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

Hugues Raimbourg^{a,b,*}, Régis Thiéry^c, Maxime Vacelet^d, Claire Ramboz^a, Nicolas Cluzel^c, Emmanuel Le Trong^a, Asuka Yamaguchi^e, Gaku Kimura^e

^a*Univ. d'Orléans, ISTO, UMR 7327, 45071, Orléans, France ; CNRS, ISTO, UMR 7327, 45071 Orléans, France ; BRGM, ISTO, UMR 7327, BP 36009, 45060 Orléans, France*

^b*IFREE, Japan Agency for Marine-Earth Science and Technology, 2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan*

^c*LMV, Laboratoire Magmas et Volcans, UMR 6524, CNRS/Clermont Université, Clermont-Ferrand, France*

^d*MINES-Paristech, Centre de Géosciences, 35, rue Saint-Honoré, 77305 Fontainebleau Cedex, France*

^e*Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

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

*Corresponding author

Email addresses: hugues.raimbourg@univ-orleans.fr (Hugues Raimbourg), r.thiery@opgc.univ-bpclermont.fr (Régis Thiéry)

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 approximatively 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. Introduction

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

To this end, the following procedure (e.g. Alderton and Bevins, 1996), which is applicable when aqueous inclusions and methane-rich gaseous inclusions are simultaneously present, is commonly used (see Table 1 for a list of symbols): If one assumes that these inclusions were trapped under the 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

properties of an aqueous CH_4 and NaCl-bearing aqueous inclusion (i.e. bulk density, bulk content, isochoric paths) using three measured phase transition temperatures: T_{mi} , melting temperature of ice; T_{hyd} , melting temperature of gas hydrate and $T_{h,aq}$, homogenization temperature. This new model is described in Section 4 after a discussion of the geological context (Section 2) and of the microthermometric analysis (Section 3).

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

2. Geological context

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

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

96 et al. (2009) describe a lateral temperature gradient from the east ($\sim 250^\circ$ C)
97 to the west ($\sim 280^\circ$ 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° 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

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

2. Using a more extensive sampling of the Hyuga unit than Kondo et al. (2005), we discovered that gaseous CH_4 -rich inclusions are restricted, in fact, to the easternmost side, while water-rich fluid inclusions are distributed throughout the whole unit (blue dots in Fig. 1). Thus, the presence of CH_4 -rich inclusions appears rather as a peculiarity, and aqueous fluids are not necessarily considered to be at equilibrium with a CH_4 -rich phase and thus to represent the liquid aqueous end-member saturated with respect to a vapour CH_4 -rich phase.

As a consequence, these preliminary observations lead us to question the effective circulation of mixtures of methane-saturated waters and CH_4 gas during the trapping of fluid inclusions.

3. Microthermometry

3.1. Apparatus

The selected quartz fragments were placed on a 200 μm -thick, 1.6 cm-wide rounded glass window on top of the silver block of the THMS-600 Linkam heating-cooling stage. Phase changes in the inclusions were observed using an Olympus BHS microscope equipped with a $\times 80$ ULWD Olympus objective and recorded by a Marlin black and white camera (CMOS 2/3" sensor, resolution 1280×1024 pixels, pixel size of 6.7 μm). Temperature was measured using a class B Pt 100 thermistance, which has an intrinsic precision of 0.15° 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

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

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

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

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

In practice, for ice, initial freezing was done at a temperature around -35 to -40°C (step 1), where ice filled instantaneously the inclusion. For gas hydrate, the temperature of initial freezing was above T_{mi} , i.e. at a state 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 $T_{h,aq}$) measured for
258 seven aqueous inclusions. Homogenization temperatures $T_{h,aq}$ 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:

$$\left\{ \begin{array}{l} n_{H_2O,1} = n_{H_2O,2} \\ n_{CH_4,1} = n_{CH_4,2} \\ n_{NaCl,1} = n_{NaCl,2} \\ \rho_2 = \rho_3 \end{array} \right. \quad (1)$$

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, H_2O , CH_4 and
 290 NaCl , between state 1 (ice melting) and state 2 (gas hydrate melting) in a
 291 fluid inclusion of 1 m^3 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 $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}$ 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: $F_1^{L_w}$, the volume proportion of the aqueous liquid
 306 at state 1; F_1^H , the volume proportion of gas hydrate at state 1; $F_2^{L_w}$, 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 H_2O -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). CH_4 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 cristallinity (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

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

In conclusion, we think that trapping occurred:

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

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

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

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

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

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

The reasons for this thermal event are not yet clear. Terranes of the Shimanto Belt on Shikoku also recorded an event of late-stage heating, with water-rich associated fluids (Sakaguchi, 1996, 1999a,b), interpreted by these authors as the result of the subduction of a paleo-ridge at Eocene time (e.g. Lewis et al. (2000)). In Hyuga *mélange*, the youngest stratigraphic ages of 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 $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}$ inclusions and gaseous CH_4 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 $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}$ inclusions. Additionally, this method is applicable
 466 even in the absence of CH_4 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 $T \sim 260\text{-}290^\circ\text{C}$ and $P \sim 175\text{-}300$ MPa and $210\text{-}250^\circ\text{C}$ 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 $\text{H}_2\text{O}-\text{CH}_4$ 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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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 H_2O and CH_4 in the gas:

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

- 563 • the number of moles of H_2O , CH_4 and NaCl in the aqueous phase:

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

- 564 • the total number of moles of H_2O , CH_4 and NaCl in a volume of 1 m^3 :

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

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/m^3) of the H_2O - NaCl aqueous solution for T ,
571 P and m_{NaCl} conditions, and v_{CH_4} is the partial molar volume (m^3/mol) of
572 dissolved CH_4 calculated by a solubility model (e.g. Duan et al., 1992).

573 References

- 574 Agard, P., Goffé, P., Touret, J.L.R., Vidal, O., 2000. Retrograde mineral and
575 fluid evolution on high-pressure metapelites (Schistes lustrés unit, Western
576 Alps). *Contrib. Mineral. Petrol.* 140, 296–315.
- 577 Alderton, D., Bevins, R., 1996. P – T conditions in the South Wales Coalfield:
578 evidence from coexisting hydrocarbon and aqueous fluid inclusions. *J.*
579 *Geol. Soc. London* 153, 265–275.
- 580 Bakker, R., 1997. Clathrates: Computer programs to calculate fluid inclu-
581 sion v-x properties using clathrate melting temperature. *Computers &*
582 *Geosciences* , 1–18.
- 583 Bakker, R., Thiéry, R., 1994. Application of clathrates to fluid inclusion
584 studies, in: De Vivo, B., Frezzotti, M. (Eds.), *Fluid inclusions in minerals:*
585 *methods and applications.*, Virginia Tech, Blacksburg, USA. pp. 191–208.

- 586 Berman, R., 1991. Thermobarometry using multi-equilibrium calculation: a
587 new technique, with petrological applications. *The Canadian Mineralogist*
588 29, 833–855.
- 589 Dalla Torre, M., DeCapitani, C., Frey, M., Underwood, M., Mullis, J., Cox,
590 R., 1996. Very low-temperature metamorphism of shales from the Diablo
591 Range, Franciscan Complex, California: New constraints on the exhuma-
592 tion path. *GSA. Bull.* 108, 578–601.
- 593 Duan, Z., Mao, S., 2006. A thermodynamic model for calculating methane
594 solubility, density and gas phase composition of methane-bearing aqueous
595 fluids from 273 to 523K and 1 to 2000 bars. *Geochim. Cosmochim. Acta*
596 70, 3369–3386.
- 597 Duan, Z., Moller, N., Greenberg, J., Weare, J., 1992. The prediction of
598 methane solubility in natural waters to high ionic strength from 0 to 250 °C
599 and from 0 to 1600 bar. *Geochim. Cosmochim. Acta* 56, 1451–1460.
- 600 Dubessy, J., Thiéry, R., Canals, M., 1992. Modelling of phase equilibria
601 involving mixed gas clathrates: Application to the determination of molar
602 volume of the vapour phase and salinity of the aqueous solution in fluid
603 inclusions. *Eur. J. Mineral.* 4, 873–884.
- 604 El Mekki-Azouzi, M., 2010. Etude expérimentale de l’eau et des solutions
605 aqueuses métastables - implications pour le milieu naturel. Ph.D. thesis.
606 ISTO. Université d’Orléans. Orléans.
- 607 Hall, R., 2002. Cenozoic geological and plate tectonic evolution of SE Asia

- 608 and the SW Pacific: Computer-based reconstruction, models and anima-
609 tions. *J. Asian Earth Sci.* 20, 353–431.
- 610 Hara, H., Kimura, K., 2008. Metamorphic cooling history of the Shimanto
611 accretionary complex, Kyushu, southwest Japan: Implications for the tim-
612 ing of out-of-sequence thrusting. *Island Arc* 17, 546–559.
- 613 Hyndman, R., Wang, K., Yamano, M., 1995. Thermal constraints on the seis-
614 mogenic portion of the southwestern Japan subduction thrust. *J. Geophys.*
615 *Res.* 100, 15,373–15,392.
- 616 Imai, I., Teraoka, Y., Okumura, K., 1971. Geologic structure and metamor-
617 phic zonation of the northeastern part of the Shimanto terrane in Kyushu,
618 Japan. *J. Geol. Soc. Jap.* 77, 207–220.
- 619 Kondo, H., Kimura, G., Masago, H., Ohmori-Ikehara, K., Kitamura, Y., Ike-
620 sawa, E., Sakaguchi, A., Yamaguchi, A., Okamoto, S., 2005. Deformation
621 and fluid flow of a major out-of-sequence thrust located at seismogenic
622 depth in an accretionary complex: Nobeoka Thrust in the Shimanto Belt,
623 Kyushu, Japan. *Tectonics* 24, 1–16.
- 624 Letouzey, J., Kimura, M., 1985. Okinawa trough genesis: Structure and
625 evolution of a backarc basin developed in a continent. *Mar. Petrol. Geol.*
626 2, 111–130.
- 627 Lewis, J., Byrne, T., Pasteris, J., London, D., Morgan VI, G., 2000. Early
628 Tertiary fluid flow and pressure–temperature conditions in the Shimanto
629 accretionary complex of southwest Japan: constraints from fluid inclusions.
630 *J. Metamorphic Geol.* 18, 319–333.

631 Lin, F., Sum, A., Bodnar, R., 2007. Correlation of methane raman ν_1 band
632 position with fluid density and interactions at the molecular level. *J. Ra-*
633 *man Spectrosc.* 38, 1510–1515.

634 Mao, S., Duan, Z., Zhang, D., Shi, L., Chen, Y., Li, J., 2011. Thermodynamic
635 modeling of binary CH₄-H₂O fluid inclusions. *Geochim. Cosmochim. Ac.*
636 75, 5892–5902.

637 Mukoyoshi, H., Hirono, T., Hara, H., Sekine, K., Tsuchiya, N., Sakaguchi,
638 A., Soh, W., 2009. Style of fluid flow and deformation in and around an
639 ancient out-of-sequence thrust: An example from the Nobeoka tectonic
640 line in the Shimanto accretionary complex, southwest Japan. *Island Arc*
641 18, 333–351.

642 Mullis, J., 1979. The system methane-water as a geological thermometer and
643 barometer from the external part of the Central Alps. *Bull. Mineral.* 102,
644 526–536.

645 Mullis, J., Dubessy, J., Poty, B., O’Neil, J., 1994. Fluid regimes during late
646 stages of a continental collision: Physical, chemical, and stable isotope
647 measurements of fluid inclusions in fissure quartz from a geotraverse in the
648 Central Alps, Switzerland. *Geochim. Cosmochim. Ac.* 58, 2239–2267.

649 Munck, J., Skold-Jorgensen, S., Rasmussen, P., 1988. Computation of for-
650 mation of gas hydrates. *Chem. Eng. Sci.* 43, 2661–2672.

651 Murata, A., 1997. Geological map of Miyazaki prefecture (1:200,000).

652 Oleskevich, D., Hyndman, R., Wang, K., 1999. The updip and downdip
653 limits to great subduction earthquakes: Thermal and structural models

654 of Cascadia, south Alaska, SW Japan and Chile. *J. Geophys. Res.* 104,
655 14,965–14,991.

656 Peacock, S., 2009. Thermal and metamorphic environment of subduction
657 zone episodic tremor and slip. *J. Geophys. Res.* 114, 1–9.

658 Pichavant, M., Ramboz, C., Weisbrod, A., 1982. Fluid immiscibility in nat-
659 ural processes : use and misuse of fluid inclusion data. I. phase equilibria
660 analysis-a theoretical and geometrical approach. *Chem. Geol.* 37, 1–27.

661 Pitzer, K., 1973. Thermodynamics of electrolytes. 1: Theoretical basis and
662 general equations. *J. Phys. Chem.* 77, 268–277.

663 Potter, R., Brown, D., 1977. The volumetric properties of aqueous sodium
664 chloride solutions from 0 °C to 500 °C at pressures up to 2000 bars based
665 on a regression of available data in the literature. preliminary steam tables
666 for NaCl solutions. *Geological Survey Bulletin* 1421-C, 1–45.

667 Powell, R., Holland, T., 1988. An internally consistent dataset with un-
668 certainties and correlations: 3. applications to geobarometry, worked ex-
669 amples and a computer program. *Journal of Metamorphic Geology* 6,
670 173–204.

671 Ramboz, C., 1980. Problèmes posés par la détermination de la compo-
672 sition de fluides carboniques complexes, à l’aide des techniques microther-
673 mométriques. *C. R. Acad. Sc. Paris, serie D* 290, 499–502.

674 Ramboz, C., Pichavant, M., Weisbrod, A., 1982. Fluid immiscibility in nat-
675 ural processes: Use and misuse of fluid inclusion data. ii. interpretation of
676 fluid inclusion data in terms of immiscibility. *Chem. Geol.* 37, 29–48.

- 677 Sadofsky, S., Bebout, G.E., 2004. Field and isotopic evidence for fluid mo-
678 bility in the Franciscan Complex: Forearc paleohydrology to depths of 30
679 kilometers. *Int. Geol. Rev.* 46, 1053–1088.
- 680 Sakaguchi, A., 1996. High paleogeothermal gradient with ridge subduction
681 beneath the Cretaceous Shimanto accretionary prism, southwest Japan.
682 *Geology* 24, 795–798.
- 683 Sakaguchi, A., 1999a. Thermal maturity in the Shimanto accretionary prism,
684 southwest Japan, with the thermal change of the subducting slab: Fluid
685 inclusion and vitrinite reflectance study. *Earth Planet. Sci. Lett.* 173, 61–
686 74.
- 687 Sakaguchi, A., 1999b. Thermal structure and paleo-heat flow in the Shimanto
688 accretionary prism Shimanto accretionary prism. *The Island Arc* 8, 359–372.
- 689 Sakai, T., Nishi, H., Saito, T., Nakaseko, K., Nishimura, A., 1984. Microfossil
690 stratigraphy of the paleogene system in Kyushu Shimanto belt, in: T., S.,
691 Okada, H., Kaiho, K. (Eds.), *Biostratigraphy and international correlation*
692 *of the Paleogene system in Japan*, Virginia Tech. pp. 95–112.
- 693 Setzmann, U., Wagner, W., 1991. A new equation of state and tables of
694 thermodynamic properties for methane covering the range from the melting
695 line to 625K at pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data* 20,
696 1061–1151.
- 697 Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equa-
698 tion of state. *Chem. Eng. Sci.* 27, 1197–1203.

- 699 Spivey, J., McCain, W., North, R., 2004. Estimating density, formation vol-
700 ume factor, compressibility, methane solubility, and viscosity for oilfield
701 brines at temperatures from 0 to 275 °C, pressures to 200 MPa, and salin-
702 ities to 5.7 mole/kg. *J. Can. Petrol. Technol* 43, 52–60.
- 703 Taira, A., Katto, J., Tashiro, M., Okamura, M., Kodama, K., 1988. The
704 Shimanto Belt in Shikoku, Japan—Evolution of Cretaceous to Miocene ac-
705 cretionary prism. *Modern Geology* 12, 5–46.
- 706 Toriumi, M., Teruya, J., 1988. Tectono-metamorphism of the Shimanto Belt.
707 *Modern Geology* 12, 303–324.
- 708 Vrolijk, P., 1987. Tectonically-driven fluid flow in the Kodiak accretionary
709 complex, Alaska. *Geology* 15, 466–469.
- 710 Vrolijk, P., Myers, G., Moore, J., 1988. Warm fluid migration along tectonic
711 melanges in the Kodiak accretionary complex, Alaska. *J. Geophys. Res.*
712 93, 10,313–10,324.

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 CH_4 -rich bubble immersed in an aqueous solution; (B) gaseous inclusion composed essentially by a CH_4 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: