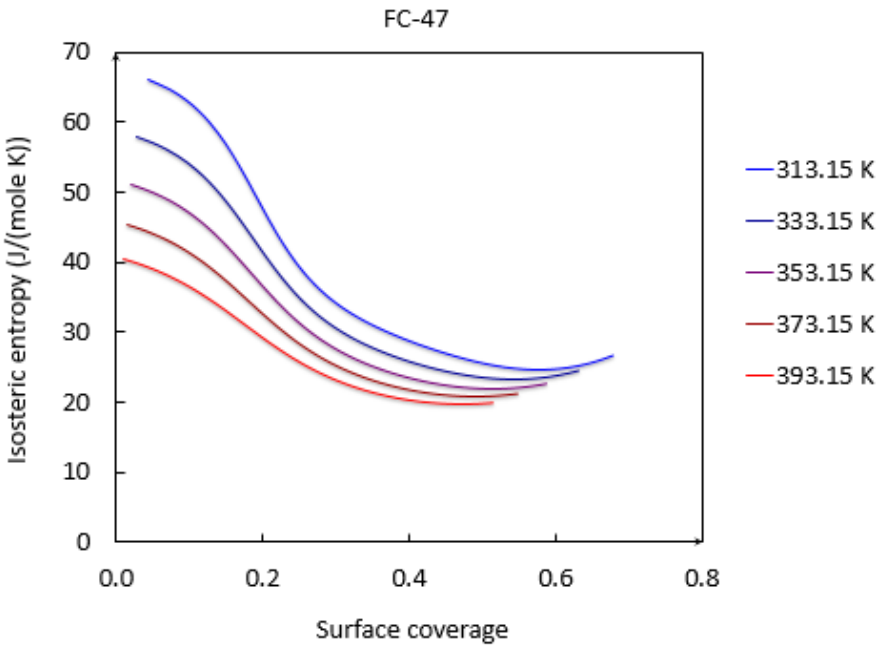

Figure S-13 Isosteric entropy as a function of surface coverage and temperature in FC-47 shales

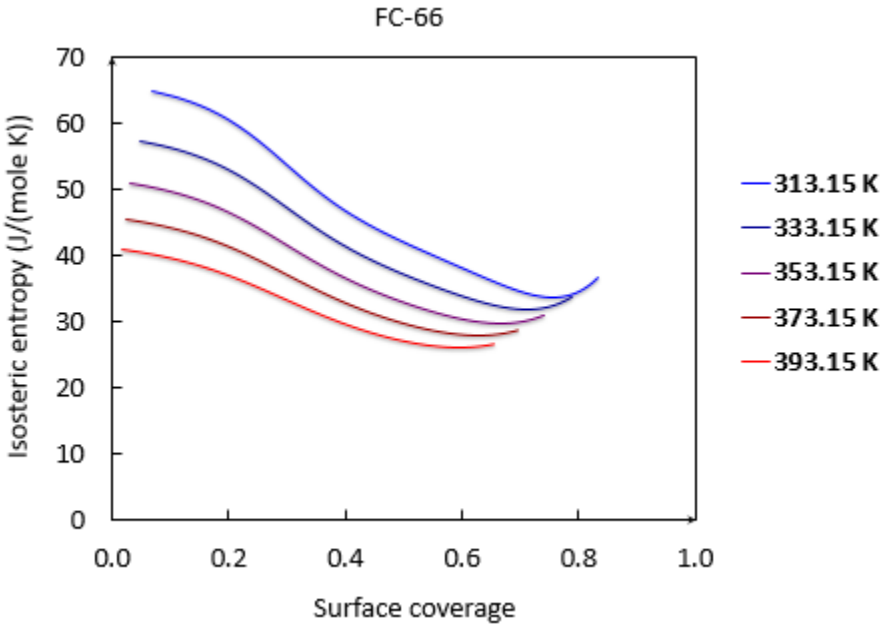

Figure S-14 Isosteric entropy as a function of surface coverage and temperature in FC-66 shales

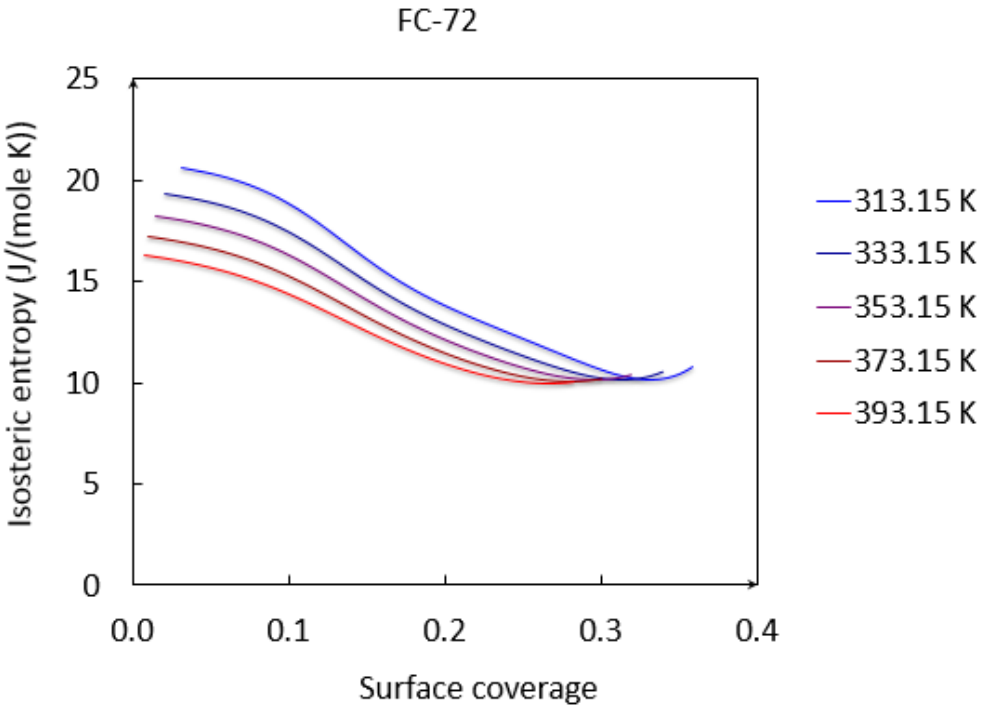

Figure S-15 Isosteric entropy as a function of surface coverage and temperature in FC-72 shales

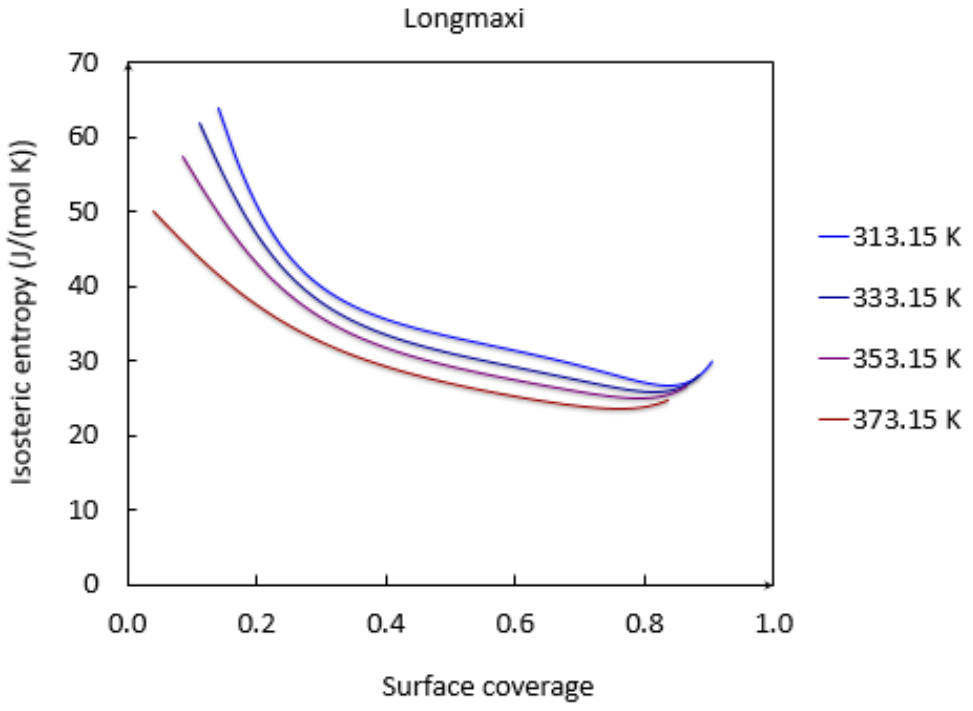

Figure S-16 Isosteric entropy as a function of surface coverage and temperature in Longmaxi shales

Section 2 Fitting parameter of 3-parameter Langmuir and SDR models for measured methane adsorption isotherms in four different shales shown in Table S1. Note, the fitting parameters for samples FC-47, FC-66 and FC-72 are originally reported in Li et al., 2017.

Table S1 Fitting parameter of 3-parameter Langmuir and SDR models for measured methane adsorption isotherms in four different shales

Sample	Tem(K)	SDR model			RMSE	Langmuir model			RMSE
		n (mmol/g)	D (mol^2/(kJ^2))	pads (mmol/cm3)		n (mmol/g)	K (1/MPa)	pads (mmol/cm3)	
FC-47	313.15	2.74	0.00731	23.00	//	2.73	0.64	24.00	//
	333.15	2.56	0.00731	20.45	//	2.52	0.62	21.45	//
	353.15	2.31	0.00731	20.20	//	2.34	0.45	21.01	//
	373.15	2.11	0.00731	19.39	//	2.17	0.35	20.32	//
	393.15	1.97	0.00731	18.89	//	2.11	0.28	18.89	//
FC-66	313.15	4.42	0.00718	25.87	//	4.41	0.59	26.87	//
	333.15	4.11	0.00718	25.31	//	4.16	0.45	26.18	//
	353.15	3.86	0.00718	24.69	//	3.84	0.39	26.25	//
	373.15	3.48	0.00718	23.50	//	3.45	0.34	25.62	//
	393.15	3.25	0.00718	21.70	//	3.34	0.27	22.57	//
FC-72	313.15	6.01	0.00700	26.56	//	5.94	0.63	27.87	//
	333.15	5.56	0.00700	25.87	//	5.44	0.51	27.68	//
	353.15	5.25	0.00700	24.13	//	5.18	0.42	26.00	//
	373.15	4.87	0.00700	23.82	//	4.74	0.36	26.68	//
	393.15	4.36	0.00700	22.44	//	4.42	0.28	23.88	//
Longmaxi	313.15	0.14	0.46645	18.90	0.0021	0.13	0.012	18.31	0.0008
	333.15	0.13	0.39184	19.09	0.0017	0.12	0.011	18.43	0.0007
	353.15	0.13	0.29655	21.53	0.0017	0.12	0.011	20.81	0.0010
	373.15	0.12	0.25475	22.76	0.0012	0.11	0.010	21.54	0.0007

Reference

Li, T., Tian, H., Xiao, X., Cheng, P., Zhou, Q., & Wei, Q. (2017). Geochemical characterization and methane adsorption capacity of overmature organic-rich Lower Cambrian shales in northeast Guizhou region, southwest China. Marine and Petroleum Geology, 86, 858-873.