Supporting Information

Abnormal Cage Occupancy of Natural Gas Hydrates in Deep Sea Floor Sediments

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Table S1. Inductively Coupled Plasma (ICP) and Energy Dispersive X-ray Fluorescence (XRF) Spectrometers of metals and some nonmetals in NGH sample (07GHP-6C).

	Al	K	Ca	Ti	Mn	Fe	Cu	Sr	Na
ppm	117.4	29.56	154.2	4.391	0.811	44.96	0.0209	1.12	7.38
%	3.846	0.968	5.0500	0.143	0.026	0.147	0.068	3.68	2.418

High resolution neutron powder diffraction (HRNPD)

The NPD patterns were determined using a high-resolution (λ= 1.8372 Å) neutron diffractometer installed at the horizontal channel ST2 of the 30MWt reactor "HANARO" of the Korea Atomic Energy Research Institute (KAERI). The resolution was variable as any of the four soller collimators with angular divergences $\alpha1$=20'. The divergence $\alpha2$=30' of the second collimator, as well as the divergence $\alpha3$=10' of the third collimator were fixed. Low-temperature neutron diffraction measurements were made using a closed cycle refrigerator (CCR) with a cooling power of 0.5 W and a Si-diode sensor installed on the neutron beam. All neutron data was modeled using the Rietveld refinement package, GSAS [1] with EXPGUI [2] interface. As a starting point we took the parameters reported by heavy ice and methane hydrate and used only the lattice constants ant thermal displacements as fit parameters [3].
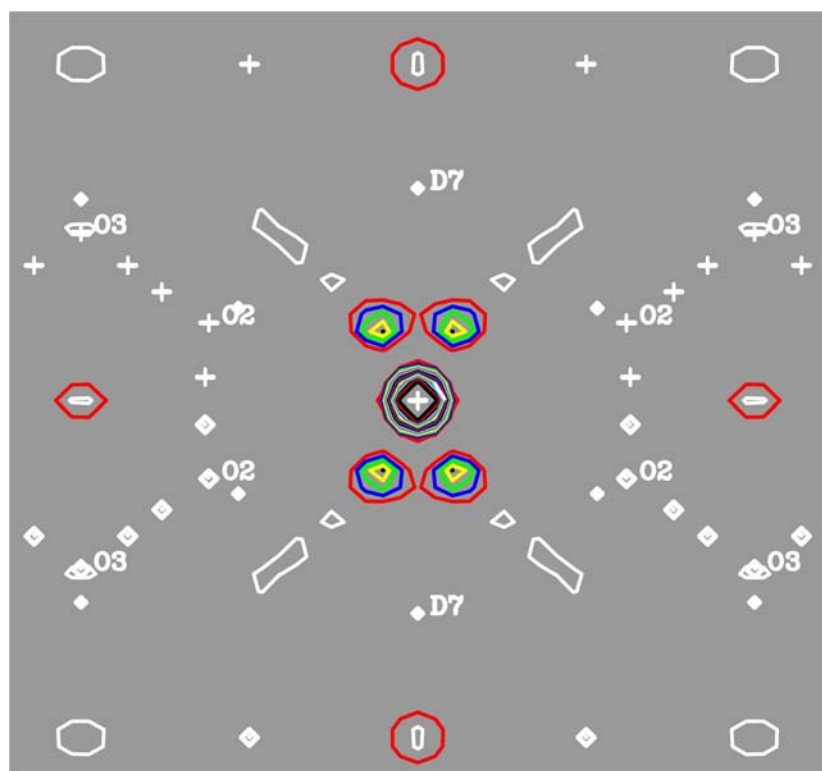
Fig. S1. Observed Fourier map of 35 wt% Na-MMT MH centered in the 5^{12} cage at (0, 0, 0). The refinement was characterized by $\chi^2 = 4.85$ and $R_{wp} = 5.45$ %.

Table S2. Rietveld refinement results for MH phase of the D_2O host lattice, CD_4 and Na guest molecules.

(35wt% Na-MMT MH at 2.7K)

| Atom	x	y	z	Occupancy	Usio
Oxygen	0.1841	0.1841	0.1841	1	0.03409
Oxygen	0.0000	0.3100	0.1154	1	0.01074
Oxygen	0.0000	0.5000	0.2500	1	0.01009
Deuterium	0.2314	0.2314	0.2314	0.5	0.51553
Deuterium	0.0000	0.4305	0.2007	0.5	0.02613
Deuterium	0.0000	0.3801	0.1614	0.5	0.06530
Deuterium	0.0000	0.3157	0.0349	0.5	0.08954
Deuterium	0.0673	0.2662	0.1373	0.5	0.06407
Deuterium	0.1177	0.2257	0.1582	0.5	0.03796
CD_4	0.25	0.5	0	1	0.45020
CD_4	0	0	0	0.55	0.0250
Na	0	0	0	0.45	0.03680
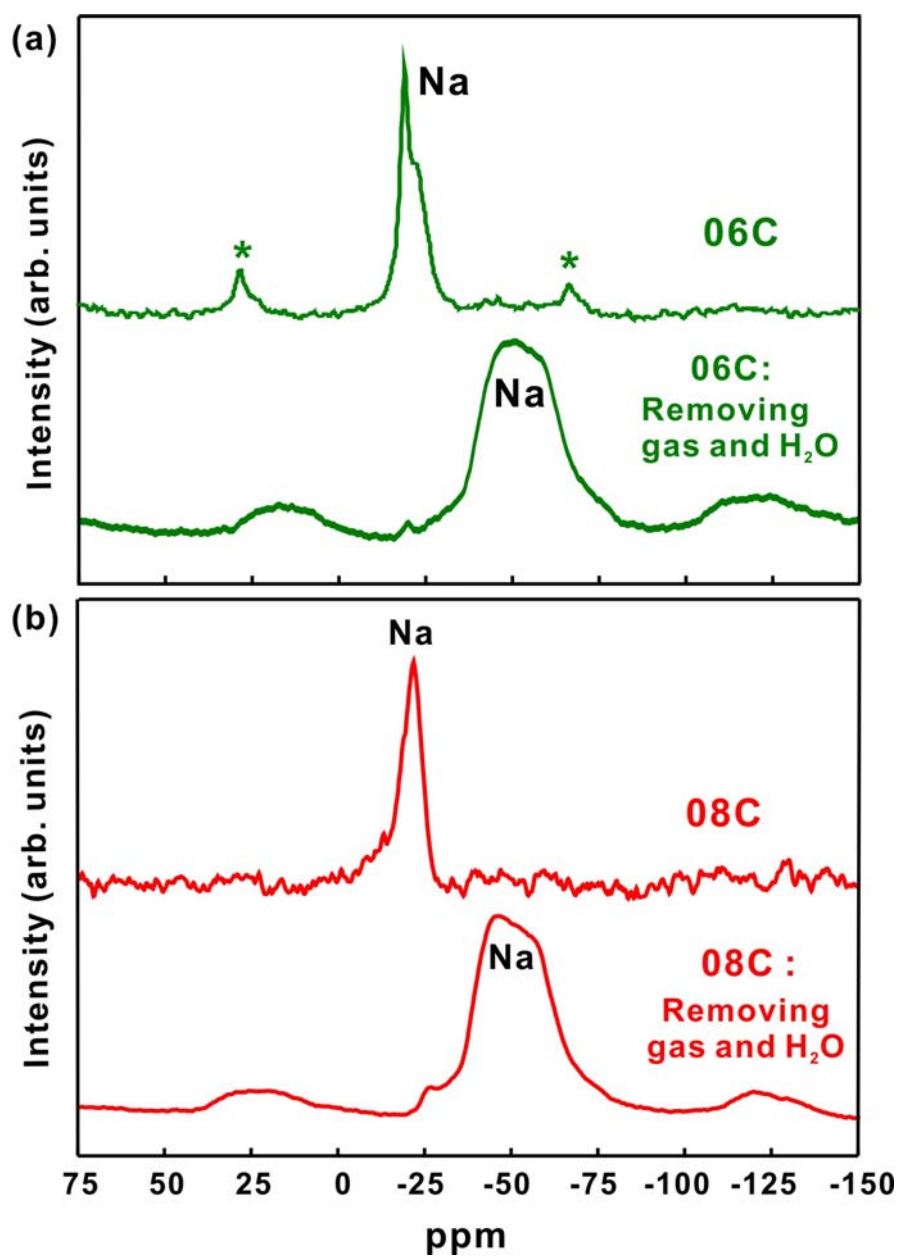
Fig. S2. ^{23}Na MAS NMR data of natural methane hydrate sample from East Sea, Korea, 06 and 08C samples. The peaks of washed and dried sediment were detected at about -50 ppm, although those of the fully swollen sediment at about -25 ppm.

References

[1] Larson A C, Dreele R B V, General Structure Analysis System (GSAS); Los Alamos National Laboratory Report LAUR 86-748 (2000)

[2] Toby B H, *J Appl Crystallogr* (2001) 34; 210.

[3] Gutt C, Asmussen B, Press W, Handa Y P, Tse J S, (2000) *J Chem Phys* 113:4713.