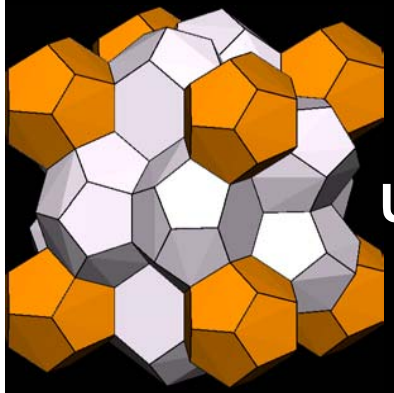
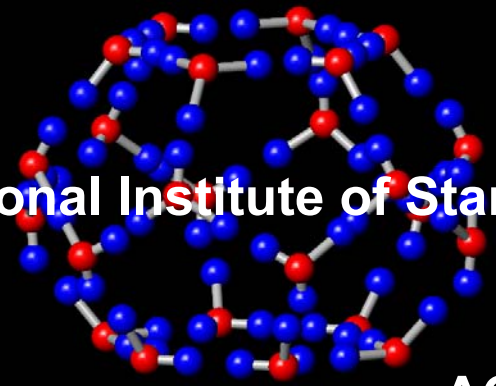
Physical and Thermodynamic Properties of Gas Clathrate Hydrates Determined by In Situ Neutron Scattering

B.C. Chakoumakos, C.J. Rawn, A.J. Rondinone,, S.L. Marshall
Oak Ridge National Laboratory, Oak Ridge, Tennessee



L.A. Stern, S.H. Kirby, S. Circone
U.S. Geological Survey, Menlo Park, California

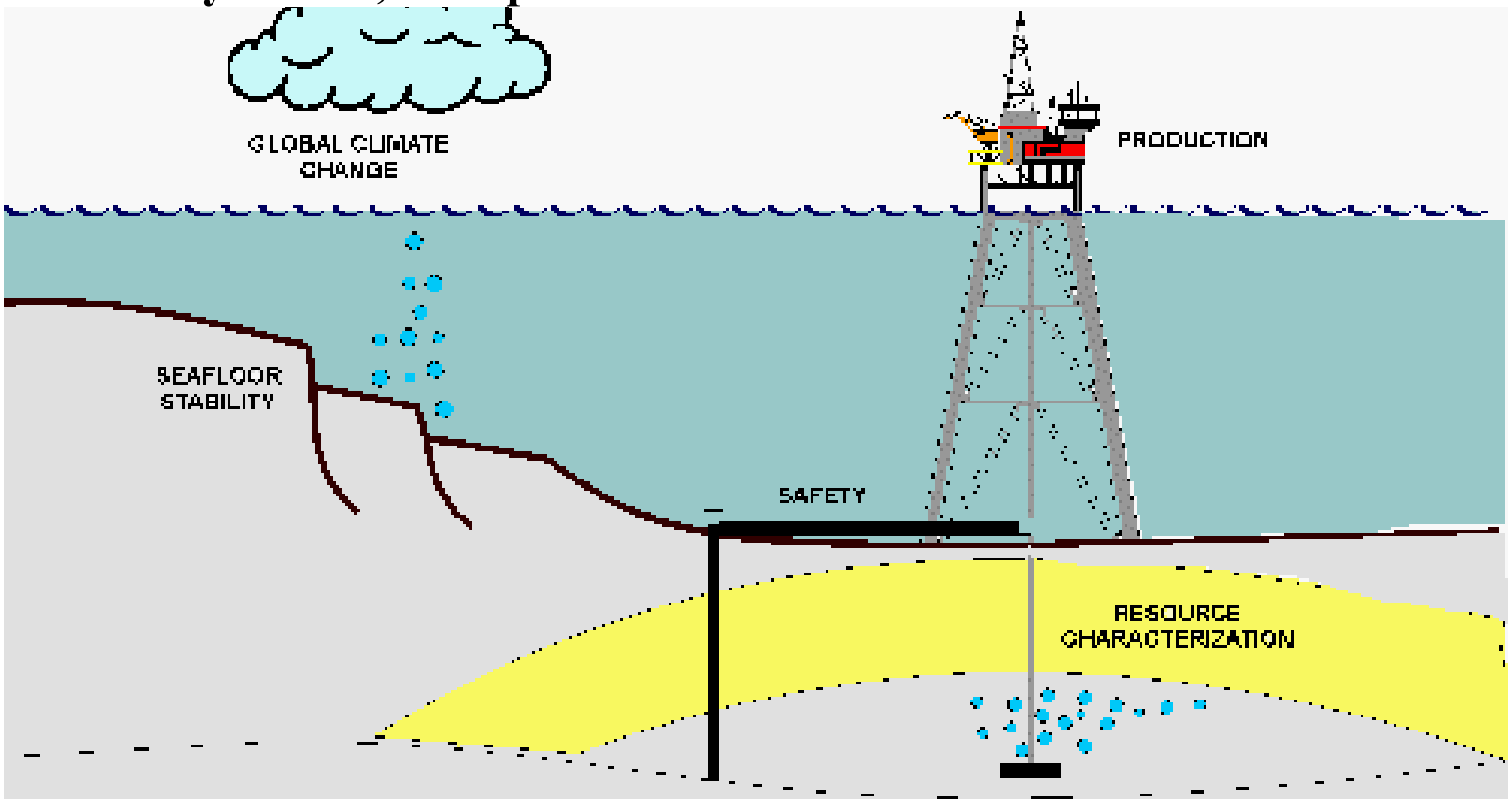
Yoshinobu Ishii
Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan

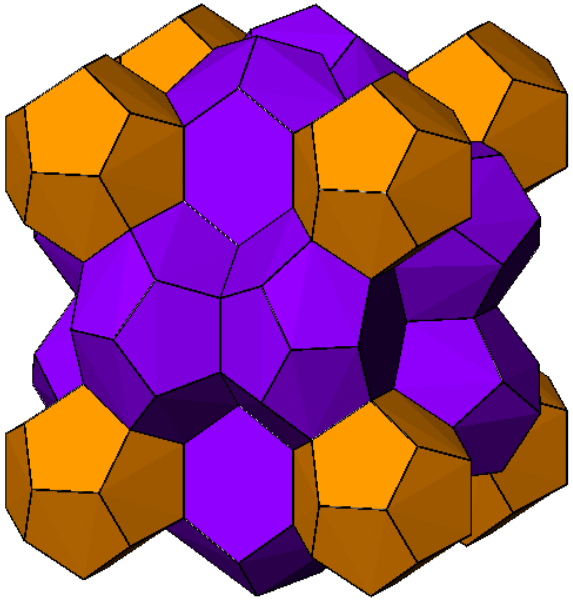


C.Y. Jones, B.H. Toby
National Institute of Standards & Technology, Gaithersburg, Maryland

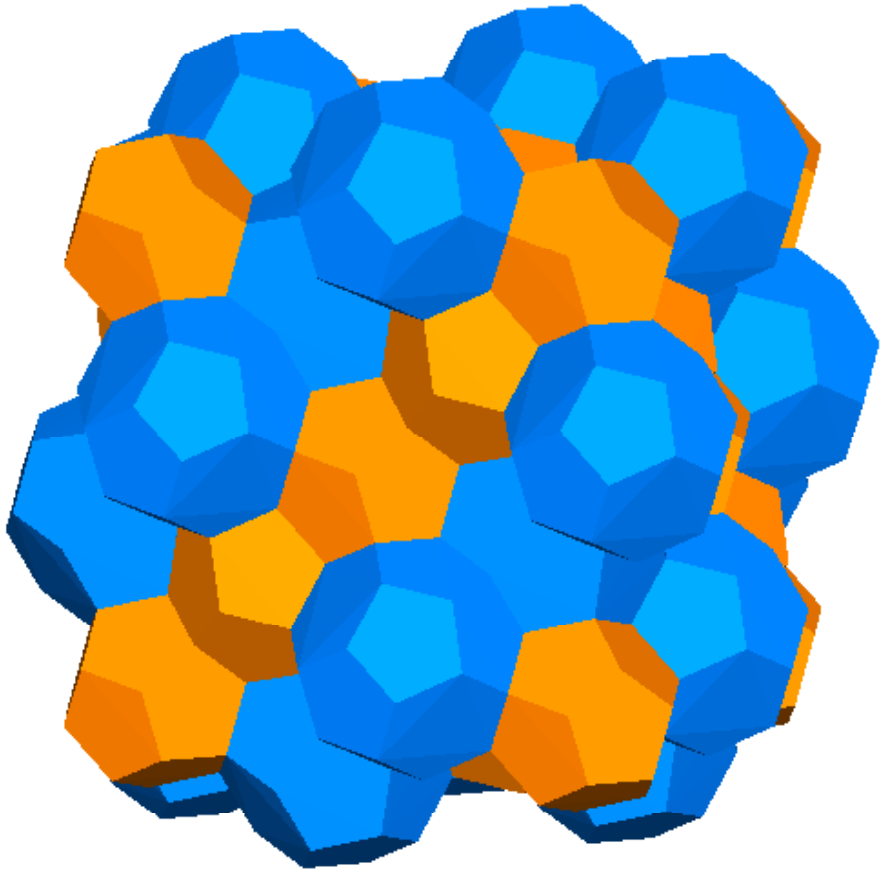
ACNS, Knoxville, June 25, 2002

- **Development of methane hydrate as a fossil fuel**
- **Understanding global carbon cycle and climate change**
- **Plugging of oil pipelines**
- **Carbon dioxide sequestration on seafloor**
- **Seafloor stability & safety of ocean drilling platforms**
- **Understanding composition and structure of icy planetary bodies**
- **New technologies, methane storage & transport medium, desalination of sea water, chemical synthesis, nanoparticle formation**





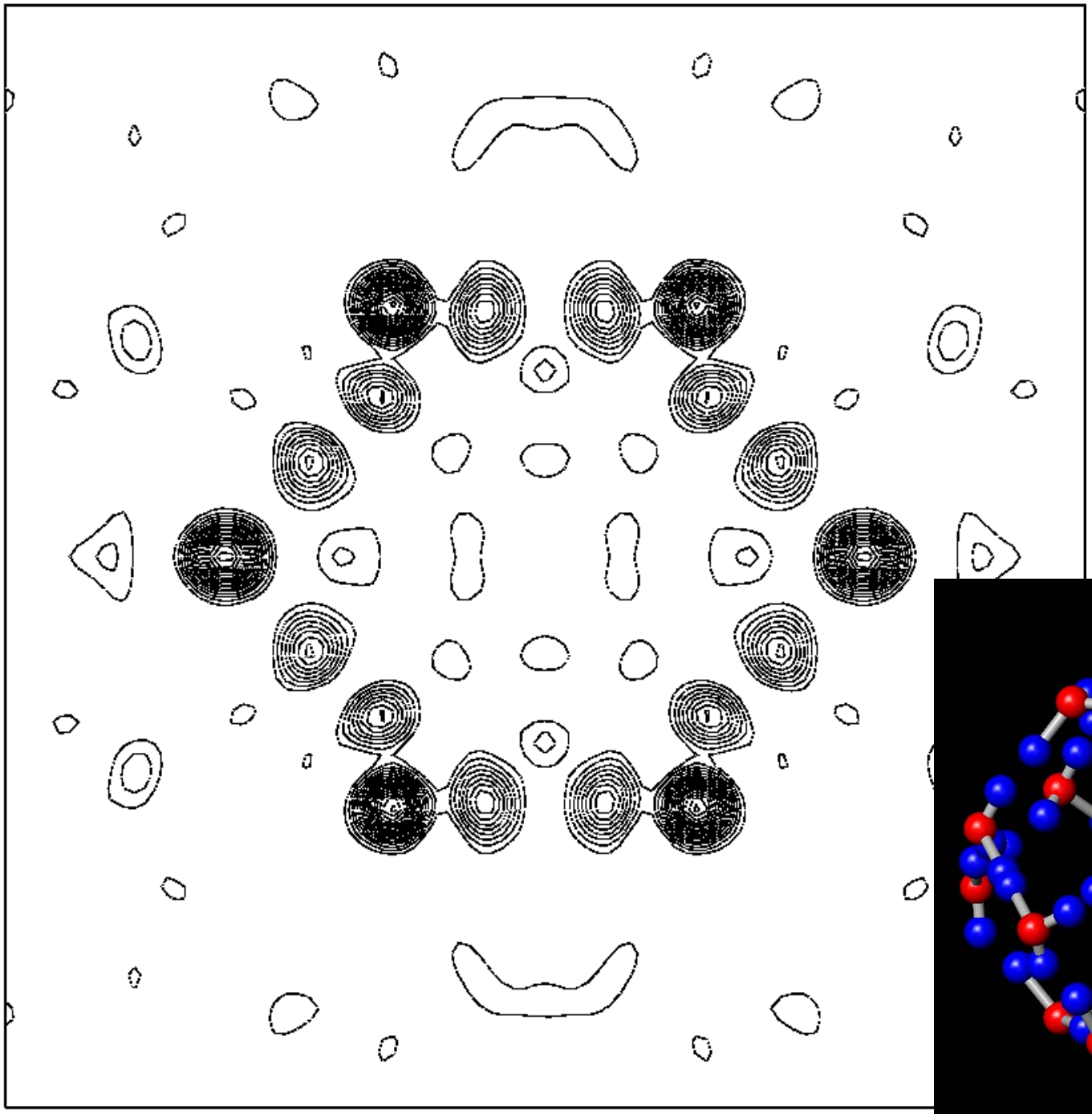
Type I
clathrate hydrate
$S_2 L_6(H_2O)_{46}$
cubic, $Pm\bar{3}n$
cell = 12 Å
$X = CH_4, CO_2$



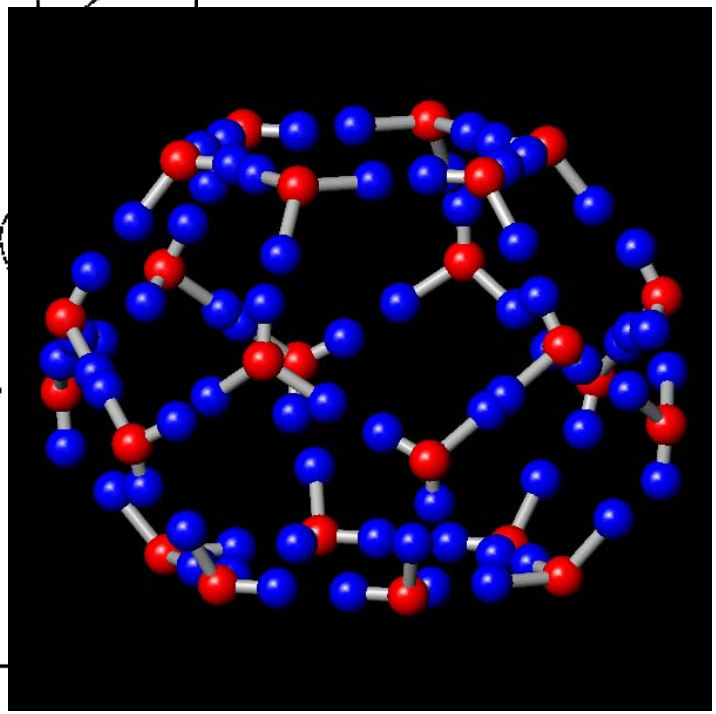
Type II
clathrate hydrate
$S_{16} L_8(H_2O)_{136}$
cubic, $Fd\bar{3}m$
cell = 17.2Å
$X = N_2, O_2, C_3H_8$

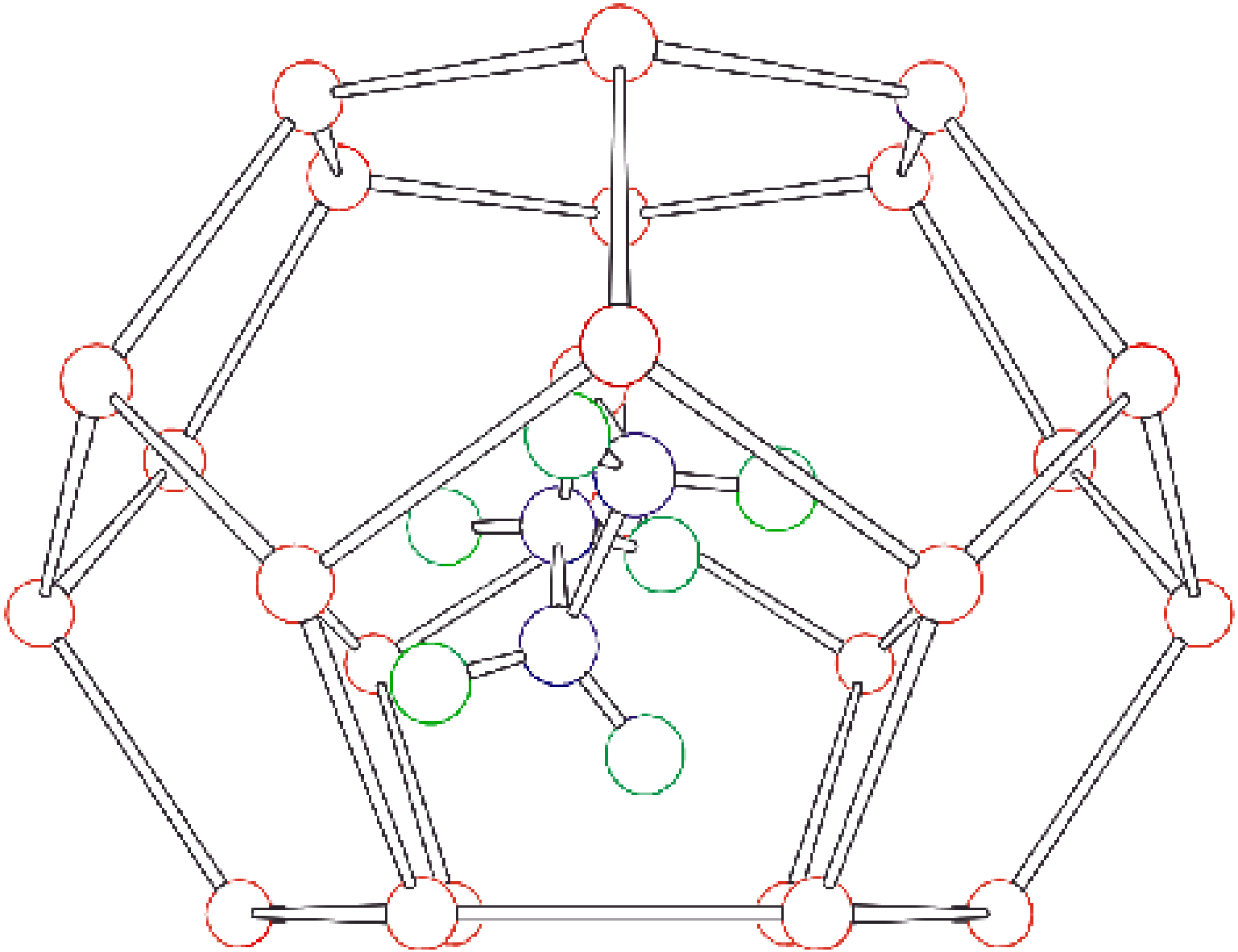
- **Methane Hydrate, structure I**
  - $CH_4 \cdot 5.75H_2O$ vs *T* — ORNL
  - $CH_4 \cdot 5.75D_2O$ vs *T* — ORNL, NIST
- **Carbon Dioxide Hydrate, structure I**
  - $CO_2 \cdot 5.75H_2O$ vs *T* — NIST
  - $CO_2 \cdot 5.75D_2O$ vs *T* — JAERI
- **Methane - Ethane Hydrate, structure II**
  - $CH_4:C_2H_6 \cdot 5.67D_2O$ vs *T* — JAERI, NIST
- **Tetrahydrofuran Hydrate, structure II**
  - $C_4H_8O \cdot 17D_2O$ vs *T* — JAERI
- **Trimethylene Oxide Hydrate, structure I and II**
  - $C_3H_6O \cdot 5.75D_2O$ vs *T* — JAERI
  - $C_3H_6O \cdot 17D_2O$ vs *T* — JAERI
- **Propane Hydrate, structure II**
  - $C_3H_8 \cdot 17D_2O$ vs *T* — JAERI
- **Methane - Ethane Hydrate, structure II**
  - $CH_4:C_2H_6 \cdot 5.67D_2O$ vs *T* — JAERI
- **Tetrahydrofuran - Hydrogen Hydrate, structure II**
  - $C_4H_8O : xH_2 \cdot 5.67D_2O$ vs *T* — JAERI

Samples We have Studied by Neutron Powder Diffraction

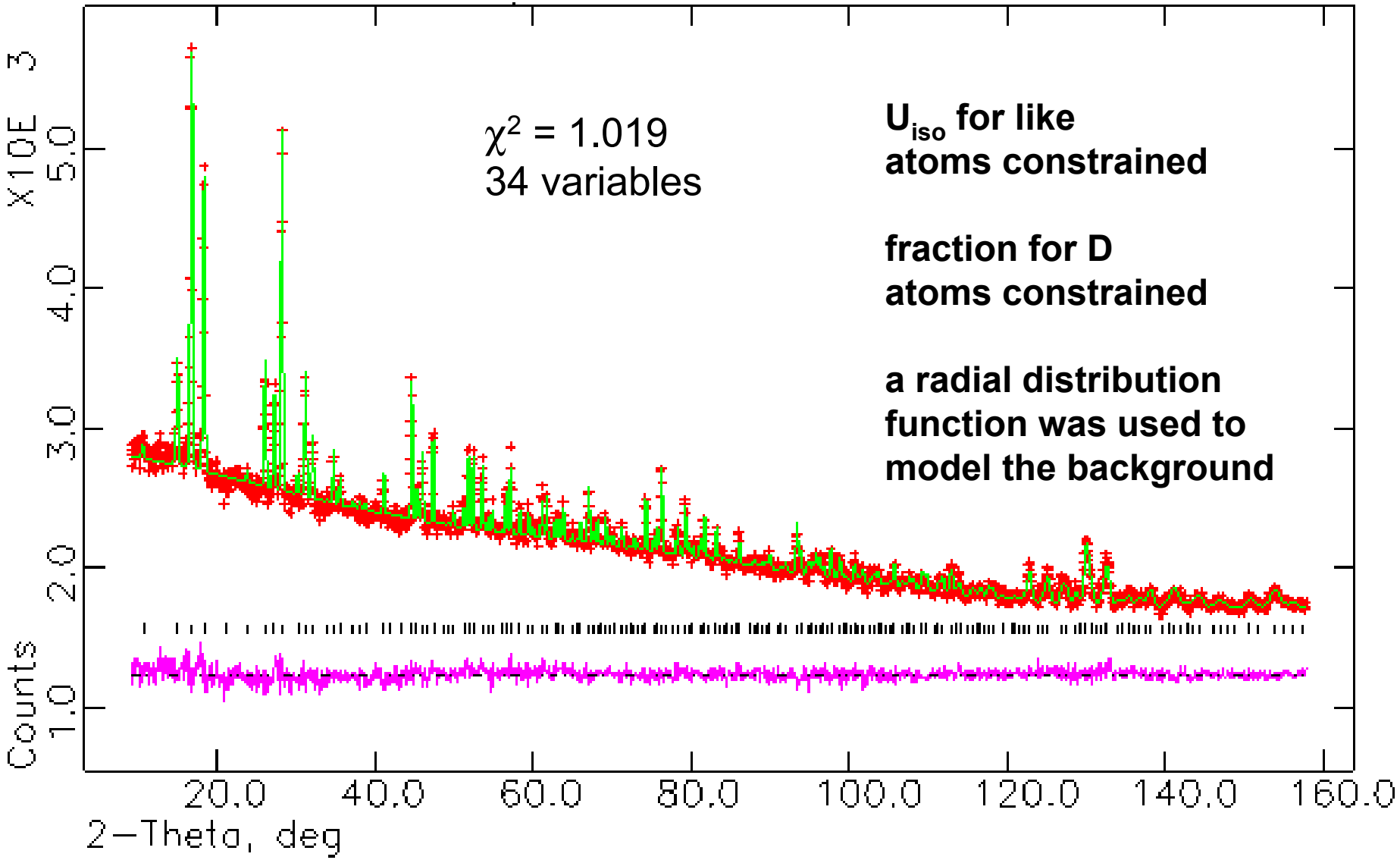


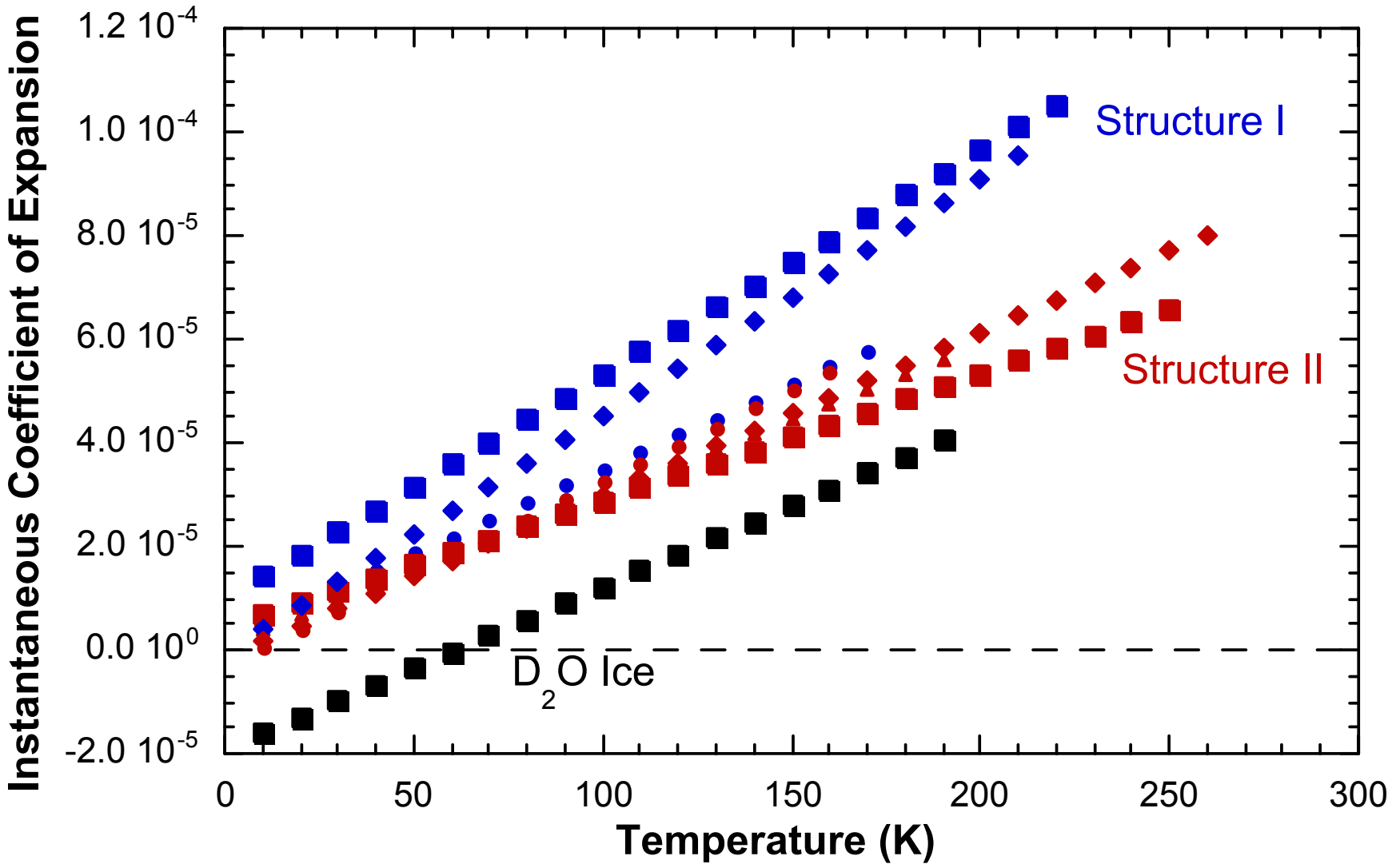
F_{obs} map
6-ring
100K
CO_2 hydrate

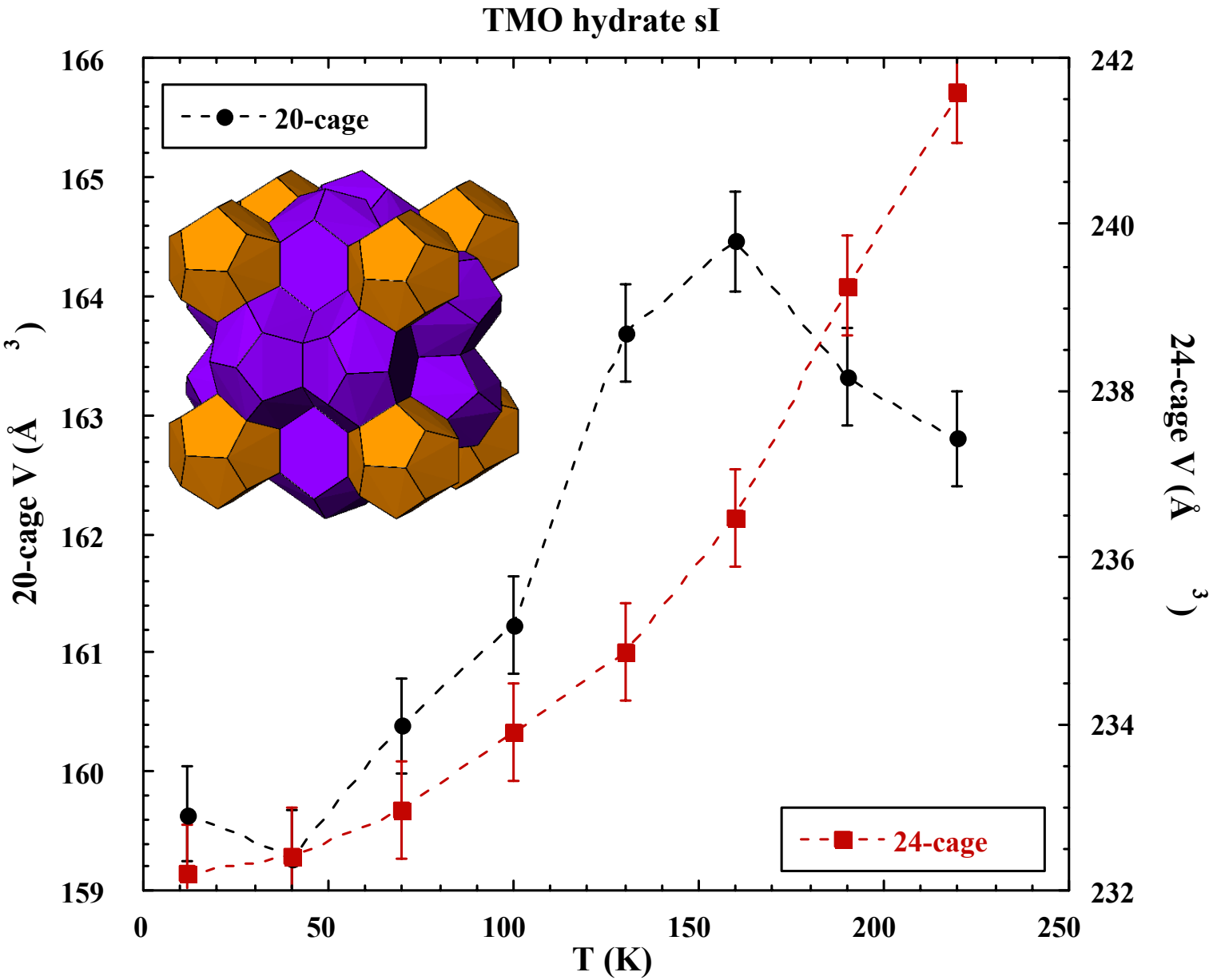


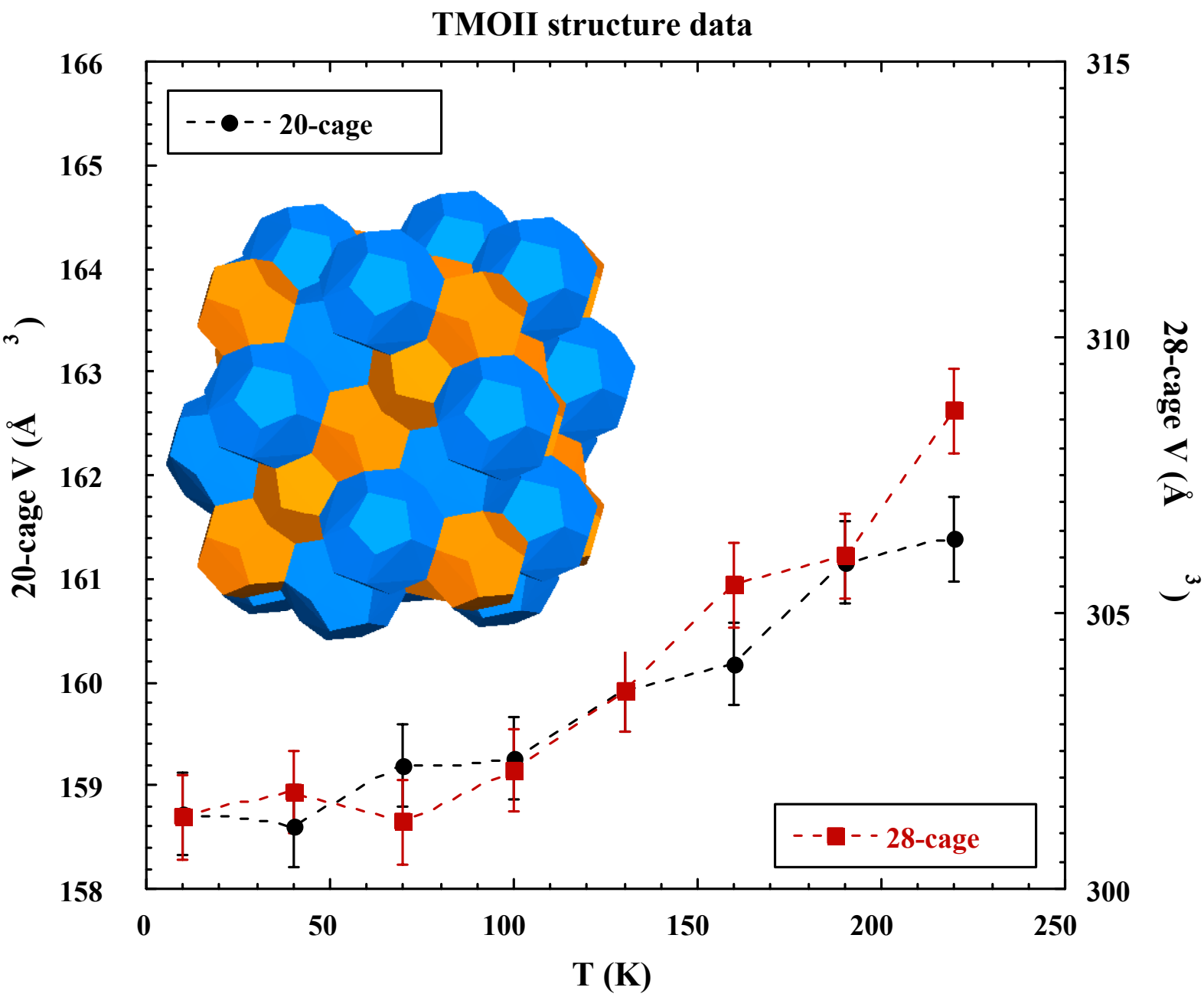


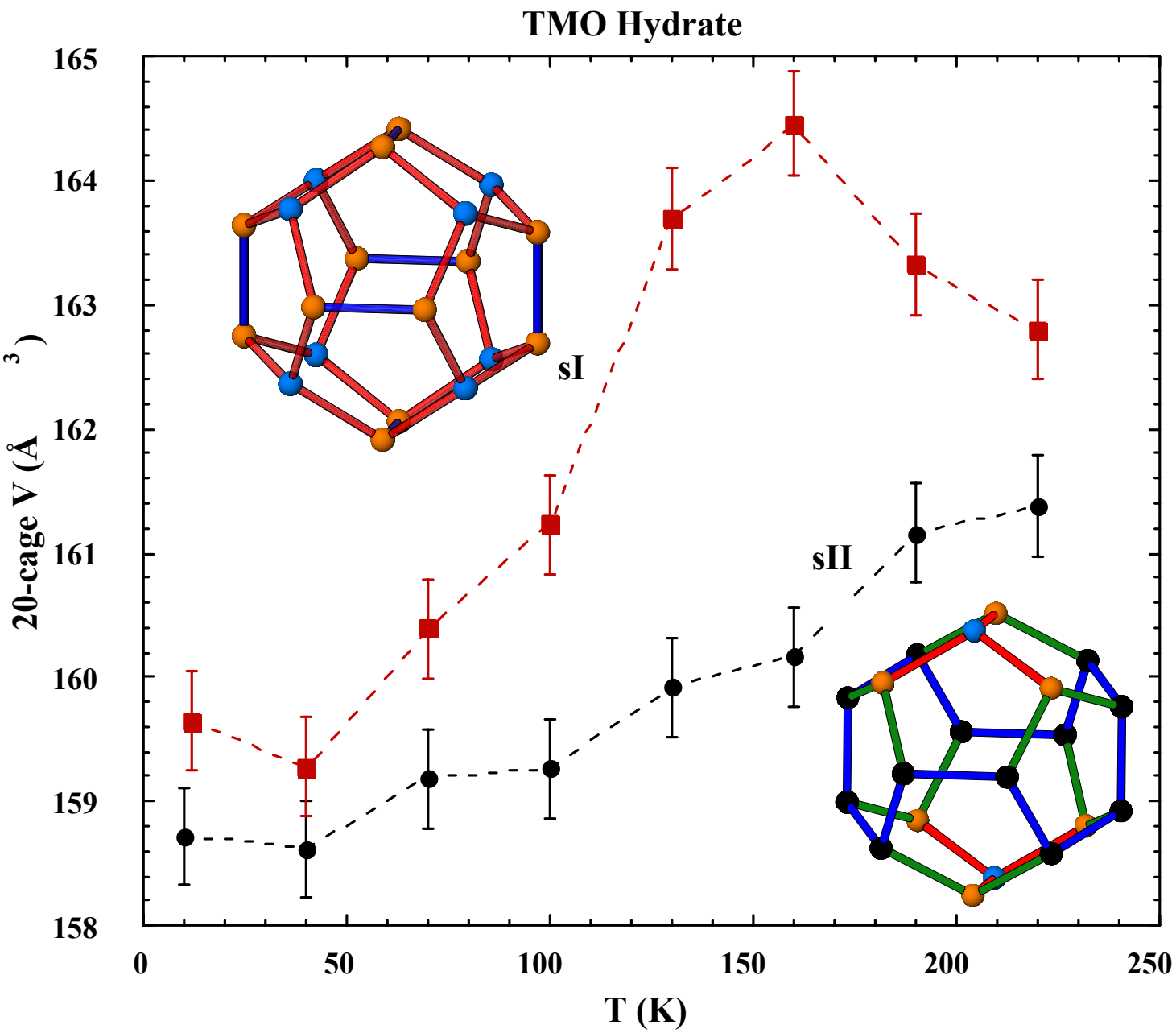
Methane hydrate



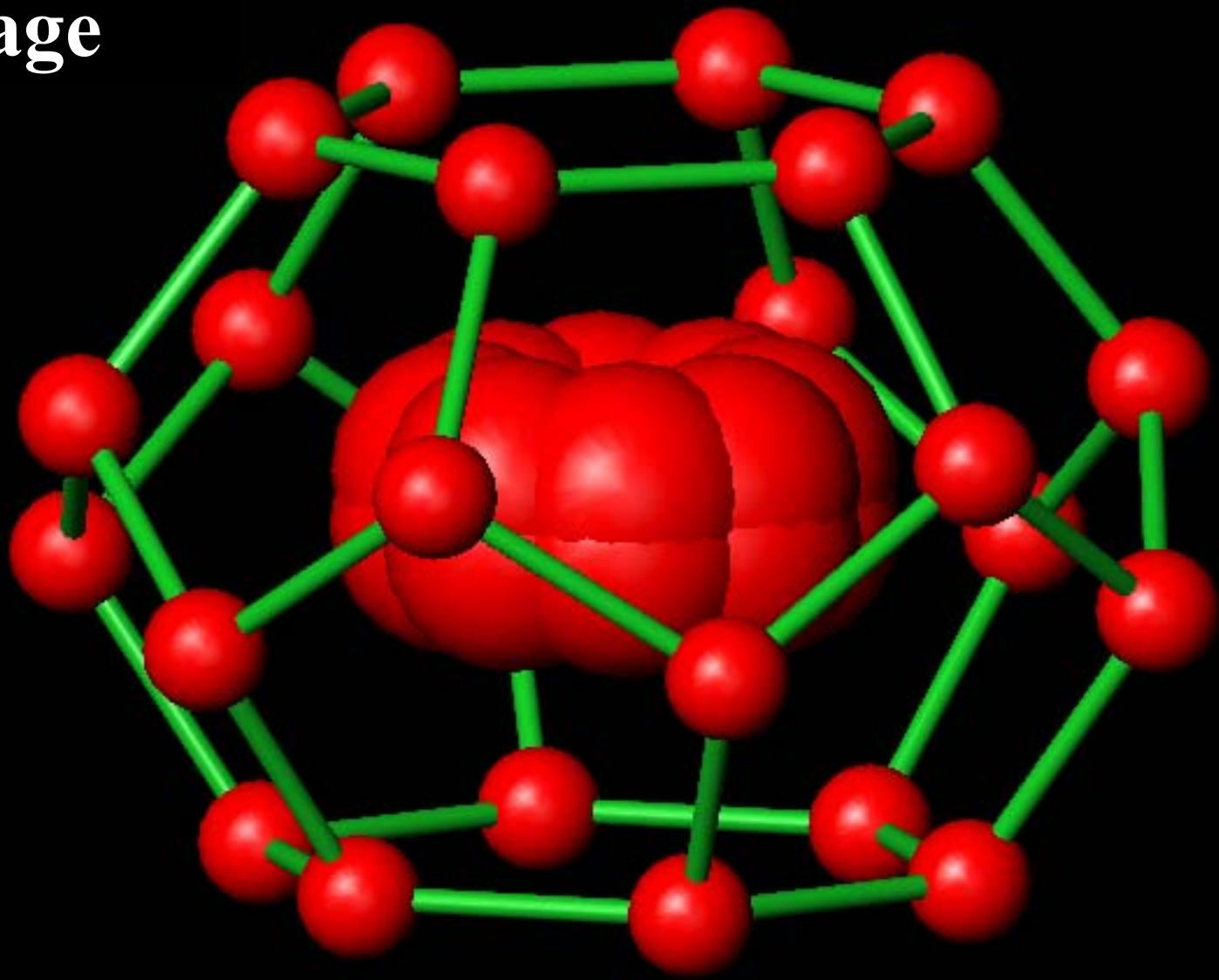

Instantaneous Coefficient of Expansion
1.2 10-4
1.0 10-4
8.0 10-5
6.0 10-5
4.0 10-5
2.0 10-5
0.0 100
-2.0 10-5
0
50
100
150
200
250
300
Temperature (K)
Structure I
Structure II
D2O Ice


TMO hydrate sI
20-cage
24-cage
20-cage V (Å 3)
24-cage V (Å 3)
T (K)
166
165
164
163
162
161
160
159
242
240
238
236
234
232
0
50
100
150
200
250

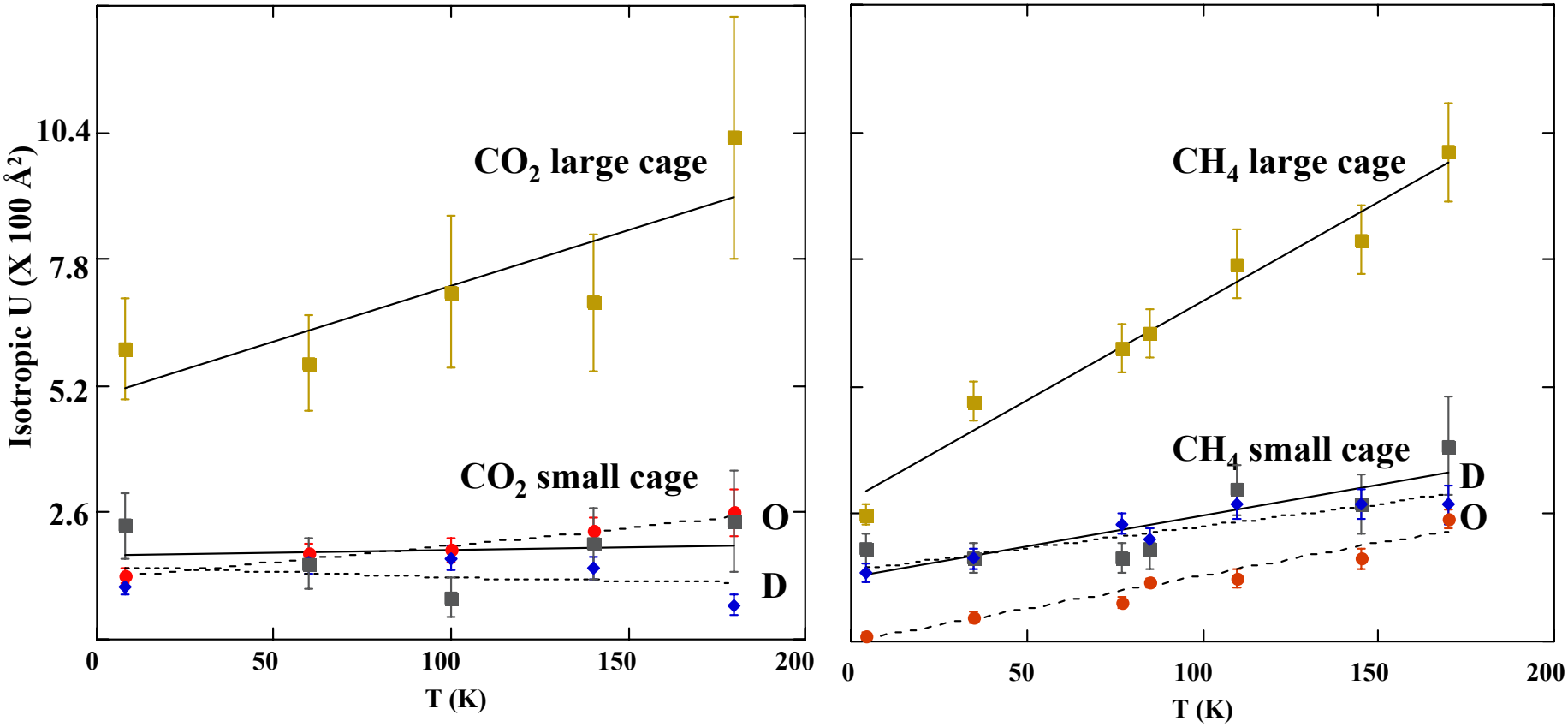

TMOII structure data
20-cage
28-cage
20-cage V (Å 3)
28-cage V (Å 3)
T (K)
166
165
164
163
162
161
160
159
158
315
310
305
300
0
50
100
150
200
250


TMO Hydrate
165
164
163
162
161
160
159
158
0
50
100
150
200
250
T (K)
20-cage V (Å 3)
sI
sII

CO_2 hydrate 8K large cage



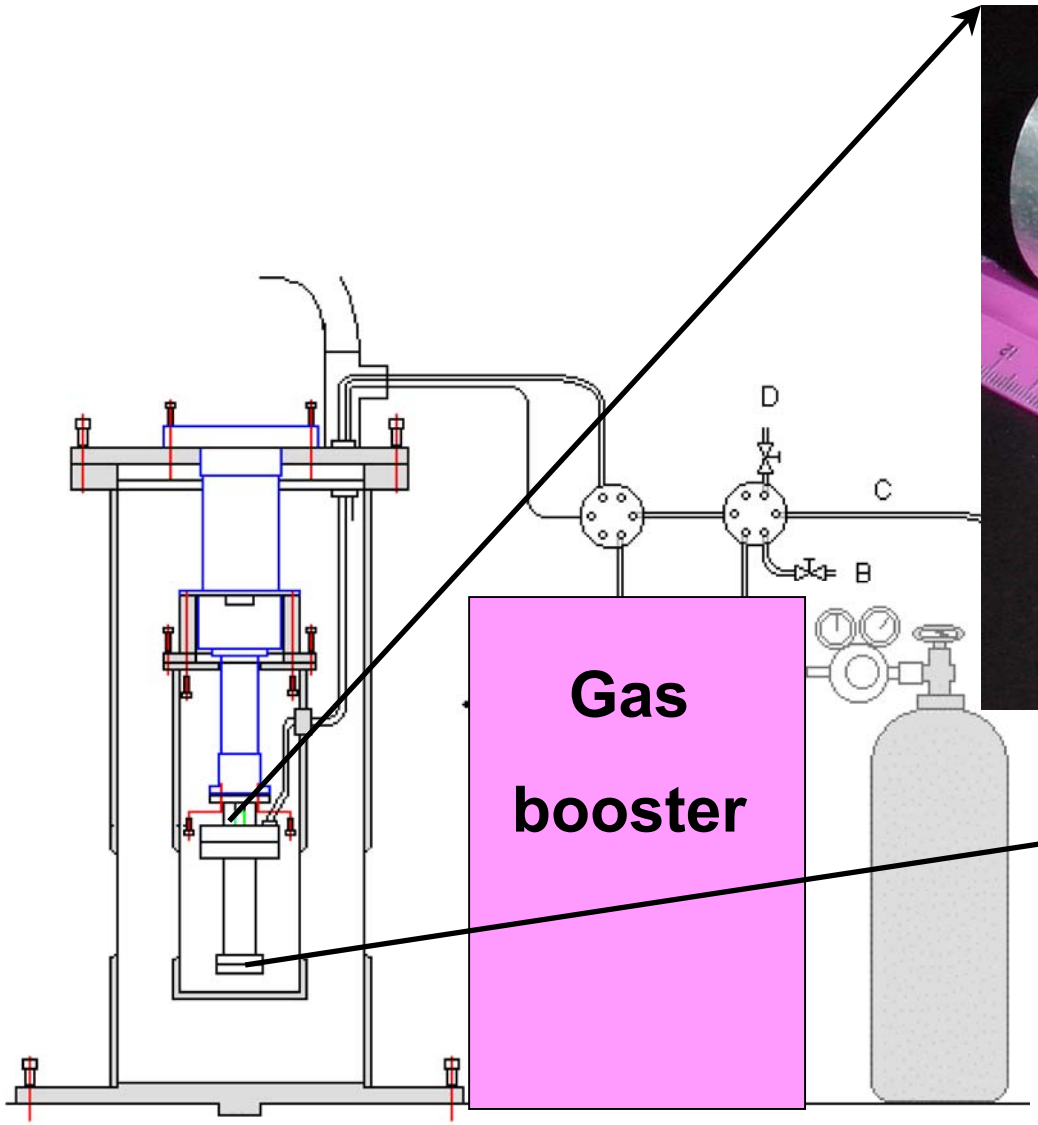
The temperature dependence of the atomic displacement parameters compared between CO_2 hydrate and CH_4 hydrate

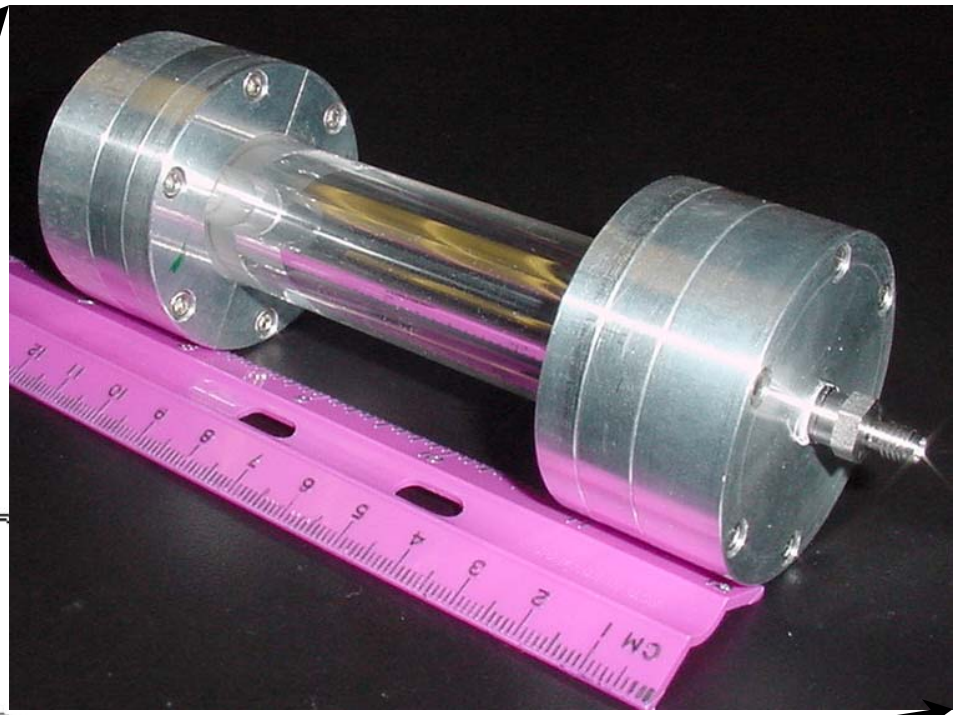


In situ Sample Cell

Operating conditions: 0.1- 350 MPa, 10-300K

Temperature control via modified closed-cycle He refrigerator





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