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## X-RAY SYNCHROTRON DIFFRACTION STUDY OF NATURAL GAS HYDRATES FROM AFRICAN MARGIN

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### Abstract:

Natural gas hydrates recovered from the Congo-Angola basin and Nigerian margins are analyzed by synchrotron X-ray powder diffraction. Biogenic methane is the most abundant gas trapped in the samples and others minor components (CO<sub>2</sub>, H<sub>2</sub>S) are co-clathrated in a type I cubic lattice structure. The refinement for the type I structure gives lattice parameters of  $a = 11.8646$  (39) Å and  $a = 11.8619$  (23) Å for specimens from Congo-Angola and Nigerian margins respectively at 90 K. These values, intermediate between the lattice constant of less pure methane specimens and pure artificial methane hydrates, indicate that lattice constants can be affected by the presence of encaged CO<sub>2</sub>, H<sub>2</sub>S and other gas molecules, even in small amounts. Thermal expansion is also presented for Congo-Angola hydrate in the temperature range 90-200 K. The coefficients are comparable with values reported for synthetic hydrates at low temperature and tend to approach thermal expansion of ice at higher temperature.

**Keywords:** natural clathrate hydrates, thermal expansion, synchrotron X-ray diffraction

## 50 1. Introduction

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Naturally occurring gas hydrates (clathrate hydrates) are ice-like inclusion solid compounds constituted of water molecules that form cages and enclose molecules of gas. Specific conditions of high pressure and low temperature are necessary to initiate the formation and stabilize the hydrate structure [Kvenvolden, 1995]. As well as they appear attractive for gas industry, natural gas hydrates can have important role in continental slope stability [Dillon *et al.*, 2001; Sultan *et al.*, 2004] or climate change [Jacobsen, 2001; Kennett *et al.*, 2000]. The knowledge of their occurrence in natural environment, their physical, chemical or thermodynamic properties are essential to prevent geohazards, to anticipate their role in climate change or to develop technologies to take advantage of this energetic resource. When intact gas hydrates can not be directly recovered by coring, the knowledge of hydrate occurrence is obtained from indirect geophysical and geochemical methods, i.e. from the quantity and nature of the gaseous decomposition products [Sassen and MacDonald, 1994] or hypothetical models [Hyndman *et al.*, 1999]. However, natural intact gas hydrates characterizations of their structure and thermal properties are of essential importance to confirm and improve such models. The molecular-scale knowledge is thus fundamental to increase understanding of hydrates at all levels. To date, only 26 sites could be sampled due to the technological difficulties to collect intact natural samples (undecomposed) [Kvenvolden, 1999; Milkov, 2005]. Recent studies have plentifully detailed the molecular and isotopic composition of the main hydrate-bound gases [Milkov, 2005] but only few physical characterizations have been conducted on recovered samples. It concerns hydrates from Gulf of Mexico [Davidson *et al.*, 1986; Yousuf *et al.*, 2004], Black Ridge [Uchida *et al.*, 1999], Mallik [Tulk *et al.*, 2000], Northeast Pacific continental margin off Oregon [Gutt *et al.*, 1999], Cascadia Margin [Yousuf *et al.*, 2004], Okhotsk sea [Takeya *et al.*, 2006], offshore Vancouver Island [Lu *et al.*, 2005] and from the Congo-Angola basin [Charlou *et al.*, 2004]. We focused recently on the physical characterization of samples from the Congo-Angola basin, the Nigerian and the Norwegian margins by detailed Raman analysis [Chazallon *et al.*, 2007]. In the present work, we extend this study on the structural property of the specimens from African margins using synchrotron X-ray diffraction measurements. Gas hydrates from the Congo-Angola margin were collected from a deep isolated pockmark (800-1000 m in diameter) during the ZAI-ROV cruise in December 2000 (ZAIANGO IFREMER/TOTAL-FINA-ELF program). The methane trapped in the hydrate structure originates from microbial CO<sub>2</sub> reduction [Charlou *et al.*, 2004]. Other natural specimens studied were retrieved in sediment cores during the NERIS II cruise (2004) in the deep province of the Niger Delta (Gulf of Guinea, West African margin) characterized by the presence of numerous pockmarks. Previous natural samples recovered by cores in these area were found in clay-rich sediments and considered as biogenic in nature with some thermogenic contribution [Brooks *et al.*, 1994; Brooks *et al.*, 1999; Cuningham and Lindolm, 2000]. Samples collected during NERIS II cruise are shown to be almost pure because there is nearly no thermogenic contribution. Only very weak signals of CO<sub>2</sub> can be detected in NERIS II samples by Raman. Because knowledge of the structure and thermal properties is of practical importance for a better understanding of natural gas hydrates occurrence, we focused this work on an original and detailed structural investigation using synchrotron X-ray diffraction measurements on ZaiAingo and NERIS II hydrate specimens.

## 95 2. Methods and material

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Gas hydrates from the Congo-Angola basin (ZaiAngo cruise) were collected at 3160 m water depth in a 12 m long sediment core [Charlou *et al.*, 2004] whereas specimens from the Nigerian margin (NERIS II cruise) were retrieved between 1147 and 1203 m water depth in a 7 m long core [Bayon *et al.*, 2007]. ZaiAingo specimens originated from deeper sediment sections at higher pressure compared to NERIS II hydrates. The recovered pieces were first stored at 190 K on board before being shipped to France where they are now preserved from decomposition in liquid nitrogen.

The natural gas hydrates are analyzed using synchrotron X-ray high-resolution powder diffraction recorded on beamline ID31 [Fitch, 2004] at the ESRF (European Synchrotron Radiation Facility) in Grenoble (France). The synchrotron light produced at the ESRF consists largely of very bright and intense X-rays. Incident beam size on the sample at ID31 is typically of 1.5 mm x 1.5 mm. The set-up allows obtaining high quality powder diffraction patterns with high signal/noise ratio, the

combination of narrow peaks, accurate positions and intensities. The typical resolution is  $\Delta d/d \sim 10^{-4}$ . White parcels of gas hydrates are inserted at low temperature in pure silica capillaries tubes suitable for adaptation onto the ID31 diffractometer and maintained at  $\sim 90$  K by a cold nitrogen gas blower. Under such cold temperatures physical (structure) and chemical properties of gas hydrates are preserved and their thermal properties can be studied under controlled conditions. The capillaries containing the samples are mounted horizontally with a spin speed set to  $\sim 60$  Hz. The experiments are conducted at wavelength  $\lambda = 0.8002$  Å in the  $1^\circ < 2\theta < 80^\circ$  range. Data are collected in continuous motion and rebinned in  $2\theta$  step of  $0.005^\circ$ . They are analyzed with the Rietveld technique [Rietveld, 1969] using GSAS software [Larson and Von Dreele, 1994].

### 3. Results and discussion

Figure 1 shows a representative pattern of the ZaiAngo specimen collected from the Congo-Angola margin.

All the reflections are indexed in the full-pattern structure refinement, with two independent phases: ice Ih and type I cubic clathrate lattice. Ice Ih is hexagonal with the space group  $P6_3/mmc$ . The structure I (with S.G.  $Pm\bar{3}n$ , sl) is the most common structure adopted by natural gas hydrates [Kvenvolden *et al.*, 1988; Sloan, 1998; Milkov and Sassen, 2001]. It consists in a body-centered cubic structure containing small gas molecules ( $4.2$  Å  $< d < 5.8$  Å). The unit cell consists of 46 water molecules (host) arranged in two pentagonal-dodecahedral D ( $5^{12}$ , a 12-faces polyhedron constituted by regular pentagons) and six tetrakaidecahedral T ( $5^{12}6^2$ , a 14-faces polyhedron having 12 regular pentagons and 2 regular hexagons) cavities. The guest molecules are statistically distributed among the different cages. In the refinement, both D and T cavities have been filled with one  $CH_4$  molecule per cage.

Five samples collected from the Congo-Angola margin and three from the Nigerian margin are investigated at 90 K. Table 1 reports the refined lattice parameter of sl. As observed in previous structural work on natural hydrates [Takeya *et al.*, 2006], ice is found in a relatively large amount in all samples (varying from  $\sim 74$  % to  $\sim 98$  %). Similarly, Bohrmann *et al.* [2007] performed a detailed study on the preservation of gas hydrates collected at Hydrate Ridge. The amount of ice Ih in their samples was comparable with values reported in our work and varied between 32 and 98 %, with 83 % as a nominal average. It is suggested that ice forms during the recovery when the hydrates are outside their p-T stability field. It may also originate from seawater that is generally attached to the gas hydrates and converts in ice when using liquid nitrogen for sample preservation. For these reasons, it is difficult to determine the exact amount of ice present on the original sample.

In figure 2, the lattice constants ( $a$ ) of ZaiAngo and NERIS II samples are displayed at 90 K. We can note a dispersion of  $a$  at 90 K ( $\sim 0.08$  % of the lattice size) for hydrate specimens from identical location (table 1, figure 2), with an average of  $a = 11.8646$  (39) Å and  $a = 11.8619$  (23) Å for ZaiAngo and NERIS samples respectively. The errors correspond to the standard deviation from the mean values. Our reported lattice constants ( $a$ ) are comparable with those obtained for sl hydrate from Cascadia margin in Pacific [Yousuf *et al.*, 2004], Okhotsk Sea [Takeya *et al.*, 2006] and synthetic methane hydrates [Kirchner *et al.*, 2004, Ogienko *et al.*, 2006]. The lattice parameters of synthetic pure methane hydrates [Kirchner *et al.*, 2004; Ogienko *et al.*, 2006, Takeya *et al.*, 2006] are typically found within  $0.02$  Å of the natural hydrates studied here. Further, the lattice parameters reported for sl hydrate from Cascadia margin at 85 K [Yousuf *et al.*, 2004] are larger than the one found in the present work, whereas those reported from Okhotsk Sea are slightly smaller or equivalent.

All the natural specimens are characterized by the mixing of methane with small amount of  $H_2S$ ,  $CO_2$  and other non-methane gases. Although not directly measured, the hydrate reported by Yousuf *et al.* [2004] is likely to contain only 97.4 %  $CH_4$  mixed with  $H_2S$  (2.6 %), and traces like  $CO_2$ ,  $C_2H_6$  or  $C_3H_8$ , whereas the ZaiAngo specimens contain 99.1 %  $CH_4$  and 0.8 %  $CO_2$  [Charlou *et al.*, 2004]. The specimens from Okhotsk Sea typically contain predominantly methane, between 1.7 % and 3.4 %  $CO_2$  and traces of  $H_2S$ . Moreover, the variations of  $a$  ( $\sim 0.01$  Å and  $\sim 0.002$  Å) observed on different areas of the same natural hydrates (ZaiAngo and NERIS II, respectively) have comparatively been reported on natural specimens from Okhotsk Sea collected at different place in the core [Takeya, personal communication]. The reasons for these variations are not clear, however the slight changes of composition and gas content which occur within each hydrate due to heterogeneousness of the samples [Chazallon *et al.*, 2007] may well influence the size of the lattice. Alternatively, we can not completely exclude some imperfections in the powder that may slightly alter the refined lattice parameters from sample to sample.

Our specimens present greater compositional similarities with the specimens recovered from Okhotsk Sea or synthetic CH<sub>4</sub>-hydrates. *Takeya et al.* [2005a] studied the lattice expansion of CH<sub>4</sub> + CO<sub>2</sub> and CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> hydrates as a function of mixed-gas composition. They showed that the lattice constant of CH<sub>4</sub> + CO<sub>2</sub> hydrates are independent of the relative gas composition (CH<sub>4</sub>/CO<sub>2</sub> ratio). The situation seems different in H<sub>2</sub>S + CH<sub>4</sub> mixtures. The substantial difference observed by *Yousuf et al.* [2004] in comparison to other natural specimens or synthetic pure methane hydrate may be due to the presence in greater amount of H<sub>2</sub>S in their samples. Independently of guest size considerations, specific guest-guest and guest-host interactions in mixed H<sub>2</sub>S/CH<sub>4</sub> hydrates may well contribute to such effect. This assumption is corroborated by molecular dynamic calculations which suggested that the nature of the guests may play an important role on clathrate lattice dimension [*Zelev et al.*, 1999]. High resolution diffraction work using synthetic mixed hydrates of different CH<sub>4</sub>/H<sub>2</sub>S ratios will be necessary to confirm clearly this point. The lattice constants of NERIS II samples are less dispersed than those of ZaiAngo samples and they are slightly lower in average. This could corroborate a higher methane purity for NERIS II samples. Furthermore, extra components are found on the diffraction pattern corresponding to NERIS II samples. They can be identified as being due to the presence of quartz, calcite and pyrite. These minerals are typical from sediments hosting the hydrates in these natural environments [*Charlou et al.*, 2004].

In figure 2 and table 2, we report measurements of the lattice constant of ZaiAngo hydrates as a function of temperature in the range 90-200 K. It is compared with the thermal evolution of the lattice expansion curves of synthetic CH<sub>4</sub>-hydrates [*Ogienko et al.*, 2006], and that of natural hydrates from Okhotsk Sea [*Takeya et al.*, 2006]. The evolution of the lattice constant with temperature  $a(T)$  is fitted to the following function from 90 to 200 K:

$$a(T) = 11.83625 (17) + 3.055 (23) \times 10^{-4} T + 7.085(81) \times 10^{-7} T^2 (\text{\AA})$$

The correlation coefficient for the fit is 0.99901. From this equation, the experimental coefficients of thermal expansion of ZaiAngo hydrate (table 2) are calculated from:  $\alpha_a = \frac{1}{a(T)} \frac{da}{dT}$ .

They are found in reasonable agreement with those obtained from synthetic pure methane hydrate (see table 2), especially at low temperature. Thermal expansion values obtained for ZaiAngo specimens are significantly larger than those reported for ice at the corresponding temperatures between 100 K and 200 K. This corroborates the fact that the thermal expansivity of hydrates is dominated by the intermolecular interactions between guest molecules and the water lattice. Further, the differences between ice and natural hydrate expansivities tend to reduce as temperature rises. This view is consistent with a less restricted motion of the guest molecules at temperature close to dissociation (~ 193 K) and a reduction of the intermolecular interactions guest-water. The hydrate thermal expansion is thus largely determined by the vibrations of the water molecules at high temperature and is not very different from ice [*Tse et al.*, 1987]. Additional experimental support for this effect has been reported for synthetic methane hydrates. A reduction of the hydrate lattice expansion takes place above the hydrate decomposition temperature (~ 193 K) [*Shpakov et al.*, 1998]. This phenomenon may be related to a self-preservation effect of the crystalline hydrates beyond the dissociation temperature [*Shpakov et al.*, 1998]. The somewhat larger discrepancies observed at 200 K for expansivities of CH<sub>4</sub>-hydrates (Table 2) may reflect a crystallite size effect on the self preservation [*Takeya et al.*, 2005b]. The driving force for the dissociation rate being governed by the slow diffusion of CH<sub>4</sub> through the ice layers, the decomposition of hydrates will take place at different temperatures under non-equilibrium conditions. This may affect the thermal expansion if equilibrium is not reached in powders containing a grain size distribution.

On the other hand, differences of  $\alpha_a$  between natural and synthetic hydrates is much more pronounced at higher temperature. Whether this effect is specific to natural hydrates containing mixed gas components or rather results from uncertainties due to the important dissociation of ZaiAngo hydrate above ~ 190 K, or even a grain size dependent self preservation effect, remains to be clarified.

Inversely, at lower temperature, the amplitude of the methane motions in the sl cages tend to decrease and the interaction with water is increased substantially due to the existence of local minima in the cage [*Tse et al.*, 1987]. This results in a perturbation of the vibrational motions of the water molecules that may experience a large anharmonic potential, and thus a large thermal expansivity [*Tanaka et al.*, 1997]. A further difference from ice would therefore be expected for natural samples containing aspherical guest molecules in high proportion that may contribute to higher anharmonicity in the crystal.

## Summary

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225 The crystal structure and thermal properties of natural gas hydrates from the African margin  
were analyzed by synchrotron X-ray powder diffraction. The studied samples, essentially composed of  
biogenic methane exhibit a type I cubic lattice structure. The average lattice constant of specimens  
230 from Congo-Angola basin and Nigerian margin at 90 K are  $a = 11.8646$  (39) Å and  $a = 11.8619$  (23) Å  
respectively. The difference between lattice constants for natural hydrates and literature data reported  
for synthetic hydrates is suggested to arise from the presence of other non methane gases in small  
proportion.

235 Thermal expansion coefficients for ZaiAngo specimen are calculated at 100 K, 150 K and 200 K.  
They are found in good agreement with thermal expansion reported for synthetic gas hydrates,  
especially at low temperature. Deviation at higher temperature needs further investigations on mixed  
clathrate system with higher hydrate content or better powder statistics. The values reported in this  
study confirm that the thermal expansivity of hydrate is significantly larger than that of hexagonal ice.  
240 This difference is shown to decrease as the temperature increases, which corroborates a less  
restricted vibrational motion of the enclathrated guests. The thermal expansivity of hydrate is thus  
dominated by the water vibrations and tends to approach ice thermal expansivity upon hydrate  
dissociation. At lower temperature, the hydrate thermal expansion is larger than that of ice due to the  
anharmonic perturbation experienced by water molecules in interaction with the guests.

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Location	Samples	$a_{sl\ hydrate}$ (Å)	WRp
<i>ZaiAngo (Congo-Angola basin)</i>	ZA_05	11.860361 (30)	0.0538
	ZA_06kin	11.874836 (44)	0.0589
	ZA_10	11.868950 (47)	0.0486
	ZA_12kin	11.869680 (54)	0.0504
	ZA_16	11.862469 (34)	0.0486
	ZA_18	11.861779 (34)	0.0577
<i>NERIS II (Nigerian margin)</i>	NE_06	11.860048 (203)	0.0488
	NE_09	11.864455 (70)	0.0513
	NE_11	11.861375 (52)	0.0529

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**Table 1.** Lattice parameters of sl hydrates for five ZaiAngo and three NERIS II samples obtained at atmospheric pressure and 90 K, except for ZA\_06kin parameters obtained at 100 K. In the refinement, the lattice parameters of hexagonal ice are fixed at  $a = 4.496385$  Å and  $c = 7.32010$  Å at 90 K [Röttger *et al.*, 1994]. Errors in parenthesis correspond to two estimated standard deviation, as calculated by GSAS.

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		T (K)			
		100	150	200	
CH <sub>4</sub> -hydrate ZA_06kin	This work	a	37.6	43.5	49.4
Synthetic CH <sub>4</sub> -hydrate	<i>Ogienko et al.</i>	a	32.2	53	73.5
Synthetic CH <sub>4</sub> -hydrate	<i>Shpakov et al.</i>	a	34.7	49.6	64.5
Pure ice Ih	<i>Rottger et al.</i>	a	11.9	25.0	38.1
	<i>Rottger et al.</i>	c	12.9	25.5	38.2

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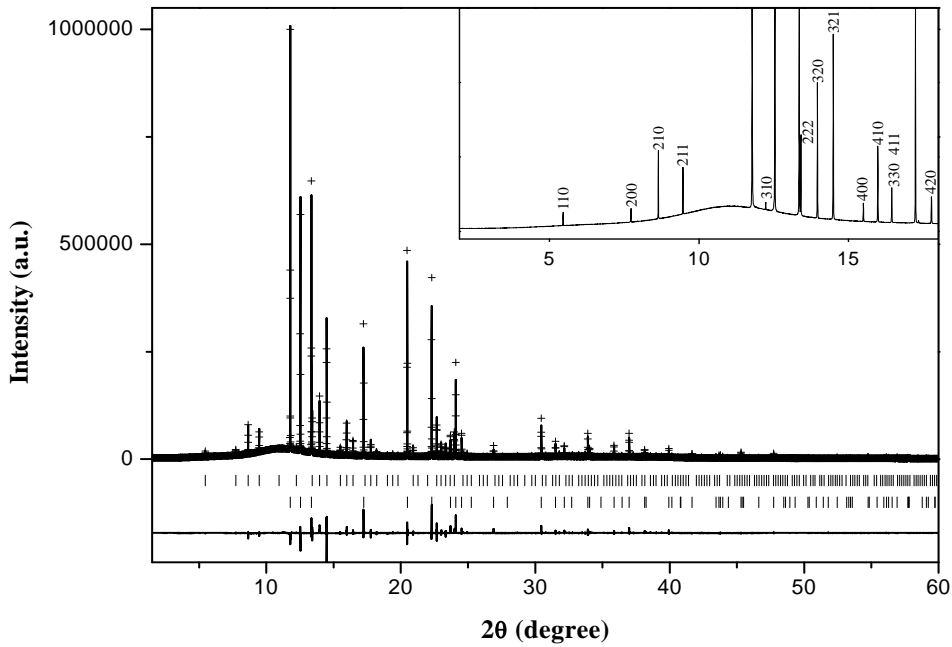
**Table 2.** Coefficient of thermal expansion ( $K^{-1}$ ,  $\times 10^{-6}$ ) for gas hydrates and ice Ih [Röttger *et al.*, 1994] at 100, 150 and 200 K. Thermal expansion coefficients for natural gas hydrate (this work) are compared with those obtained for synthetic gas hydrates [Ogienko *et al.*, 2006; Shpakov *et al.*, 1998].

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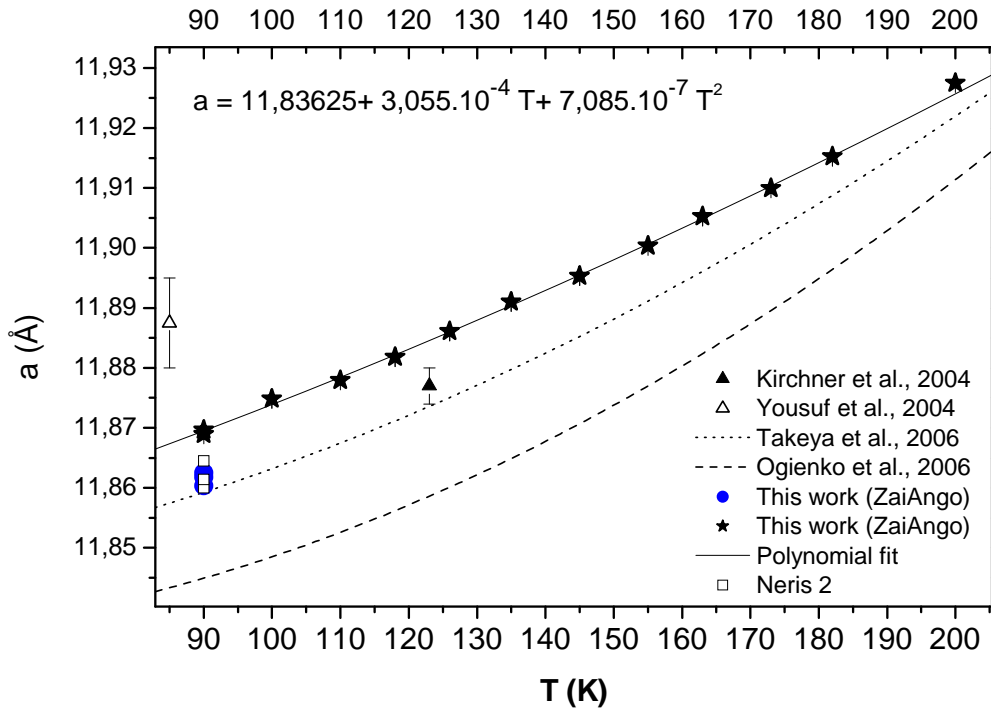
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435 **Figure 1:** X-ray diffraction profile of ZaiAngo sample collected at 90 K. The lower line corresponds to the difference between observed (plus signs) and calculated profiles. The upper tick marks indicate the reflection positions for the type I hydrate and the lower tick marks indicate the peak positions for hexagonal ice. The insert shows the enlarged portion of profile with Miller index of first diffraction peaks corresponding to type I hydrate.



440 **Figure 2:** Lattice expansion as a function of temperature for natural hydrates and pure synthetic methane hydrates. Lattice constants of ZaiAngo and NERIS II samples are compared with parameters of natural samples from Cascadia margin [Yousuf *et al.*, 2004], the Sea of Okhotsk [Takeya *et al.*, 2006] and with synthetic hydrates [Kirchner *et al.*, 2004; Ogienko *et al.*, 2006].

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