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A new method of reconstructing the P - T conditions of fluid circulation in an accretionary prism (Shimanto, Japan) from microthermometry of methane-bearing aqueous inclusions

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Abstract

In paleo-accretionary prisms and the shallow metamorphic domains of orogens, circulating fluids trapped in inclusions are commonly composed of a mixture of salt water and methane, producing two types of fluid inclusions: methane-bearing aqueous and methane-rich gaseous fluid inclusions. In such geological settings, where multiple stages of deformation, veining and fluid influx are prevalent, textural relationships between aqueous and gaseous inclusions are often ambiguous, preventing the microthermometric

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determination of fluid trapping pressure and temperature conditions.

To assess the P - T conditions of deep circulating fluids from the Hyuga unit of the Shimanto paleo-accretionary prism on Kyushu, Japan, we have developed a new computational code, applicable to the H_2O - CH_4 - NaCl system, which allows the characterization of CH_4 -bearing aqueous inclusions using only the temperatures of their phase transitions estimated by microthermometry: T_{mi} , the melting temperature of ice; T_{hyd} , the melting temperature of gas hydrate and $T_{h,\text{aq}}$, homogenization temperature. This thermodynamic modeling calculates the bulk density and composition of aqueous inclusions, as well as their P - T isochoric paths in a P - T diagram with an estimated precision of approximately 10 %.

We use this computational tool to reconstruct the entrapment P - T conditions of aqueous inclusions in the Hyuga unit, and we show that these aqueous inclusions cannot be cogenetic with methane gaseous inclusions present in the same rocks. As a result, we propose that pulses of a high-pressure, methane-rich fluid transiently percolated through a rock wetted by a lower-pressure aqueous fluid. By coupling microthermometric results with petrological data, we infer that the exhumation of the Hyuga unit from the peak metamorphic conditions was nearly isothermal and ended up under a very hot geothermal gradient.

In subduction or collision zones, modeling aqueous fluid inclusions in the ternary H_2O - CH_4 - NaCl system and not simply in the binary H_2O - NaCl is necessary, as the addition of even a small amount of methane to the water raises significantly the isochores to higher pressures. Our new code provides therefore the possibility to estimate precisely the pressure conditions of fluids

circulating at depth.

Keywords: fluid inclusions, microthermometry, Raman spectroscopy, gas hydrates, H₂O-CH₄-NaCl

1 **1. Introduction**

2 Using observation of thousands of fluid inclusions in quartz veins from the
3 Central Alps, Mullis (1979) and Mullis et al. (1994) recognized the correspon-
4 dence of the nature of the fluid with metamorphic grade: Methane-bearing
5 aqueous fluids are dominant at low metamorphic grade, up to $\sim 300^\circ$ C. Simi-
6 larly, water and methane have been identified as the major components of the
7 fluid in many worldwide paleo-accretionary prisms, including the Shimanto
8 Belt in Japan (Sakaguchi, 1999a; Lewis et al., 2000; Kondo et al., 2005),
9 Kodiak Island in Alaska (Vrolijk et al., 1988) and the Franciscan Complex
10 in California (Dalla Torre et al., 1996; Sadofsky and Bebout, 2004). Fluid
11 inclusions carry invaluable information regarding pressure (P) - temperature
12 (T) conditions of the fluid at the time of trapping and, indirectly, of the host
13 terrane, in the shallow portion ($P \sim 0 - 500$ MPa) of subduction and colli-
14 sion zones where the analysis of complex phase assemblages with the help of
15 thermodynamic databases and software (e.g. THERMOCALC, (Powell and
16 Holland, 1988) or TWEEQU (Berman, 1991)) is not possible.

17 To this end, the following procedure (e.g. Alderton and Bevins, 1996),
18 which is applicable when aqueous inclusions and methane-rich gaseous in-
19 clusions are simultaneously present, is commonly used (see Table 1 for a list
20 of symbols): If one assumes that these inclusions were trapped under the
21 same conditions, then the trapping pressure (P_t) and temperature (T_t) can

22 be estimated on a P - T diagram from the intersection of the isochores of
23 gaseous inclusions with the isotherm $T = T_{h, \text{aq}}$ of aqueous inclusions (where
24 $T_{h, \text{aq}}$ is the homogenization temperature of aqueous inclusions). The central
25 assumption of this method is that the two types of fluid inclusions derive
26 from the entrapment of the two end-members of an immiscible mixture of a
27 CH_4 ($\pm\text{H}_2\text{O}$) gas in equilibrium with a dense H_2O - NaCl ($\pm\text{CH}_4$) solution. In
28 other words, this method assumes that aqueous and gaseous inclusions are
29 cogenetic.

30 This assumption is commonly based on the distribution and the geometry
31 of the inclusions (e.g. primary inclusions of the two kinds trapped in the
32 same crystal). However, in orogenic settings, where rocks have experienced
33 multiple stages of deformation and fluid influx, most inclusions are secondary
34 and textures are often ambiguous.

35 Thus, one must assess if there was a single fluid at depth or if the two
36 kinds of inclusions correspond to two unrelated fluids, trapped at either the
37 same or even different P - T conditions. To this end, an approach alternative
38 to texture analysis is to determine, from microthermometric measurements,
39 the possibility for several populations of fluid inclusions to be thermody-
40 namically in equilibrium (Pichavant et al., 1982; Ramboz et al., 1982). To
41 prove their cogenetic character, several conditions must be met, including
42 a similar temperature for total homogenization. This transition is readily
43 observable in water-rich fluid inclusions by the disappearance of thermally
44 agitated bubbles of methane. In methane-rich inclusions, the water phase,
45 occupying a low volume fraction and forming a meniscus on the rim of the
46 inclusion, is often not visible, hence total homogenization cannot be mea-

47 sured optically. An alternative solution was developed by Mullis (1979), who
48 showed good agreement between the estimated molar fraction of methane in
49 water-rich inclusions and the saturation concentration of methane in water for
50 the P - T conditions of equilibrium between water-rich and methane-rich fluid
51 inclusions. This method is nevertheless restricted to exceptionnally large
52 water-rich fluid inclusions where the density of the bubble of methane can
53 be estimated with a freezing stage. In general, however, it is often difficult
54 to check the cogenetic character of methane-rich and water-rich inclusions.

55 The above mentioned difficulties present themselves when working with
56 aqueous H_2O - NaCl - CH_4 inclusions in rocks of the Shimanto paleo-accretionary
57 complex (Japan). In particular, small ($\sim 5\mu\text{m}$), aqueous inclusions are asso-
58 ciated with some gaseous CH_4 inclusions, whose cogenetic character cannot
59 be clearly supported by texture analysis. Unfortunately, such ambiguous
60 textural relationships are common in orogenic contexts, limiting the scope of
61 microthermometry in these formations.

62 Regardless, aqueous inclusions exhibit one additional phase transition,
63 which is the melting of a gas hydrate in the presence of a vapour phase. Its
64 temperature can be measured by microthermometry, generally between 0°C
65 and 15°C , and this data gives us one additional constraint to characterize
66 aqueous inclusions in terms of bulk content and density. Two models to this
67 end (Dubessy et al., 1992; Mao et al., 2011) already exist in the literature,
68 but none can be applied to Shimanto paleo-accretionary complex: Dubessy
69 et al. (1992) does not take into account $T_{h,\text{aq}}$, whereas Mao et al. (2011)
70 does not take into account the presence of dissolved salts. We have, there-
71 fore, built a new algorithm allowing the complete characterization of the

72 properties of an aqueous CH₄ and NaCl-bearing aqueous inclusion (i.e. bulk
73 density, bulk content, isochoric paths) using three measured phase transition
74 temperatures: T_{mi} , melting temperature of ice; T_{hyd} , melting temperature
75 of gas hydrate and $T_{h,aq}$, homogenization temperature. This new model is
76 described in Section 4 after a discussion of the geological context (Section 2)
77 and of the microthermometric analysis (Section 3).

78 Section 6 synthesizes the main results, which have been obtained from this
79 microthermometric work and thermodynamic modeling and shows that the
80 Hyuga unit has experienced important fluid composition changes in the past
81 (methane-rich and water-rich fluids in disequilibrium) as well as variations
82 in thermal regime.

83 **2. Geological context**

84 The Hyuga Group is part of the Shimanto Belt on Kyushu, Japan (Fig.
85 1). This belt is interpreted as a paleo-accretionary complex formed dur-
86 ing the subduction of the Pacific plate below the Eurasian Plate (Taira
87 et al., 1988). It is divided by the Nobeoka Tectonic Line (NTL), an out-of-
88 sequence megathrust, several hundreds of kilometers long, marking a large
89 stratigraphic and metamorphic gap (Imai et al., 1971; Toriumi and Teruya,
90 1988).

91 The Hyuga *mélange* is the uppermost unit of the Hyuga Group and consti-
92 tutes the footwall of the NTL. It was strongly deformed and affected by meta-
93 morphism, with peak temperature conditions estimated around 250-300°C
94 on the basis of vitrinite reflectance (Kondo et al., 2005) or illite cristallinity
95 (Hara and Kimura, 2008; Mukoyoshi et al., 2009). In addition, Mukoyoshi

96 et al. (2009) describe a lateral temperature gradient from the east ($\sim 250^\circ \text{C}$)
97 to the west ($\sim 280^\circ \text{C}$). Furthermore, based on prehnite-pumpellyite meta-
98 morphic assemblages in greenstones included in the *mélange*, Toriumi and
99 Teruya (1988) estimated the peak metamorphic conditions as 3-5 kbars and
100 200-300 $^\circ \text{C}$.

101 The Hyuga *mélange* has a block-and-matrix structure, where blocks are
102 made of lenses of sandstone/siltstone or early stage quartz veins and matrix is
103 rich in phyllosilicates. The ductile deformation, associated with peak meta-
104 morphic conditions, is pervasive and apparent in (1) the foliation, defined
105 both from the elongated shape of the blocks and the preferential orientation
106 of the phyllosilicates in the matrix, (2) top-to-SE shear zones in the ma-
107 trix and (3) stretching/necking of the blocks. At the grain scale, ductilely
108 deformed quartz grains are preferentially elongated parallel to the foliation
109 and show undulose extinction, subgrains and bulging grain boundaries (Fig.
110 2A_2). Note that the plastic deformation of quartz is more apparent in the
111 west of the Hyuga *mélange* unit, in agreement with the slightly higher meta-
112 morphic conditions, than along the eastern coast, which somehow explains
113 why it is not described in Kondo et al. (2005).

114 The *mélange* rocks have been pervasively affected by quartz veining through-
115 out their history. We define early-stage veins as those containing quartz
116 grains that have been plastically deformed and late-stage veins as those cross-
117 cutting the ductile deformation microstructures and containing grains devoid
118 of plastic deformation. The latter veins are preferentially orientated perpen-
119 dicular to the foliation and are often restricted to the blocks of the *mélange*,
120 i.e. not propagating into the phyllosilicate-rich matrix.

121 All the quartz grains in veins contain fluid inclusions, most often with
122 a very high density (Fig. 2). As plastic deformation of host quartz grains
123 can potentially affect their volume, fluid inclusions predating or synchronous
124 with the ductile phase cannot be studied by microthermometric methods,
125 which assume an isochoric evolution of the inclusions from their trapping.
126 Our study is thus necessarily restricted to late-stage quartz veins, devoid of
127 plastic deformation (Fig. 2A and B).

128 In the Hyuga *mélange* (Fig. 1), Kondo et al. (2005) described two kinds of
129 fluid inclusions in quartz veins: aqueous inclusions and gaseous CH₄-bearing
130 inclusions (Fig. 3). Assuming that these inclusions were cogenetic, Kondo
131 et al. (2005) could derive the minimum P_t and T_t conditions of trapping from
132 the intersection of the isochore of CH₄ inclusions with the $T_{h,aq}$ isotherm (e.g.
133 Mullis, 1979).

134 Our own analysis (microthermometry and Raman microspectrometry) of
135 samples of Kondo et al. (2005) confirmed the presence of aqueous and gaseous
136 CH₄-rich inclusions. All these inclusions, distributed within late-stage veins,
137 have very irregular shapes (Fig. 2A_3 and B_3). In some cases, they are
138 clearly organized as planes of inclusions (Fig. 2B_3), i.e. they are secondary
139 inclusions; in other cases their nature is obscure. The cogenetic nature of
140 these two kinds of inclusions, if possible, is questionable in two respects:

- 141 1. There is no textural evidence, apart from their presence in the same
142 crystals, to the fact that water-rich and methane-rich fluid inclusions
143 were trapped together and are thus representative of the two end-
144 members of coexisting liquid and vapour fluid phases. In particular,
145 the gaseous CH₄-rich inclusions are all contained within fracture planes

146 that do not contain any aqueous inclusion. We found neither primary
147 fluid inclusions of the two kinds in the same crystal or secondary inclu-
148 sions of the two kinds in the same fracture plane.

149 2. Using a more extensive sampling of the Hyuga unit than Kondo et al.
150 (2005), we discovered that gaseous CH₄-rich inclusions are restricted,
151 in fact, to the easternmost side, while water-rich fluid inclusions are
152 distributed throughout the whole unit (blue dots in Fig. 1). Thus,
153 the presence of CH₄-rich inclusions appears rather as a peculiarity, and
154 aqueous fluids are not necessarily considered to be at equilibrium with
155 a CH₄-rich phase and thus to represent the liquid aqueous end-member
156 saturated with respect to a vapour CH₄-rich phase.

157 As a consequence, these preliminary observations lead us to question the
158 effective circulation of mixtures of methane-saturated waters and CH₄ gas
159 during the trapping of fluid inclusions.

160 **3. Microthermometry**

161 *3.1. Apparatus*

162 The selected quartz fragments were placed on a 200 μ m-thick, 1.6 cm-wide
163 rounded glass window on top of the silver block of the THMS-600 Linkam
164 heating-cooling stage. Phase changes in the inclusions were observed using an
165 Olympus BHS microscope equipped with a $\times 80$ ULWD Olympus objective
166 and recorded by a Marlin black and white camera (CMOS 2/3" sensor, reso-
167 lution 1280 \times 1024 pixels, pixel size of 6.7 μ m). Temperature was measured
168 using a class B Pt 100 thermistance, which has an intrinsic precision of 0.15°
169 to 1.35°C between 0° and 600°C. Temperature is sampled every ~ 300 ms by

170 a Eurotherm 902 controller which allows analogic output. The temperature
171 cycles of the stage (heating - cooling rate and temperature steps) are con-
172 trolled using a LabVIEW® computer program. In the vicinity of the phase
173 transitions, we chose slow heating rates about $\sim 1^\circ\text{C}/\text{min}$.

174 The stage was calibrated according to the procedure detailed in El Mekki-
175 Azouzi (2010) between -56.6°C and 573°C against 8 reference temperatures.
176 The standards used were:

- 177 1. either natural and synthetic fluid inclusions: melting point of CO_2 at
178 -56.6°C , melting point of ice : 0°C ,
- 179 2. or ceramics: solid - solid transitions at 37°C and 47°C in CsPbCl_3 and
180 at 180°C in $\text{Pb}_3(\text{PO}_4)_2$,
- 181 3. or salts : $b/g \rightarrow a$ transition at 147°C in AgI and subsequent melting
182 at 557°C ,
- 183 4. or minerals : $a \rightarrow b$ transition in quartz at 573°C .

184 Based on the calibration, the temperature accuracy is around $\pm 1^\circ\text{C}$ over
185 the whole investigation temperature range, from -120°C to $+290^\circ\text{C}$, but much
186 better, of the order of $\pm 0.1^\circ\text{C}$ in the temperature range from -10° to $+20^\circ\text{C}$,
187 where ice and gas hydrate melting occurs.

188 3.2. Gaseous methane-rich fluid inclusions

189 These inclusions are restricted to the easternmost, coastal side of the
190 Hyuga unit. They are monophasic at ambient temperature. Upon cool-
191 ing, they nucleate a bubble below -82.7°C (the critical temperature of pure
192 methane) and thus, we measured these homogenization temperatures (T_h) to
193 liquid. T_h distribution is roughly unimodal, with a principal peak between

194 -115°C and -105°C (Fig. 4), similar to what was described in Kondo et al.
195 (2005).

196 3.3. Aqueous fluid inclusions

197 Water-rich fluid inclusions were collected in the whole Hyuga unit (Fig.
198 1), including the eastern sides, where methane-rich inclusions are also present.
199 At ambient temperature, they are biphasic, with a methane-rich bubble of
200 vapor embedded in a water-rich liquid (Fig. 3). Upon heating, the size of
201 the methane vapor bubble is progressively reduced, up to its complete dis-
202 solution in the liquid phase at the homogenization temperature ($T_{h,aq}$). In
203 the final steps of heating, when the bubble has sufficiently shrunked, it is
204 systematically affected by thermal agitation. The bubble rapid movement
205 can be easily observed, even in very small (below 5 μm) inclusions, so that
206 $T_{h,aq}$ estimation can be carried out efficiently on a large pool of inclusions of
207 various size and shape. Homogenization temperatures are reproducible with
208 a precision of $\sim 1^\circ\text{C}$. In the inclusions where all phase transitions were observ-
209 able (Tab. 2), $T_{h,aq}$ range from 200 to 280°C, i.e. similar to measurements
210 by Kondo et al. (2005).

211 On the other hand, the measurements of the temperatures of ice melting
212 (T_{mi}) and gas hydrate disappearance (T_{hyd}) are more difficult to carry out.
213 In theory, T_{mi} and T_{hyd} can be estimated, during heating, by visual obser-
214 vation of the disappearance of ice and gas hydrate, respectively. However,
215 in practice, the inclusions are either too small or too crowded, so that the
216 ice and and gas hydrate crystals are not visible. Fortunately, their presence,
217 at the interface between the liquid and the vapor bubble, can be indirectly
218 detected by their influence on the bubble shape, size or position within the

219 inclusion. As a consequence, we restricted the complete microthermometric
220 observations to the largest fluid inclusions, and we had to apply a specific
221 procedure of cyclic heating and cooling (Ramboz, 1980) to measure T_{mi} and
222 T_{hyd} .

223 The method of Ramboz (1980) is based on successive cycles of heating
224 and cooling, which allow to determine the temperature of disappearance
225 of ice/gas hydrate. It can be described as follows (Fig. 5 and movies in
226 Supplementary Material):

- 227 1. First, freeze the inclusion up to formation of ice/gas hydrate.
- 228 2. Heat slowly the inclusion to melt progressively the ice/gas hydrate, up
229 to a given temperature (let's say T_i for the cycle #i).
- 230 3. Then freeze very rapidly the inclusion and observe possible variations
231 in its size, shape of location.
- 232 4. Repeat steps (2) and (3) for increasing T_i temperatures, until for some
233 T_n , rapid freezing has no effect on the vapour bubble (no shrinkage
234 and no deformation). This indicates that ice/gas hydrate seeds have
235 completely disappeared.

236 The melting temperature (T_m , i.e either T_{mi} or T_{hyd}) of ice/gas hydrate
237 is then approximated by $T_{n-1} < T_m < T_n$. The precision depends on the
238 temperature increments, and it can be set up to the precision of the mi-
239 crothermometric equipment (i.e. a precision of 0.1°C).

240 In practice, for ice, initial freezing was done at a temperature around
241 -35 to -40°C (step 1), where ice filled instantaneously the inclusion. For
242 gas hydrate, the temperature of initial freezing was above T_{mi} , i.e. at a state
243 where the fluid inclusion contains three phases (gas hydrate, aqueous solution

244 and gas bubble).

245 For ice, the measurement of T_{mi} is systematically reproducible within \pm
246 0.1°C , as the bubble shrinkage caused by ice formation is easily detectable.
247 However, for gas hydrates, the procedure is much less efficient. As the bulk
248 content of CH_4 is very low, the volumetric proportion of gas hydrate is also
249 very low. Thus, its growth does not affect much the gas bubble, and its effect
250 is only detectable in favourable cases, when the gas hydrate deforms the shape
251 of the vapor bubble or changes its position in the inclusion. Hence, only a
252 fraction of the inclusions showed some response to freezing/heating cycles.
253 Moreover, in some of these inclusions, it was noted that the measurements
254 of T_{hyd} were not reproducible after a complete freezing below $\sim -40^\circ\text{C}$. We
255 postulate that the reason is a change in the position of the gas hydrate crystal
256 seed, but had to discard the results of these inclusions.

257 Table 2 gives the complete data set (T_{mi} , T_{hyd} and $T_{h,\text{aq}}$) measured for
258 seven aqueous inclusions. Homogenization temperatures $T_{h,\text{aq}}$ range from \sim
259 200° to 280°C . On the other hand, T_{mi} and T_{hyd} are restricted to relatively
260 narrow ranges, from -3.15° to -1.9°C and from 5.3° to 10.4°C , respectively.

261 4. Thermodynamic modeling of aqueous inclusions

262 The fluid inclusions of this study can be ascribed to the $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}$
263 system. Thus, if they contain sufficient CH_4 , they undergo the following
264 phase transitions from low to high temperatures (Bakker, 1997; Bakker and
265 Thiéry, 1994):

- 266 • first (state 1), melting of the last ice crystal in the presence of a gas
267 hydrate (H), an aqueous solution (L_w) and a gas bubble (G) at a tem-

268 perature $T_1 = T_{mi}$,

- 269 • then (state 2), melting of the last gas hydrate crystal in the presence
- 270 of an aqueous solution and a gas bubble at a temperature $T_2 = T_{hyd}$,
- 271 • and eventually (state 3), disappearance of the gas bubble (homogeniza-
- 272 tion point) at a temperature $T_3 = T_{h,aq}$.

273 To our knowledge, at least two thermodynamic models (Dubessy et al.,
274 1992; Mao et al., 2011) have been devised to characterize such fluid inclu-
275 sions exhibiting gas hydrates. However, none of them can be applied to the
276 present study: the model of Dubessy et al. (1992) does not make use of
277 homogenization temperatures and the model of Mao et al. (2011) does not
278 allow for the presence of NaCl. Therefore, specific thermodynamic modeling
279 has to be developed to interpret our microthermometric data. The method
280 proposed here is an extension of the model of Dubessy et al. (1992), which
281 has been associated to a CH_4 solubility model (e.g. Duan and Mao, 2006) for
282 NaCl-bearing aqueous solutions.

283 Our algorithm is based on the assumption that fluid inclusions behave as
284 closed and isochoric systems. Thus, the key equations can be given by the
285 following set of expressions:

$$\left\{ \begin{array}{l} n_{\text{H}_2\text{O},1} = n_{\text{H}_2\text{O},2} \\ n_{\text{CH}_4,1} = n_{\text{CH}_4,2} \\ n_{\text{NaCl},1} = n_{\text{NaCl},2} \\ \rho_2 = \rho_3 \end{array} \right. \quad (1)$$

286 where the meaning of the symbols used here (and in all what follows) is given
287 in Table 1. The volume conservation between states 1 and 2, and between
288 states 2 and 3, as well, is implicitly expressed in these equations. The first
289 three equations express the mass balance of, respectively, H₂O, CH₄ and
290 NaCl, between state 1 (ice melting) and state 2 (gas hydrate melting) in a
291 fluid inclusion of 1 m³ of volume. The last equation formulates the mass
292 conservation between state 2 and state 3 (homogenization).

293 As a consequence, this set of four equations represents a closed form of the
294 constraints (volume and matter conservation) imposed on a fluid inclusion
295 in the H₂O-CH₄-NaCl system. These equations are further developed in
296 Appendix A. Other thermodynamic quantities do not explicitly appear in
297 the equations above, but are implicitly required. In particular, this is the case
298 of pressures of gas hydrate dissociation (P_1 and P_2), which are calculated by
299 a thermodynamic model describing gas hydrate melting (e.g. Munck et al.,
300 1988). NaCl activities in aqueous solutions are also needed and are calculated
301 by a model for activity coefficients of dissolved salts (Pitzer, 1973). Molar
302 volumes (V^G) of the gas phase are calculated by the equation of state of
303 Soave (1972). Additional details are given in Dubessy et al. (1992).

304 At the end, in the whole set of equations (1), it appears that there
305 are only four unknowns: F_1^{Lw} , the volume proportion of the aqueous liquid
306 at state 1; F_1^H , the volume proportion of gas hydrate at state 1; F_2^{Lw} , the
307 volume proportion of aqueous solution at state 2; and $m_{\text{NaCl},2}$, the NaCl mo-
308 lality in the aqueous solution at state 2. Thus, with four unknowns for four
309 equations, the problem is completely solvable. Only one solution is found
310 by using an iterative Newton algorithm for a given set of microthermometric

311 measurements (T_{mi} , T_{hyd} and $T_{h,aq}$). Therefore, the present procedure rep-
312 resents an interesting enhancement of the method of Dubessy et al. (1992),
313 which could not fully characterize the bulk properties of the fluid inclusion
314 without relying upon the imprecise estimation of the bubble filling degree
315 F_2^G at T_2 .

316 One discussion point is concerned with the error propagation produced by
317 the successive equations of state used in our calculations. From the literature
318 indications, the solubility models deviate at most by around 6% from exper-
319 imental data (Duan and Mao, 2006; Spivey et al., 2004). Density models for
320 H₂O-NaCl solutions are more accurate with deviations within 1 % (Spivey
321 et al., 2004; Duan and Mao, 2006). We have tested different combinations
322 of thermodynamic models (Duan and Mao, 2006; Spivey et al., 2004; Duan
323 et al., 1992; Potter and Brown, 1977; Pitzer, 1973) and we found no deviation
324 above 12% in the calculated methane concentration, which is well consistent
325 with the precision degree we estimated for our calculations.

326 **5. Reconstitution of paleo pressures and temperatures**

327 *5.1. P-T-X trapping conditions of the Hyuga mélange unit*

328 The thermodynamic modeling described in the preceding section has been
329 applied to analyse the microthermometric data obtained on fluid inclusions
330 from the Hyuga unit. Computed salinities and bulk methane concentrations
331 are given in Table 2. Both show large relative variations, even within samples
332 collected in the same area, either in the west (HN48, HN51 and HN87) or
333 on eastern coast (Kon-NB26). CH₄ concentrations are positively correlated
334 with homogenization temperatures, reflecting the fact that solubility at high

335 P and T is mostly controlled by the temperature (Duan and Mao, 2006).
336 Salinities are systematically below oceanic levels.

337 Monophasic isochores of gaseous inclusions, calculated from the web page
338 <http://webbook.nist.gov/chemistry/fluid/> from the National Institute of Stan-
339 dards and Technology using the equation of state by Setzmann and Wagner
340 (1991) and biphasic liquid-gas isochores of aqueous inclusions, calculated us-
341 ing Duan and Mao (2006), are plotted in Fig. 6. From this diagram, one
342 important conclusion emerges: isochores of gaseous inclusions do not inter-
343 sect biphasic isochores of aqueous inclusions. They run even at much higher
344 pressures than homogenization pressures of aqueous inclusions. Thus, aque-
345 ous and gaseous inclusions cannot be cogenetic.

346 As a consequence, the inclusions have registered, at least, two types of
347 fluid circulations with marked composition differences: one involving dense
348 aqueous solutions with some minor dissolved methane, and another one com-
349 posed of light methane-rich gas. Methane pulses have probably occurred at
350 larger pressures than aqueous solutions, but at this stage, other arguments
351 must be searched to constrain further the trapping pressures and tempera-
352 tures of these fluids.

353 The problem can be partially solved by considering the rock maximum
354 temperature (T_{\max}), as recorded by the vitrinite reflectance (Kondo et al.,
355 2005) or the illite crystallinity (Hara and Kimura, 2008; Mukoyoshi et al.,
356 2009). Here, T_{\max} is of the order of $250\text{-}280^{\circ}\text{C} \pm 30^{\circ}\text{C}$, i.e. a temperature
357 range in line with the highest of $T_{h,\text{aq}}$ values (Fig. 6 and Tab. 2).

358 It is always possible that circulating fluids were significantly hotter than
359 the host rock, but were not abundant enough to influence the bulk rock tem-

360 perature (i.e. $T_t > T_{\max}$). However, a large temperature discrepancy between
 361 T_t and T_{\max} is unlikely, as the rocks considered here are pervasively filled by
 362 quartz veins, corresponding originally to circulating fluids. Furthermore, in
 363 the case of a large $T_t - T_{\max}$ disequilibrium, fluids would be trapped at various
 364 temperatures ranging from T_{\max} (for small fluid pulses, locally buffered by the
 365 bulk rock temperature) up to the fluid source temperature (for larger fluid
 366 pulses, not buffered). Consequently, we should expect a broad distribution
 367 for trapping temperatures T_t in this case.

368 However, Fig. 6 suggests a simpler solution. Indeed, it is striking that
 369 the bulk rock peak temperatures (T_{\max}) are roughly of the same magnitude
 370 as:

- 371 1. either $T_{h, \text{aq}}$ temperatures of aqueous inclusions (inclusions: Kon-NB26-
 372 ech27 inclusion 26, HN51-4c, HN48b-inc a and inc b, HN87-inc c). In
 373 this case, $T_t = T_{h, \text{aq}}$ and $P_t = P_{h, \text{aq}}$. Most of the aqueous inclusions
 374 have recorded these $P_t - T_t$ conditions.
- 375 2. or temperatures of intersection points between monophasic isochores
 376 of aqueous and gaseous inclusions (inclusions: Kon-NB26-ech27 inclu-
 377 sions 27 and 30). In this case, $T_t = T_{\max}$ and $P_t = P_{\text{aq}}(T_t) = P_g(T_t)$
 378 (where P_g is the pressure of gaseous inclusions along their monophasic
 379 isochores). Both aqueous and gaseous inclusions have recorded these
 380 $P_t - T_t$ conditions, but, as aqueous fluid inclusions are undersaturated
 381 in methane (as they are in the single-phase domain, see Fig. 6), they
 382 are not at equilibrium with gaseous inclusions. In other words, two
 383 fluids penetrated the rock for these $P-T$ conditions, but they were not
 384 at equilibrium with each other, hence not cogenetic. This case is an

385 illustration of the conditions to be fulfilled for two fluids to be at equi-
386 librium, as developed in Ramboz et al. (1982): they must not only
387 share the same P and T but also, in terms of composition, be exactly
388 on the immiscibility surface between a methane-rich and a water-rich
389 fluid. This latter condition can also be expressed as that the common
390 P - T conditions must coincide with the saturation in methane for the
391 aqueous inclusion.

392 In conclusion, we think that trapping occurred:

- 393 1. for roughly constant temperatures $T_t \sim T_{\max}$ with fluids in thermal
394 equilibrium with hosting rocks at temperatures between 250 and 280°C,
- 395 2. but in a retrometamorphic context featured by a large decrease in fluid
396 pressure, from 250 to 50 MPa.

397 Furthermore, in both cases exposed above, aqueous fluids appear to be
398 methane-undersaturated at their (P_t, T_t) trapping conditions, i.e. water-rich
399 and methane-rich fluids, even when trapped for similar P-T conditions, are
400 not at equilibrium with each other. Thus, during exhumation, we should not
401 imagine the rock as being soaked by a single fluid mixture, but rather tran-
402 siently percolated by pulses of higher-pressure, methane-rich fluids coming
403 from the depth and in chemical disequilibrium with the local, lower-pressure
404 aqueous fluid, undersaturated in methane.

405 5.2. Geothermal evolution of the unit of the Hyuga melange unit

406 The trapping conditions inferred in the preceding section correspond to
407 a late-stage event in the polyphased history of the rocks, as aqueous and

408 gaseous inclusions are contained into late-stage veins that postdate the meta-
409 morphic assemblages formed at peak conditions. When comparing the P-T
410 evolution from the metamorphic peak to this late-stage event, pressure de-
411 creased from 300-500 MPa, while temperature remained in the same range
412 (Toriumi and Teruya, 1988), in other words, Hyuga unit was exhumed along
413 a nearly isothermal path (Fig. 6). This exhumation pattern involves a sharp
414 change in the thermal regime, from a geothermal gradient, for peak condi-
415 tions, similar to the current subduction margin of SW Japan (Oleskevich
416 et al., 1999; Hyndman et al., 1995; Peacock, 2009) to a much higher gradient
417 during its late-stage evolution.

418 To estimate precisely this late-stage geothermal gradient from fluid in-
419 clusion data, one needs to know where the fluid pressure is placed between
420 hydrostatic and lithostatic pressure. Assuming hydrostatic fluid pressure
421 yields a lower bound on the gradient; taking sedimentary rock volumic mass
422 as 2.7 g/cm^3 , the lowest fluid pressure recorded by aqueous fluid inclusions,
423 50 MPa (Fig. 6), converts into a lithostatic pressure of 135 MPa, for a
424 temperature of $\sim 250^\circ\text{C}$. This gradient is even higher than in the Cascadia
425 subduction zone, the "hottest" modern margin for which thermal models are
426 available (Oleskevich et al., 1999; Peacock, 2009).

427 The reasons for this thermal event are not yet clear. Terranes of the
428 Shimanto Belt on Shikoku also recorded an event of late-stage heating, with
429 water-rich associated fluids (Sakaguchi, 1996, 1999a,b), interpreted by these
430 authors as the result of the subduction of a paleo-ridge at Eocene time (e.g.
431 Lewis et al. (2000)). In Hyuga *mélange*, the youngest stratigraphic ages of
432 blocks embedded in the matrix are Early Oligocene (Sakai et al., 1984). The

433 thermal event, which postdates the metamorphic deformation of these rocks,
434 must therefore be significantly younger than Early Oligocene, hence cannot
435 be explained by the Eocene paleo-ridge subduction. Another candidate is
436 the subduction of the Shikoku Basin spreading center, on the Philippines sea
437 plate, which was active from Early to Middle Miocene and which subducted
438 nearly perpendicular to the margin (Letouzey and Kimura, 1985; Hall, 2002).
439 As a result, the geothermal gradient in Middle Miocene, resulting from the
440 subduction of an active ridge, was much higher than the modern one or
441 the one that prevailed during the metamorphic deformation of the Hyuga
442 *mélange*. Thermal models for the subduction along the SW Japan of a 15
443 (i.e. the actual margin), 10 and 5 Ma old crust by Hyndman et al. (1995),
444 give for the latter, young and hot oceanic crust, results in relative agreement
445 with the late-stage gradient recorded by the aqueous fluid inclusions. One
446 can also note that the Middle Miocene corresponds to a stage of widespread
447 magmatism, as evidenced by numerous granite and granodiorite intrusions
448 along the margin (Fig. 1), which may have further contributed to heat the
449 deep rocks of the Shimanto accretionary prism. Although precise radiomet-
450 ric dating are not yet available, we tentatively attribute the heating event
451 recorded by the late-stage, aqueous inclusions analyzed here to the Middle
452 Miocene tectonic and paleogeographic settings.

453 *5.3. A sensitive tool for pressure estimations in accretionary prisms*

454 To assess the P - T conditions of fluid circulating at depth, fluid inclusions
455 have been exploited in previous studies in accretionary prisms, like Kodiak
456 in Alaska (Vrolijk, 1987; Vrolijk et al., 1988) or Shimanto in Japan (Lewis
457 et al., 2000; Sakaguchi, 1999a; Kondo et al., 2005). These studies assume that

458 aqueous H₂O-CH₄-NaCl inclusions and gaseous CH₄ inclusions are cogenetic.
459 This hypothesis is attractive as it allows to get a first approximate of the
460 trapping P_t - T_t conditions. However, in practice, the coevality of these fluid
461 inclusions is extremely difficult to ascertain in rocks affected by multiple
462 stages of deformation. Thus, the assumption of cogenetic trapping is no
463 more satisfactory. The procedure we proposed here overcomes the problem
464 and permits to get an independent estimation of trapping pressures P_t of
465 aqueous H₂O-CH₄-NaCl inclusions. Additionally, this method is applicable
466 even in the absence of CH₄ inclusions, as it is often the case in the Hyuga
467 melange unit of the Shimanto Belt in Kyushu. And finally, this procedure
468 is quite sensitive to small variations of bulk methane contents and trapping
469 pressures.

470 To illustrate this point, let's consider the water-rich inclusions described
471 in Vrolijk (1987) and Lewis et al. (2000), whose trapping conditions were
472 determined as $T \sim 260$ - 290°C and $P \sim 175$ - 300 MPa and 210 - 250°C and 80 -
473 100 MPa, respectively. These two examples give an idea of the P - T range
474 of trapping conditions, with a relatively narrow range in temperature and a
475 much larger range in pressure. Using our thermodynamic modeling, we have
476 performed simulations for two inclusions in the system H₂O-CH₄ with the
477 same homogenization temperature $T_{h, \text{aq}} = 250^\circ\text{C}$ and a gas hydrate melting
478 temperature of 9°C and 19°C , respectively (Fig. 7 and Table 3, inclusions a
479 and b). For $T > T_{\text{hyd}}$, inclusions are constituted of two phases, liquid and va-
480 por, and evolve along an isochore up to $T_{h, \text{aq}}$, where the last bubble of vapor
481 disappears. The two inclusions show a much different isochoric evolution up
482 to $T_{h, \text{aq}}$, with a very large pressure increase for inclusion b, up to $P_{h, \text{aq}} = 215$

483 MPa, and a much smaller pressure increase for the inclusion a, up to $P_{h,aq}=48$
484 MPa. The strong contrast between the two inclusions is primarily controlled
485 by the very steep slope of the melting gas hydrate curve. A small increment
486 in T_{hyd} results in a relatively large increase in the inclusion pressure, hence
487 in the density of the methane in the bubble at temperature near ambient
488 conditions: in inclusion a, P_{hyd} is 3 times larger than in inclusion b (Table
489 3). As a result, bulk concentration of methane is larger, so that the pres-
490 sure conditions required to dissolve completely the methane in the water, i.e.
491 $P_{h,aq}$, are much higher. One can note that the influence of T_{hyd} on methane
492 concentration is dominant over volumic fraction: Inclusion a is less concen-
493 trated in methane though the volumic fraction of methane bubble at ambient
494 T is larger than inclusion b. The conclusion of this fictive example is that
495 even a small quantity of methane in the inclusion strongly affects the P-V-T
496 properties of the inclusions and raises their isochoric evolution towards high
497 pressure. Therefore, in accretionary prisms (e.g. Vrolijk (1987); Sakaguchi
498 (1999a)) or collision zones (e.g. Mullis (1979)) where dissolved methane is
499 present in water, the estimation of realistic fluid pressure conditions requires
500 to model the fluid in the ternary system H_2O-CH_4-NaCl . In other words,
501 considering the fluid only in the simplified $H_2O-NaCl$ system, whose liquid-
502 vapor equilibrium curve runs at very low pressure, leads to underestimating
503 the fluid pressure. Our new approach, which solves this systematic bias and
504 can be used even for very low concentrations in methane, calls for a reap-
505 praisal of cases, such as the high-pressure metamorphic stage recorded in the
506 Schistes Lustrés in the Alps (Agard et al., 2000), where a large gap between
507 fluid and mineral pressure was observed.

508 6. Conclusion

509 Fluid inclusions contained in rocks deformed in accretionary prisms or in
510 orogenic contexts are the only key to unravel the composition, temperature
511 and pressure of the fluids circulating at depth.

512 In this work, we have developed a new procedure to study methane-
513 bearing aqueous inclusions, commonly found in such geodynamical contexts.
514 The method depends only on microthermometric data, i.e.: the melting
515 temperature of ice, T_{mi} the melting temperature of gas hydrate, T_{hyd} and
516 the homogenization temperature, $T_{h,aq}$. It completely describes the physico-
517 chemical properties of the aqueous inclusions (bulk density, composition,
518 phase diagram) and $P - T - composition$ of the circulating fluids. This
519 method is based on an integrated algorithm, involving several state-of-the-
520 art thermodynamic models for the H_2O-CH_4-NaCl system (solubility and
521 density calculations, phase equilibria modeling) and has a relative precision
522 within 10 %.

523 Modeling methane-bearing aqueous inclusions in the system H_2O-CH_4-
524 $NaCl$, and not in the simplified $H_2O-NaCl$ system, is necessary to reconstruct
525 reliable fluid pressures in the depths of accretionary prisms or orogens. Fur-
526 thermore, in cases where gaseous CH_4 inclusions are present in addition to
527 aqueous ones, our method enables to discuss the cogenetic character of the
528 two kinds of inclusions, without invoking any textural argument, often ques-
529 tionable in strongly deformed rocks.

530 We have applied this new method to the case study of the Hyuga unit
531 from the Shimanto Belt (Japan). After careful microthermometric measure-
532 ments, we show that aqueous and gaseous inclusions cannot be cogenetic,

533 in other words two fluids (a water-rich and a methane-rich one), in disequi-
534 librium, were trapped in the rock at depth. $P - T$ conditions recorded by
535 aqueous inclusions show that after a nearly isothermal exhumation, a very
536 hot geothermal gradient prevailed during the latest stage of the Hyuga unit
537 evolution.

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545 Raman spectrometry was done at the Thermodynamics Laboratory of the
546 Blaise Pascal University (Clermont-Ferrand).

547 **Appendix A. Detailed equations**

548 Detailed equations, which are given below, are involved in the formulation
549 of mass balance and volume conservation (equation (1)). For the sake of
550 simplicity, it is understood that these equations are expressed for a fluid
551 inclusion having a volume of 1 m^3 .

552 *Appendix A.1. State 1: ice melting*

553 First, when the last piece of ice disappears (state 1) at $T_1 = T_{mi}$, one has:

554

- the number moles of CH₄ and H₂O in the gas:

$$\begin{cases} n_{\text{H}_2\text{O},1}^G = \frac{x_{\text{H}_2\text{O},1}^G (1 - F_1^{Lw} - F_1^H)}{V_1^G} \\ n_{\text{CH}_4,1}^G = \frac{(1 - x_{\text{H}_2\text{O},1}^G) (1 - F_1^{Lw} - F_1^H)}{V_1^G} \end{cases} \quad (\text{A.1})$$

555

- the number of moles of CH₄ and H₂O in the gas hydrate:

$$\begin{cases} n_{\text{H}_2\text{O},1}^H = \frac{F_1^H \rho_1^H x_{\text{H}_2\text{O},1}^H}{M_{\text{CH}_4} x_{\text{CH}_4,1}^H + M_{\text{H}_2\text{O}} x_{\text{H}_2\text{O},1}^H} \\ n_{\text{CH}_4,1}^H = \frac{F_1^H \rho_1^H x_{\text{CH}_4,1}^H}{M_{\text{CH}_4} x_{\text{CH}_4,1}^H + M_{\text{H}_2\text{O}} x_{\text{H}_2\text{O},1}^H} \end{cases} \quad (\text{A.2})$$

556

- and the number of moles of H₂O, CH₄ and NaCl in the aqueous solution:

$$\begin{cases} n_{\text{H}_2\text{O},1}^{Lw} = \frac{F_1^{Lw} \rho_1^{Lw}}{M_{\text{H}_2\text{O}} (1 + M_{\text{CH}_4} m_{\text{CH}_4,1} + M_{\text{NaCl}} m_{\text{NaCl},1})} \\ n_{\text{CH}_4,1}^{Lw} = \frac{F_1^{Lw} \rho_1^{Lw} m_{\text{CH}_4,1}}{1 + M_{\text{CH}_4} m_{\text{CH}_4,1} + M_{\text{NaCl}} m_{\text{NaCl},1}} \\ n_{\text{NaCl},1}^{Lw} = \frac{F_1^{Lw} \rho_1^{Lw} m_{\text{NaCl},1}}{1 + M_{\text{CH}_4} m_{\text{CH}_4,1} + M_{\text{NaCl}} m_{\text{NaCl},1}} \end{cases} \quad (\text{A.3})$$

557

The mole numbers of H₂O, CH₄ and NaCl is then obtained from:

$$\begin{cases} n_{\text{CH}_4,1} = n_{\text{CH}_4,1}^G + n_{\text{CH}_4,1}^{Lw} + n_{\text{CH}_4,1}^H \\ n_{\text{H}_2\text{O},1} = n_{\text{H}_2\text{O},1}^G + n_{\text{H}_2\text{O},1}^{Lw} + n_{\text{H}_2\text{O},1}^H \\ n_{\text{NaCl},1} = n_{\text{NaCl},1}^{Lw} \end{cases} \quad (\text{A.4})$$

558

where different quantities are yielded by equations A.1, A.2 and A.3.

559 *Appendix A.2. State 2: gas hydrate melting*

560 In the same way, similar equations are derived for state 2 (i.e. when the
561 last nugget of gas hydrate melts at $T_2 = T_{\text{hyd}}$):

- 562 • the number of moles of H₂O and CH₄ in the gas:

$$\begin{cases} n_{\text{H}_2\text{O},2}^G = \frac{x_{\text{H}_2\text{O},2}^G (1 - F_2^{Lw})}{V_2^G} \\ n_{\text{CH}_4,2}^G = \frac{x_{\text{CH}_4,2}^G (1 - F_2^{Lw})}{V_2^G} \end{cases} \quad (\text{A.5})$$

- 563 • the number of moles of H₂O, CH₄ and NaCl in the aqueous phase:

$$\begin{cases} n_{\text{H}_2\text{O},2}^{Lw} = \frac{F_2^{Lw} \rho_2^{Lw}}{M_{\text{H}_2\text{O}} (1 + M_{\text{CH}_4} m_{\text{CH}_4,2} + M_{\text{NaCl}} m_{\text{NaCl},2})} \\ n_{\text{CH}_4,2}^{Lw} = \frac{F_2^{Lw} \rho_2^{Lw} m_{\text{CH}_4,2}}{1 + M_{\text{CH}_4} m_{\text{CH}_4,2} + M_{\text{NaCl}} m_{\text{NaCl},2}} \\ n_{\text{NaCl},2}^{Lw} = \frac{F_2^{Lw} \rho_2^{Lw} m_{\text{NaCl},2}}{1 + M_{\text{CH}_4} m_{\text{CH}_4,2} + M_{\text{NaCl}} m_{\text{NaCl},2}} \end{cases} \quad (\text{A.6})$$

- 564 • the total number of moles of H₂O, CH₄ and NaCl in a volume of 1 m³:

$$\begin{cases} n_{\text{H}_2\text{O},2} = n_{\text{H}_2\text{O},2}^G + n_{\text{H}_2\text{O},2}^{Lw} \\ n_{\text{CH}_4,2} = n_{\text{CH}_4,2}^G + n_{\text{CH}_4,2}^{Lw} \\ n_{\text{NaCl},2} = n_{\text{NaCl},2}^{Lw} \end{cases} \quad (\text{A.7})$$

565 where right-hand terms are calculated by equations A.5 and A.6.

566 *Appendix A.3. Bulk volume conservation*

567 And finally, the bulk densities of the fluid inclusion at states 2 and 3, are
568 given respectively by:

$$\begin{cases} \rho_2 = F_2^{L_w} \rho_2^{L_w} + (1 - F_2^{L_w}) \frac{M_{\text{CH}_4} x_{\text{CH}_4,2}^G + M_{\text{H}_2\text{O}} x_{\text{H}_2\text{O},2}^G}{V_2^G} \\ \rho_3 = \rho_3^{L_w} \end{cases} \quad (\text{A.8})$$

569 where densities $\rho_2^{L_w}$ and $\rho_3^{L_w}$ of the aqueous solution are obtained from:

$$\begin{cases} \rho_2^{L_w} = \frac{1 + M_{\text{CH}_4} m_{\text{CH}_4,2} + M_{\text{NaCl}} m_{\text{NaCl},2}}{1/\rho_2^* + m_{\text{CH}_4,2} v_{\text{CH}_4}} \\ \rho_3^{L_w} = \frac{1 + M_{\text{CH}_4} m_{\text{CH}_4,3} + M_{\text{NaCl}} m_{\text{NaCl},3}}{1/\rho_3^* + m_{\text{CH}_4,3} v_{\text{CH}_4}} \end{cases} \quad (\text{A.9})$$

570 where ρ^* is the density (kg/m³) of the H₂O-NaCl aqueous solution for T ,
571 P and m_{NaCl} conditions, and v_{CH_4} is the partial molar volume (m³/mol) of
572 dissolved CH₄ calculated by a solubility model (e.g. Duan et al., 1992).

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713 **Tables**

Table 1: List of symbols

Table 2: Summary of data for seven representative aqueous inclusions from the Hyuga formation. Input data (T_{mi} , T_{hyd} and $T_{h, aq}$ temperatures obtained by microthermometry) permit to characterize the fluid inclusion at different states (in particular, homogenization point and gas hydrate melting point).

Table 3: P-V-T-composition properties of the two fictive inclusions described in 5.3 and in Fig. 7.

714 **Figures**

Figure 1: Simplified geological map of the Shimanto Belt on eastern Kyushu, Japan, from Murata (1997); Taira et al. (1988). The Nobeoka Tectonic Line (NTL) constitutes a major tectonic boundary between northern and southern Shimanto. All the samples studied here in microthermometry (red stars) were collected in the highly deformed Hyuga *mélange* unit, in the footwall of the NTL. Blue dots corresponds to other samples of the same unit, where two-phased, aqueous fluid inclusions are also present. Methane-rich inclusions could be found only near the easternmost extension of the NTL, i.e. near sample Kon-NB26.

Figure 2: Structures of quartz grains and included fluid inclusions. A: A early-stage vein of quartz, elongated parallel to the foliation, is crosscut by a late-stage vein, visible by its lower density in fluid inclusions. The quartz grains constituting the early-stage veins are elongated parallel to the foliation and show undulose extinction, subgrain formation and grain boundary bulging, while the late-stage vein is virtually undeformed. The late-stage vein contains aqueous fluid inclusions, two-phased at ambient temperature. These inclusions are aligned along fracture planes parallel to the vein walls and have themselves an elongated shape parallel to the same direction. B- Undeformed quartz vein showing a variable density of fluid inclusions. Note in picture 2 that a single quartz grain hosts domains of low and high density of inclusions. Fluid inclusions have the same composition and geometry as A. All pictures: optical microscope, A.2 and B.2 with crossed nicols.

Figure 3: Aqueous and gaseous inclusions were the two types of fluid inclusions, which could be easily identified by their very different microthermometric properties and Raman spectra at ambient temperatures. (A) aqueous inclusion, exhibiting a CH₄-rich bubble immersed in an aqueous solution; (B) gaseous inclusion composed essentially by a CH₄ fluid; (C and D) normalized Raman spectra focused on different parts (x, y or z) of the inclusions pictured above. The broad peak of water between 3000 and 3800cm⁻¹ and the ν_1 sharp peak near 2918cm⁻¹ of the methane vapour are well visible (Lin et al., 2007).

Figure 4: Distribution of homogenization temperatures $T_{h,aq}$ of gaseous inclusions in the sample NB25-#46-zoneB, collected near sample Kon-NB26 in Fig. 1.

Figure 5: Determination procedure of T_{mi} (a to d) and T_{hyd} (e to h). We start at low temperatures to nucleate ice (a) or gas hydrate (e). Then, we slowly heat up to some fixed temperature T_i (b and f) and we freeze rapidly the fluid inclusion (c and g). If the freezing triggers movement/deformation of the methane vapor bubble, this means that some ice (gas hydrate) was still present at T_i . Thus, we repeat a new heating/freezing cycle, but with a T_i incremented by 0.1 °C, until the freezing does not induce any detectable change of the bubble behaviour (d and h). The last T_i yields then a good approximation of the disappearance temperature of ice (or gas hydrate).

Figure 6: P - T diagram illustrating the main results obtained from microthermometry and thermodynamic modeling. Black lines are monophasic isochores of gaseous CH_4 inclusions, homogenizing mostly between -115 and -95°C . Blue lines are isochores calculated for the aqueous inclusions: solid curves represent biphasic liquid-gas isochores, whereas dashed lines are monophasic liquid isochores. Biphasic isochores start from gas hydrate melting points (filled diamonds) and end at homogenization points (empty diamonds). The shaded area represents the peak temperatures of host formation estimated from petrological analyses. The dark arrow symbolizes the earliest stage of isothermal exhumation of the formation, starting from peak metamorphic conditions (empty rectangle, from Toriumi and Teruya (1988)), down to the trapping conditions of aqueous fluid inclusions.

Figure 7: P - T evolution of two fictive inclusions in the system H_2O - CH_4 , with the same $T_{h,\text{aq}}=250^\circ\text{C}$ but contrasted T_{hyd} , either 9°C (a) or 19°C (b). Each inclusion is three-phased (liquid+vapour+gas hydrate) from T_{mi} to T_{hyd} , two-phased (liquid+vapour) from T_{hyd} to $T_{h,\text{aq}}$, then single-phased (vapour) for $T > T_{h,\text{aq}}$. Phase transitions occur along the gas hydrate melting curve and the methane solubility curve corresponding to methane concentration of each inclusion. From the comparison of the two inclusion, one can see that a small increase in gas hydrate melting temperature results in a large increase in pressure at homogenization.

715 Supplementary Material: Movies illustrating the cycling procedure to
716 estimate precisely T_{mi} and T_{hyd} . Each cycle is composed of a slow heating
717 phase, followed by rapid freezing. The presence/absence of a crystal of ice or
718 gas hydrate at the maximum temperature T_i of each cycle is detected by the
719 rapid crystal growth upon freezing, which triggers the shrinkage, movement
720 or deformation of the gas bubble. Note that the temperature embedded in
721 the movies needs a correction determined by calibrating the heating/freezing
722 stage.

723 Movie 1: Cycle i to measure T_{mi} . As T is slowly increased up to T_i , the
724 bubble expands. Rapid freezing results in bubble shrinkage, showing that ice
725 was still present at T_i .

726 Movie 2: Cycle j to measure T_{mi} . As T is slowly increased up to T_j , the
727 bubble expands. Rapid freezing has no effect on the bubble, showing that
728 ice was no longer present at T_j .

729 Movie 3: Cycle i to measure T_{hyd} . As T is slowly increased up to T_i , the
730 bubble moves and deforms. Rapid freezing results in the movement of the
731 bubble towards the bottom of the picture, showing that gas hydrate was still
732 present at T_i .

733 Movie 4: Cycle j to measure T_{hyd} . As T is slowly increased up to T_j ,
734 the bubble moves and deforms. Rapid freezing has no effect on the bubble,
735 showing that gas hydrate was no longer present at T_j .

Symbol	Signification
subscript i	component (i either H ₂ O or CH ₄ or NaCl)
superscript j	phase ($j = H$ for gas hydrate; $j = L_w$ for aqueous solution; and $j = G$ for gas)
subscript k	state ($k = 1$ for ice disappearance point; $k = 2$ for gas hydrate disappearance point; $k = 3$ for homogenization point)
n_i	bulk mole density of component i (mol/m ³)
T	temperature
T_{mi}	ice melting temperature
T_{hyd}	gas hydrate melting temperature
$T_{h,aq}$	homogenization temperature of aqueous inclusions
T_h	homogenization temperature
T_t	trapping temperature
T_{max}	rock maximum temperature
P	pressure
P_t	trapping pressure
$P_{h,aq}$	homogenization pressure of aqueous inclusions
P_g	pressure of a gaseous isochore along its monophasic isochore
ρ	bulk mass density of a fluid inclusion (kg/m ³)
ρ_k^j	mass density of phase j at state k
ρ^*	density of a H ₂ O-NaCl aqueous solution
n_i^j	number of moles of component i in phase j
$n_{i,k}^j$	number of moles of component i in phase j

Sample	Kon-NB26-ech			27	HN51	HN48B		HN87
Inclusion	26	29	30	4c	inc a	inc b	inc c	
Data								
T_{mi} (°C)	-3.15	-2.9	-2.3	-3	-1.9	-2	-1.9	
T_{hyd} (°C)	9.5	8.7	8.5	10.25	6.7	5.3	10.4	
$T_{h,aq}$ (°C)	239	198	207	252	248	275	277	
State 3 (homogenization point)								
$P_{h,aq}$ (MPa)	80.9	80.3	69.9	83.0	44.7	35.3	64.1	
ρ_3^{Lw} (kg/m ³)	892	934	914	876	849	809	819	
$m_{CH_4,3}$ (mol/kg H ₂ O)	0.85	0.53	0.57	1.02	0.70	0.76	1.26	
$m_{NaCl,3}$ (mol/kg H ₂ O)	0.83	0.77	0.60	0.77	0.49	0.52	0.46	
State 2 (gas hydrate melting)								
P_2 (MPa)	8.6	7.8	7.3	9.2	5.8	5.1	8.6	
F_2^G %	15	10	12	16	18	22	21	

Table 2:

Sample	a	b
Data		
T_{mi} (°C)	0	0
T_{hyd} (°C)	9	19
$T_{h, aq}$ (°C)	250	250
State 3 (homogenization point)		
$P_{h, aq}$ (MPa)	47.6	215.6
ρ_3^{Lw} (kg/m ³)	824	891
$m_{CH_4, 3}$ (mol/kg H ₂ O)	0.83	1.72
$m_{NaCl, 3}$ (mol/kg H ₂ O)	0	0
State 2 (gas hydrate melting)		
P_2 (MPa)	6.6	20.9
F_2^G %	0.19	0.13

Table 3:

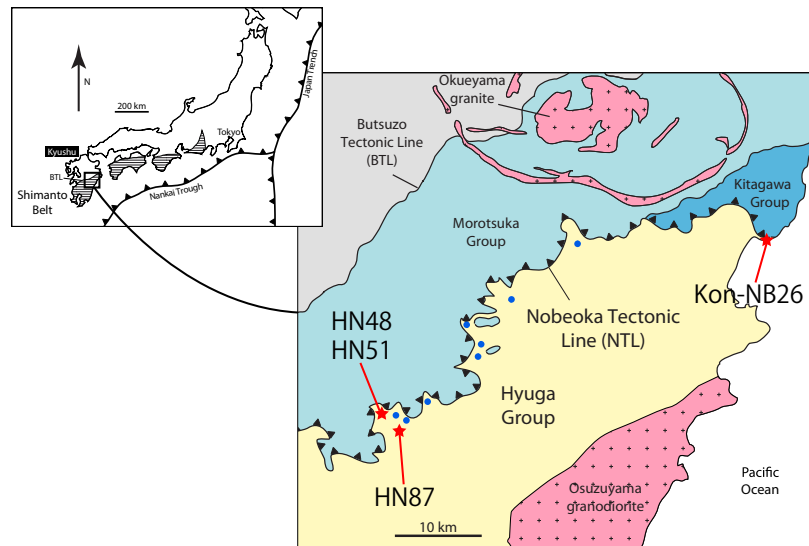


Figure 1:

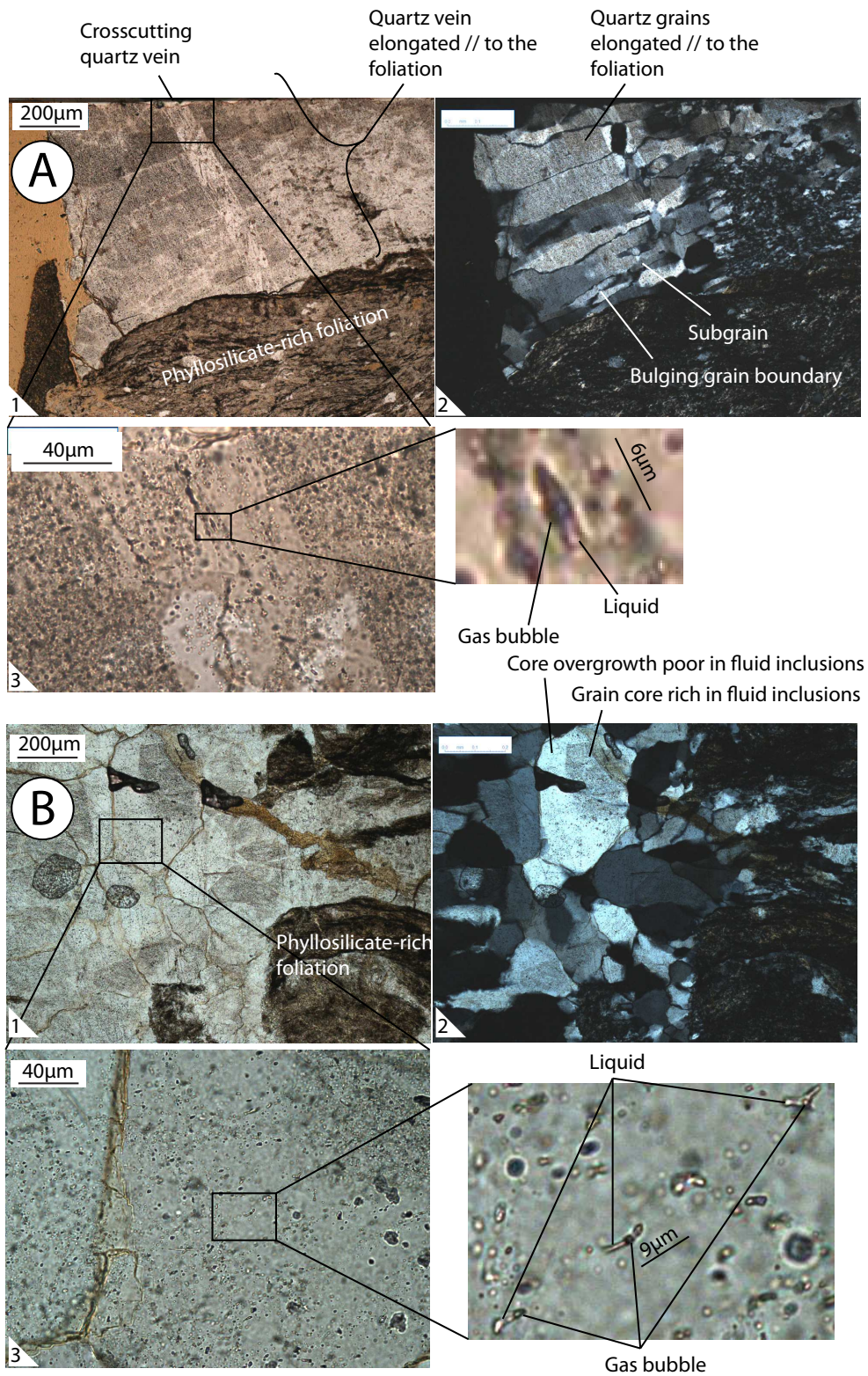


Figure 2:

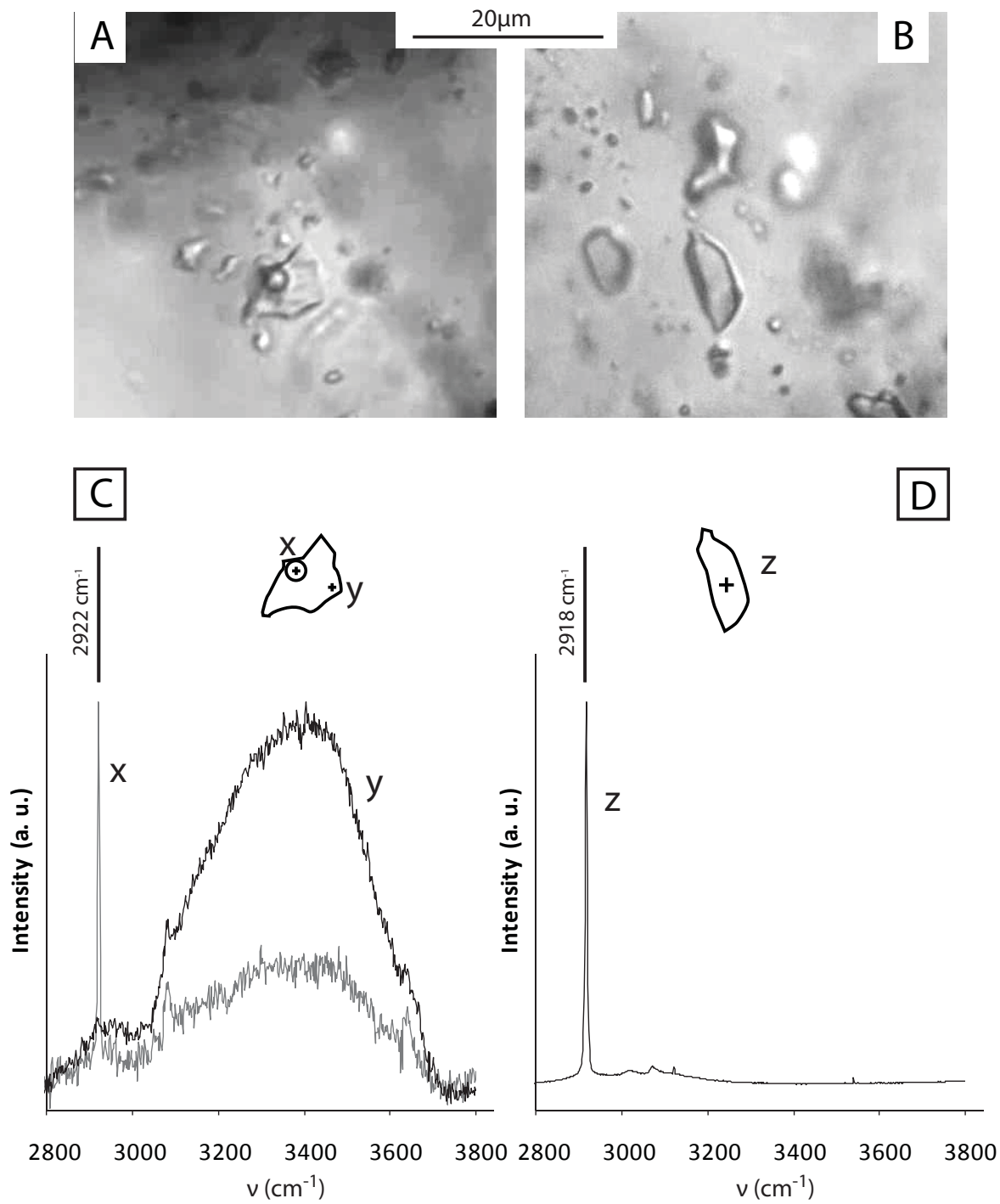


Figure 3:

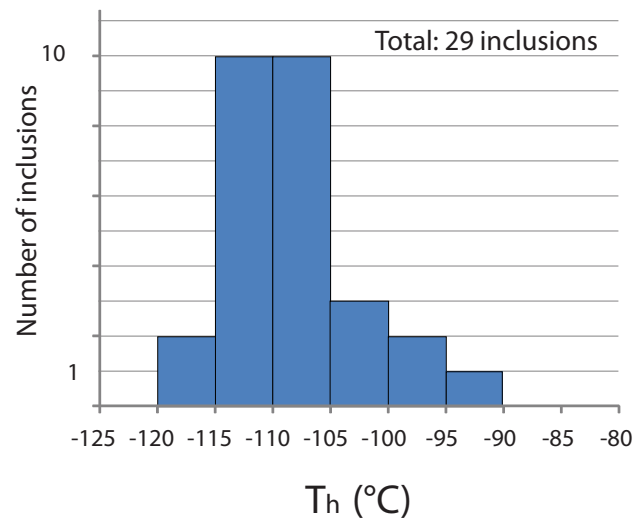


Figure 4:

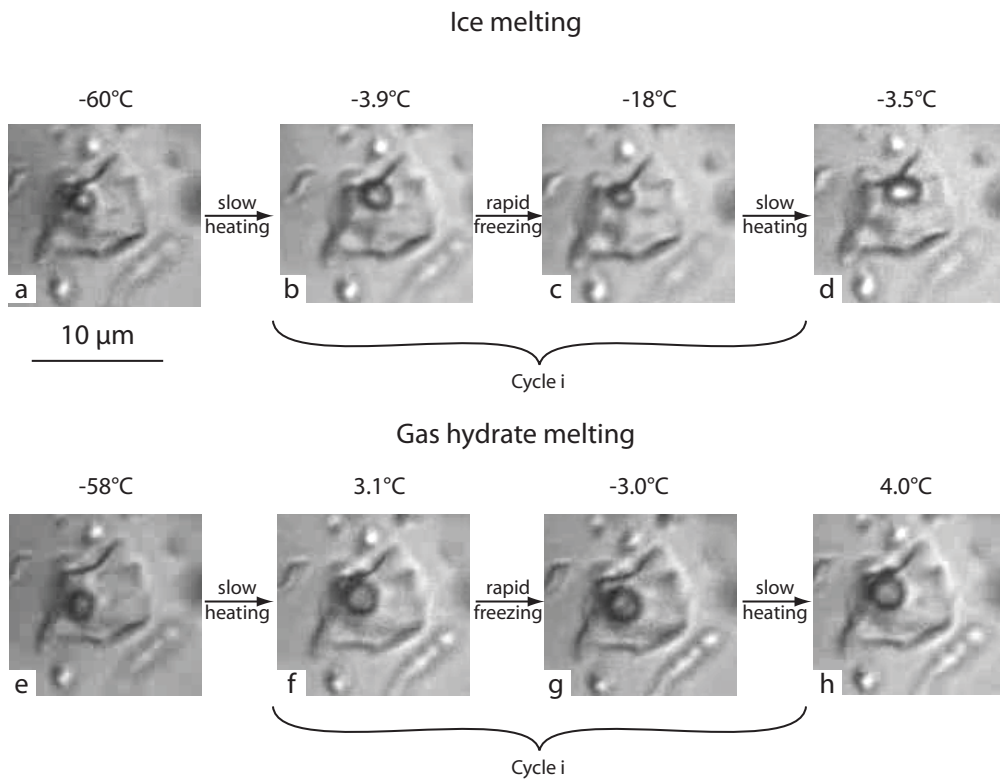


Figure 5:

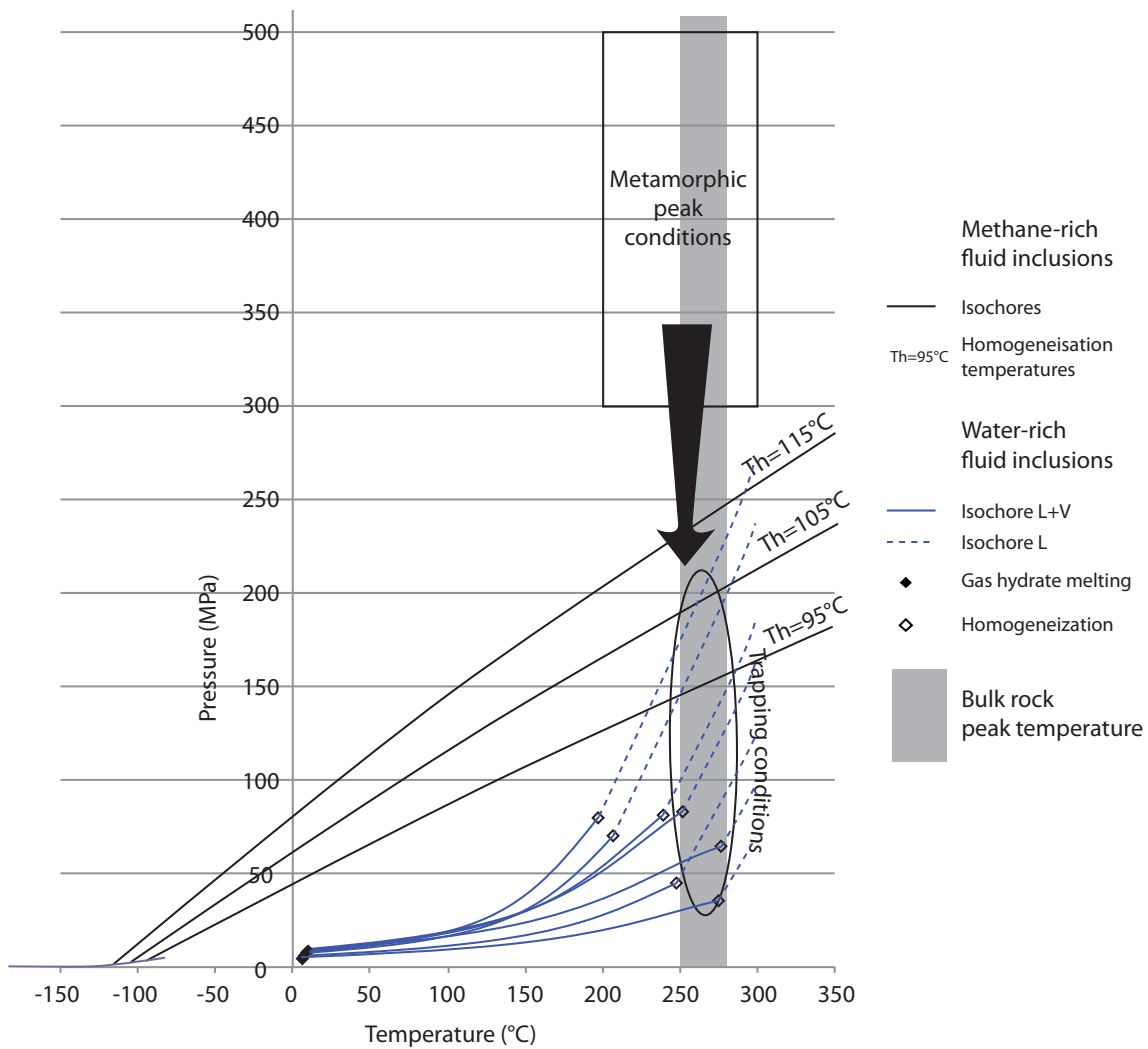


Figure 6:

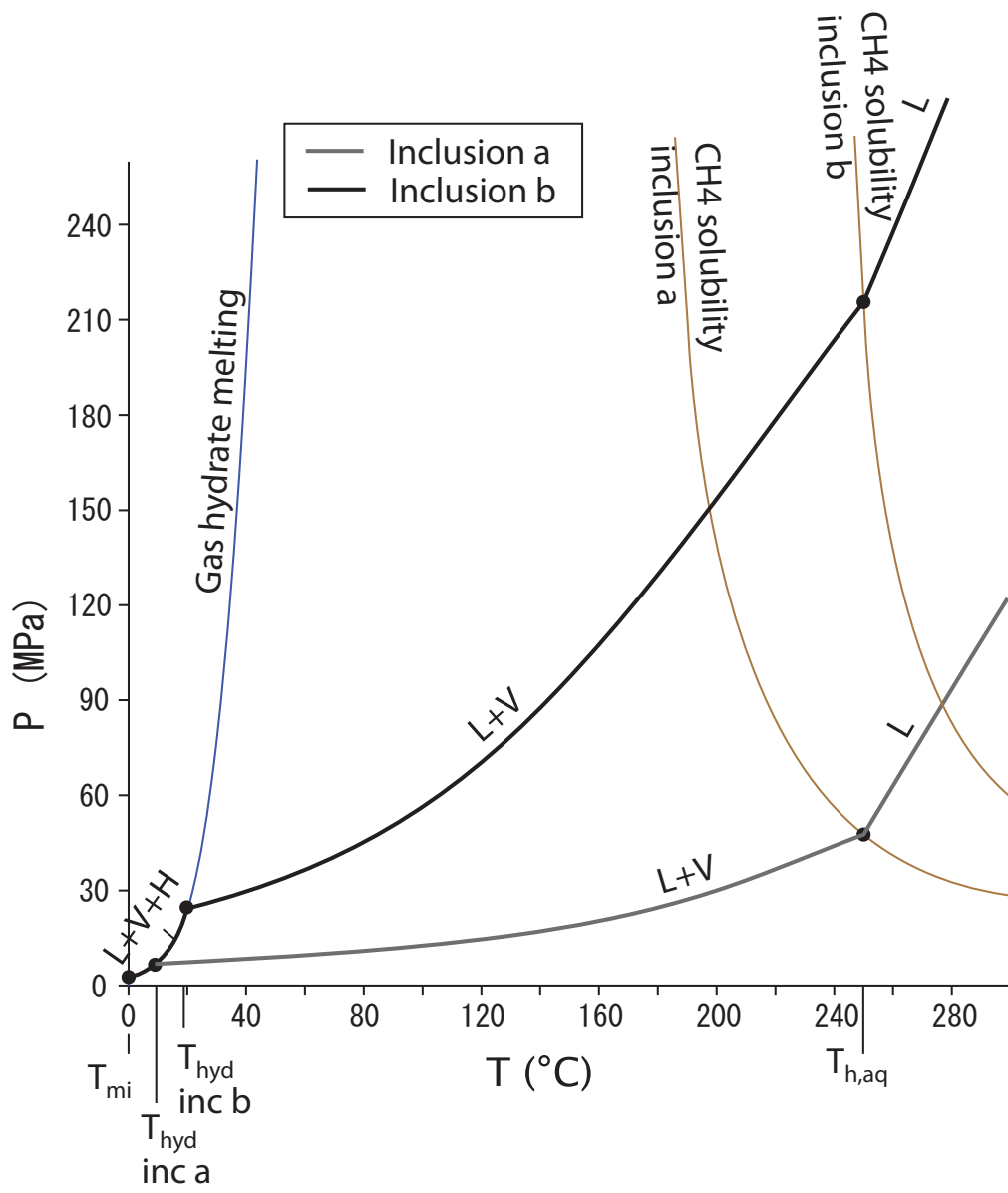


Figure 7: