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1 **Metamorphic reactions and their implication for the fluid budget in metapelites at seismogenic depths**
2 **in subduction zones**

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13 **Abstract**

14 In order to determine fluid-mineral reactions and the fluid budget in subduction zones, we have examined
15 rocks from two accretionary complexes, the Kodiak (Alaska) and Shimanto (Japan), that were buried at
16 the temperature conditions of the seismogenic zone. Maximum burial temperatures based on Raman
17 spectroscopy of carbonaceous material in both examples range from 230 to 350°C, whereas pressures
18 reached up to ~3 and ~4kbars (based on multi-equilibrium modelling) in the higher-grade units of the
19 Japanese and Alaskan complexes, respectively. At 230-260°C, chlorite is interpreted as a coproduct of the
20 lower-grade smectite-to-illite transformation. Chlorite content increases as temperature increases to 330-
21 350°C, as a result of illite-to-chlorite transformation. Other reactions include pyrite oxidation, dissolution
22 of titanite and precipitation of anatase. Whole-rock chemistry points to the absence of systematic
23 chemical variations in the temperature range between 250 and 350°C and only local transport of quartz
24 and albite from the matrix, to veins nearby, is observed. Qualitative analyses of the composition of fluid
25 inclusions using decrepitation method show that the composition of the fluid is significantly different from
26 the original seawater trapped in pores. In addition, the salinity of fluid inclusions in the quartz veins at
27 230-260°C, analyzed using the Raman spectrum of water, is lower than seawater and interpreted as
28 dilution of the original seawater by the fresh water released by the smectite-to-illite transformation. In

29 contrast, veins formed at 330-350°C contain fluid inclusions with a salinity on the order of or higher than
30 that of seawater. The increase in salinity for temperatures of 250-350°C reflects hydration reactions,
31 which are mostly controlled by chlorite crystallization. This study demonstrates an uptake of pore fluid by
32 mineral reactions at temperature corresponding to the base of the seismogenic zone, which is in contrast
33 to the general trend of dehydration reactions occurring along rock burial in subduction zones.

34 **1. Introduction**

35 Fluids are heavily involved in the majority of subduction zone processes. For instance, the presence of
36 pore fluids highly impacts the rheological behavior of subducted lithologies (e.g., Fagereng et al., 2018;
37 Hacker et al., 2003; Muñoz-Montecinos, Angiboust, & Garcia-Casco, 2021), and influences seismic activity
38 via pore fluid pressure variations (Audet & Schwartz, 2013; Davis et al., 1983; Saffer & Tobin, 2011).
39 Dehydration reactions in deeply subducted lithologies are also responsible for the generation of arc
40 magmas due to the melting action of volatile species of the mantle (Bebout, 1991; Elliott, 2003; Hacker,
41 2008; Stern, 2011). Because fluids are reactants or products of metamorphic reactions, their abundance,
42 nature and chemistry change with burial. Beyond the drilling reach of ODP/IODP programs (<5 km), our
43 knowledge of fluid composition mostly relies on studies of fluid inclusions and mineral transformations in
44 rocks from exhumed subducted complexes (e.g., Agard et al., 2000; Herviou et al., 2021; Raimbourg et al.,
45 2018; Scambelluri et al., 2015). In veins that have trapped deep fluids as fluid inclusions, the most
46 commonly retrieved property is salinity, converted to NaCl equivalent with the assumption that NaCl is
47 the dominant species (Agard et al., 2000; Brantley & Fisher, 1997; Herviou et al., 2021; Kondo et al., 2005;
48 Nishiyama et al., 2021; Raimbourg, 2015, 2018; Rossetti et al., 2006; Rowe et al., 2009; Sadofsky & Bebout,
49 2004). However, few studies have actually analyzed the chemistry of the occluded fluid (e.g., Scambelluri
50 et al., 2004, 2015; Yoshida et al., 2015).

51 Sediments are the major carriers of fluids (mostly water) into subduction zones (Jarrard, 2003; Plank,
52 2014; Stern, 2002), together with the altered and serpentinized oceanic lithosphere (Peacock, 1993;
53 Schmidt & Poli, 2014; Reynard, 2013; Rupke, 2004). Average seafloor shales contain up to 70 vol.% of pore
54 fluids that are chemically similar to sea water, and about 7 wt.% as crystal-bound H₂O (Plank, 2014). During
55 burial, most of the interstitial water is expelled from sediments at shallow depths by compaction and
56 cementation processes; leaving only <10 vol.% in pore spaces (Fagereng et al., 2018; Kastner et al., 2014;
57 Kominz & Pekar, 2001; Saffer & Tobin, 2011). Following pore collapse, the occurrence of prograde
58 metamorphic reactions controls the water budget (Rupke, 2004; Schmidt & Poli, 2014). The smectite-to-
59 illite transformation occurs in the temperature range 60-150°C and releases significant amount of H₂O

60 that is bounded in minerals, thus, it reduces the salinity of pore fluids (e.g., Kastner et al., 2014; Saffer et
61 al., 2012). Upon further burial, several important dehydration reactions have been reported above 400°C,
62 such as carpholite and chlorite breakdown in the blueschist facies or the glaucophane, as well as lawsonite
63 and chlorite breakdown in the eclogite facies (Agard et al., 2001; Angiboust & Agard, 2010; Bebout, 1991;
64 Bebout et al., 2013; Becker et al., 2000; van Keken et al., 2002; Lefeuvre et al., 2020; Muñoz-Montecinos
65 et al., 2021; Peacock, 1993; Simons et al., 2010; Spandler et al., 2003). Beside dehydration reactions, other
66 mineral transformations may strongly impact to the chemical composition of fluids, such as the
67 transformation of biotite into chlorite, which is correlated to the transition of CH₄-dominated to CO₂-
68 dominated fluids (Dubessy et al., 1983; Ferry, 1981; Hall, 1986; Tarantola et al., 2007, 2009).

69 Only few metamorphic reactions have been identified in subducted sediments in the range 150-350°C,
70 such as the formation of lawsonite and Mg-Fe carpholite (Goffé & Chopin, 1986; Lefeuvre et al., 2020).
71 Many exhumed sub-greenschist and greenschist facies rocks (peak-metamorphism at 150-350°C) contain
72 evidence of ancient fluid pathways in form of metamorphic veins, such as the Kodiak accretionary prism
73 in Alaska (Brantley & Fisher, 1997; Fisher et al., 1995; Fisher & Brantley, 2014; Vrolijk et al., 1988), the
74 Shimanto Belt in Japan (Nishiyama et al., 2021; Raimbourg et al., 2015, 2018), the Franciscan Complex in
75 California, or the Otago Schists in New Zealand (Breeding & Ague, 2002; Fagereng et al., 2011). However,
76 the mineral reactions and the influence of reactions on the pore fluid budget is relatively poorly
77 documented compared to deeper metamorphism (e.g., Fagereng & Cooper, 2010; Frey, 1978; Kameda et
78 al., 2011a; Rahn et al., 1994; Raimbourg et al., 2009; Schmidt et al., 1997; Wang, 1996).

79 The objective of this study is to fill this knowledge gap, by describing the prograde evolution of mineral
80 assemblages, the scale of chemical transport and the fluid budget in sediments subducted and buried
81 down to greenschist facies. To do so, we targeted two accretionary prisms: Kodiak and the Shimanto Belt,
82 because the peak-metamorphic conditions are well preserved and constrained to 200-350°C at both
83 localities (Brantley & Fisher, 1997; Palazzin et al., 2016; Raimbourg et al., 2014, 2021; Rowe et al., 2009;
84 Vrolijk et al., 1988). First, we studied changes in microstructures, mineralogy and whole-rock chemistry
85 with increasing temperature. Mineral chemistry was then used to test the mineral equilibrium for possible
86 estimations of the pressure-temperature conditions based on multi-phase equilibrium model (Dubacq et
87 al., 2010; Vidal et al., 2006). Finally, we studied fluid inclusions as fluid witnesses of the deep metamorphic
88 reactions. Based on these results, we propose several mineral reactions and evaluate fluid-rock
89 interactions, as well as changes in the salinity among subduction-related fluids from the two paleo-

90 accretionary complexes. Our results are of importance for quantifying the fluid budget of sediments
91 undergoing burial in the greenschist facies realm during subduction.

92

93 **2. Geological settings and sampling strategy**

94 We sampled metapelites and adjacent veins along various units of the two selected accretionary prisms
95 (Fig. 1; Palazzin et al., 2016; Raimbourg et al., 2021) to investigate the dependence of fluid-mineral
96 reactions on peak-metamorphic temperature and pressure. The list of samples and their peak-
97 metamorphic conditions is presented in Table 1.

98 **2.1. Kodiak accretionary complex**

99 Kodiak is a paleo-accretionary complex exposed in Kodiak archipelago, southern Alaska, which consists of
100 coherent slices of metasediments and tectonic mélanges (Fig. 1a) that decrease in age towards the
101 modern trench (Byrne & Fisher, 1987; Connelly, 1978; Moore et al., 1983; Plafker et al., 1994). The Kodiak
102 accretionary complex is classically divided into several trench-parallel units (Fig. 1a). The Late Cretaceous
103 Kodiak Formation consists of deep trench sediments. The formation is subdivided into three belts
104 (Landward, Central and Seaward Belts), which are also characterized by the peak-metamorphic
105 temperature and structural fabric variations (Brantley & Fisher, 1997; Rowe et al., 2009; Sample & Fisher,
106 1986; Vrolijk et al., 1988). The Kodiak Landward Belt (KLB) in Uyak Bay consists of intercalated
107 sandstone/siltstone and mudstone beds (Fig. 2a), with occasionally disrupted strata closer to its northern
108 boundary marked by the Uganik Thrust (Fisher & Byrne, 1987; Rowe et al., 2009). The veins from Landward
109 Belt are Mode 1 (Mode 1 veins refer to mineralized fractures characterized by the opening direction
110 perpendicular to the fracture plane; Bons et al., 2012) quartz-calcite veins oriented almost perpendicular
111 to the bedding stratification (Fig. 2a) and are interpreted as forming in the sediments during
112 underthrusting, where the maximum compressive stress (σ_1) is in sub-vertical position (Byrne & Fisher,
113 1990; Fisher & Byrne, 1990). The temperatures derived from fluid inclusions in Mode 1 quartz veins are in
114 the range of 215-255°C for the Landward Belt at Raspberry and Afognak islands (Vrolijk et al., 1988). The
115 Kodiak Central Belt (KCB), investigated in Seal Bay, is characterized by a sub-horizontal bedding
116 stratification and foliation (S_1), with top-to-the-trench shear bands and recumbent folds (Raimbourg et
117 al., 2021; Sample & Fisher, 1986; Sample & Moore, 1987). In Seal Bay, two types of veins have been
118 observed: Shear veins at low angle to the foliation with a fibrous structure parallel to the stretching
119 direction on foliation plane, and Mode 1 quartz veins, often in form of en échelon arrays (Fig. 2c). En

120 échelon veins cut across the foliation but are folded perpendicular to the foliation and are interpreted as
121 formed at peak metamorphic conditions (Fisher & Brantley, 2014; Raimbourg et al., 2021). The Central
122 Belt experienced the highest metamorphic conditions of the Kodiak Formation, reaching temperatures of
123 $\sim 330^{\circ}\text{C}$ as determined from Raman spectroscopy of carbonaceous material (RSCM; Raimbourg et al.,
124 2021). Towards the southeast, the Kodiak Seaward Belt (KSB) is characterized by intercalated sandstone
125 and shale layers. This belt experienced horizontal noncoaxial shortening with top-to-the-SE thrust faults
126 (Sample & Moore, 1987). Vitrinite reflectance in the Kodiak Formation has an average value of 3.73 and
127 corresponds to a temperature of $\sim 225^{\circ}\text{C}$ (Sample & Moore, 1987).

128 **2.2. Shimanto Belt, Japan**

129 The Shimanto Belt is a paleo-accretionary wedge (Taira, 1988) exposed on the islands of Honshu, Kyushu
130 and Shikoku in Japan. It is composed of several parallel units elongated SW-NE and stacked from the NW
131 to the SE, this general trend is consistent with the active Nankai Trough (Fig. 1b). The Shimanto Belt in
132 Kyushu is also divided into several units, among which two are selected for this study, the Foliated
133 Morotsuka and the Hyuga Tectonic Mélange.

134 The Foliated Morotsuka (FM) is composed of sheared and strongly foliated lithologies, including deep-sea
135 sediments and basaltic lenses embedded within a metapelitic matrix. The age of the sediments range from
136 the Cenomanian to the Turonian (Saito et al., 1996). A strong metamorphic foliation is present, along with
137 a N-S and NNW-SSE stretching lineation (Raimbourg et al., 2009, 2014; Ujiie et al., 2018). The Foliated
138 Morotsuka is separated from the Hyuga Group by the Nobeoka Tectonic Line (NTL; Teraoka & Okumura,
139 1992), an out-of-sequence thrust (Kondo et al., 2005). Based on metamorphic assemblages in basaltic
140 lenses, the pressure-temperature conditions in the FM were estimated to be 3-5 kbar and $300\text{-}350^{\circ}\text{C}$
141 (Toriumi & Teruya, 1988). RSCM yielded a maximum temperature of $345 \pm 30^{\circ}\text{C}$ for the FM (Palazzin et
142 al., 2016). Similarly to the veins from the KCB, the examined veins from the FM are Mode 1 fractures often
143 arranged as en échelon arrays (Fig. 2d), cutting across the foliation and shortened perpendicular to the
144 foliation (Raimbourg et al., 2021).

145 The Hyuga Group is divided into Hyuga Tectonic Mélange (HTM) and Coherent Hyuga. In this study the
146 Hyuga Tectonic Mélange is examined, which consists of strongly sheared sandstone lenses embedded in
147 a pelitic matrix. Based on microfossil assemblages, the sedimentation age is from the Middle Eocene to
148 the Early Oligocene (Nishi, 1988; Sakai et al., 1984). Based on RSCM, the peak-temperature of deformation
149 was estimated to $\sim 245 \pm 30^{\circ}\text{C}$ (Palazzin et al., 2016). The dominant veins in the HTM are Mode 1 quartz-

150 filled extension fractures oriented perpendicular to the NW-SE stretching direction of sandstone lenses
151 (Fig. 2b; Raimbourg et al., 2014).

152

153 **3. Analytical methods**

154 **3.1. Whole-rock chemistry**

155 Samples for major element whole-rock analysis were crushed after removing any visible macro- and
156 micro-veins in order to estimate the chemical composition of the pelitic matrix. Major elements were
157 analyzed by X-ray fluorescence (XRF) at ALS lab (Loughrea Galway, Ireland; analytical code ME_XRF26). To
158 prepare glass beads, crushed samples (~0.5 g) were fused using a platinum mold into a fusion disk and
159 mixed with lithium metaborate as a flux. The disks were then analyzed by XRF, where the concentrations
160 of major elements (oxides) were determined in conjunction with loss-on-ignition (LOI) at 1000°C.
161 Analyzed elements and parameters are Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, K, P, S, Sr, Ba and LOI. Elements
162 were calibrated in oxide weight percentage form.

163 **3.2. X-Ray Diffraction**

164 X-ray diffraction (XRD) measurements were carried at BRGM, Orléans, France, using a BRUKER D8 Advance
165 X-ray diffractometer equipped with a Cu K α radiation ($\lambda_{K\alpha} = 0.15406$ nm) operating at 40 kV and 40 mA.
166 X-Ray diffraction on bulk-powder was used for a first-order estimation of the mineralogy, including the
167 nature of phyllosilicates. Samples were micronized in ethanol using an XRD Mill McCrone (Retsch), dried
168 at 40°C and homogenized. XRD patterns were recorded on randomly oriented powder samples from 4 to
169 90°2 θ , with a step of 0.03°2 θ and a step time of 480 seconds. Quantitative analyses of X-ray diffractograms
170 were carried out using the SiroQuant™ program, version 4 (Taylor & Clapp, 1991).

171 The <2 μ m fraction was then isolated from the bulk samples. To do so, the crushed powder was firstly
172 treated with acetate (pH = 5.0) to dissolve carbonates, secondly with 0.01 M CaCl₂ to saturate interlayer
173 space of clay minerals if present, and finally washed with pure water. Then clay particles were dispersed
174 by ultrasonics in deionised water and the suspension was left to rest 100 minutes. Then <2 μ m fraction
175 was isolated by sampling the upper part of the suspension and deposited on a thin section. X-ray
176 diffraction patterns were acquired firstly on the oriented deposit dried at 50°C, then saturated with
177 ethylene glycol under vapor tension at 60°C for at least 16 hours, to identify the clay mineral varieties.
178 XRD patterns were recorded on oriented deposits from 2 to 35°2 θ , with a step of 0.03°2 θ and a step time
179 of 1.5 seconds.

180

3.3. SEM-Backscatter Electron images and Electron microprobe

181 Mineral petrography was carried by optical microscopy and a Merlin Compact ZEISS scanning electron
182 microscope (SEM) equipped with backscattered electron (BSE) detector BSD4 at the Institut des Sciences
183 de la Terre, Orléans (ISTO). The SEM-BSE was operated at 15 kV voltage and a dwell time of 50 ms.
184 Backscattered electron images were further processed with the software ImageJ (Schneider et al., 2012)
185 to semi-quantify the amount of each mineral phase and to prepare phase maps.

186 The chemical composition of the main mineral phases was determined by using a Cameca SX Five electron
187 microprobe equipped with five wavelength-dispersive spectrometers (WDS), housed at ISTO-BRGM joint
188 facilities in Orléans. Measurements were performed at 15 kV voltage, a 10 nA beam current and a 1 μm
189 spot size. Analyzed elements were Si, Ti, Al, Fe, Mn, Mg, Ca, Na and K. The standards used for calibration
190 were MgO (Mg), albite (Si, Al), andradite (Ca), orthoclase (K), MnTiO₃ (Mn, Ti) and hematite (Fe). For the
191 elemental maps, the step size and dwell time were 1 μm and 150 ms, respectively. The maps were
192 processed using the software XMapTools (Lanari et al., 2014).

193

3.4. Thermobarometric estimates

194 The crystallization temperature of chlorite was estimated with the chlorite-quartz-H₂O thermodynamic
195 model and the parameters described in Vidal et al. (2006). Pressure was estimated via equilibrium with
196 illite using the solid solution model from Dubacq et al. (2010). The approach relies on the phengite-
197 chlorite-quartz model first presented by Vidal & Parra (2000) and applied to metapelites over a wide range
198 of conditions from LP-LT (Árkai et al., 2003; Battaglia, 2004) to HP-LT terrains (e.g., Plunder et al., 2012).
199 In chlorite and mica, substitutions are modeled with end-members. The model accounts for the following
200 substitutions: Fe=Mg²⁺; Tschermak [Si+(Mg,Fe²⁺)=Al^{IV}+Al^{VI}] in illite and chlorite; di/trioctahedral
201 [\square^{VI} +Al^{VI}+Al^{VI}=3(Fe²⁺,Mg)] in illite and chlorite, and pyrophyllitic [(Na,K)+Al= \square^{XII} +Si] and paragonitic [K=Na]
202 in illite (Dubacq et al., 2010; Masci et al., 2019; Vidal & Parra, 2000; Zane et al., 1998). Incorporation of
203 water in the interlayer space of low-temperature illite is modeled via a vacancy-water [\square =H₂O]
204 substitution (see Dubacq et al., 2010). The resulting set of solid solution end-members is pyrophyllite (PrI),
205 hydrated pyrophyllite (PrI·1H₂O), muscovite (Ms), Mg- and Fe-celadonite (Mg-Cel and Fe-Cel) for illite, and
206 clinocllore (Clin), daphnite (Daph), sudoite (Sud), Fe- and Mg-amesite (Fe-Am and Mg-Am) for chlorite.
207 Additional phases are quartz (Qtz) and H₂O with an activity set at unity. With this set of phases, 124
208 reactions may be written, out of which six are independent. Equilibrium is inferred when independent
209 reactions appear reasonably close to one another in P-T space (e.g., less than 20°C and 1 kbar).

210

3.5. Raman spectroscopy

211 From each locality where deformation structures were studied, a thick section oriented in the X-Z plane
212 of kinematic reference was prepared from metasedimentary samples for the purpose of RSCM. Analyzed
213 particles were chosen far from shear bands to avoid shear-enhanced thermal maturation of carbonaceous
214 material.

215 A Raman Renishaw InVia Reflex micro-spectrometer was used at BRGM, Orléans. A silicon standard was
216 used for calibration. The light source was a 514.5 nm Ar laser with a power of ~1 mW, focused by a Leica
217 DM2500 microscope at a magnification of 100x. The signal was analyzed by a CCD NIR/UV detector. 15-
218 20 points were analyzed per sample on 150-200 μm thick, polished sections. The final deconvolution was
219 made following the method of Lahfid et al. (2010), applicable for the temperature range from ~200°C to
220 ~320°C. Raman spectra were processed with the software PeakFit 4.12 for subtracting the baseline and
221 fitting each corrected spectrum with five Lorentzian bands. From the area below five Lorentzian bands,
222 RA1 ratio was calculated by the equation $RA1 = (D1 + D4) / (D1 + D2 + D3 + D4 + G)$. The final temperature
223 was estimated following the equation $T (^{\circ}\text{C}) = 1217.6 \times RA1 - 450.66$ (Lahfid et al., 2010). The uncertainty
224 of the method is ~30°C (Lahfid et al., 2010). Fifteen to twenty points were analyzed in each sample,
225 average values and standard deviations (1σ) are reported in Table 1.

226 The Raman spectrum of water originates from OH stretching vibrations, which vary as a function of salinity
227 (e.g., Caumon et al., 2014, 2015). The salinity of water-rich fluid inclusions was estimated using a Raman
228 Renishaw InVia Qontor micro-spectrometer at CEMHTI CNRS, Orléans. A silicon standard was used for the
229 calibration, and the light source was a 514.5 nm solid state laser. Applied power was 50 mW, focused on
230 standards or fluid inclusions with Leica DM2700 microscope at a magnification of 100x (0.9 NA). The signal
231 was acquired by a CCD NIR/UV "centrus" detector. Acquiring time was 60 s for each point. For calibration,
232 12 solutions with known NaCl molarity were prepared (0.125 M, 0.25 M, 0.375 M, 0.5 M, 0.625 M, 0.75
233 M, 0.875 M, 1 M, 1.25 M, 1.5 M, 1.75 M and 2 M). The solutions were placed into the borosilicate circular
234 capillaries with outer and inner radius of 0.33 and 0.2 mm, respectively. Borosilicate capillaries are
235 transparent to Raman signal. The Raman spectrum of the OH stretching vibrations can be divided into two
236 sub-bands (Sun et al., 2010), strong- (HBs, with the peak centered around 3200 cm^{-1}) and weak-hydrogen
237 band (HBw, with the peak centered around 3450 cm^{-1}). For each solution, the deconvolution process is
238 made following the method of Sun et al. (2010) using the software PeakFit 4.12. After the baseline was
239 subtracted, two Gaussian sub-bands were used to fit the obtained Raman Spectrum (Fig. 3a). Based on

240 the intensity (I) and full width at half maximum (FWHM) of each band, the equilibrium constant is
241 calculated as:

$$242 \quad K' = \frac{\left(\frac{I}{FWHM}\right)_{HBw}}{\left(\frac{I}{FWHM}\right)_{HBs}}$$

243 Finally, the linear correlation between K' value and salinity of prepared solutions (Fig. 3b) leads to a
244 formula for the salinity estimation in fluid inclusions:

$$245 \quad \text{Cl}^- \text{ Molarity (M)} = -0.6843*(K')^2 + 5.6135*K' - 6.3693.$$

246 Fluid inclusions were analyzed with the same conditions as the standards. To avoid biases due to the effect
247 of host mineral birefringence (Caumon et al., 2015), circular polarization was applied to the beam.
248 Additionally, the salinity of 22 fluid inclusions with wide range of salinities determined by Raman
249 Spectroscopy were also measured by microthermometry by using a Linkam THMSG600 heating-cooling
250 stage (Fig. 3c), wherein the salinity was estimated using the last ice-melting temperature (Bodnar, 1993).

251 **3.6. Decrepitation of fluid inclusions**

252 Qualitative chemical analysis of major cations and anions in individual fluid inclusions was carried out from
253 evaporate mounds after decrepitating fluid inclusions, following the method by Kontak (2004). Double-
254 polished quartz sections were rapidly heated by THMS-600 Linkam stage to 500-600°C and quenched for
255 5-15 minutes, until decrepitation was observed. The system was then rapidly cooled down to room
256 temperature. The chemical maps of evaporate mounds were acquired by SEM-EDS at the voltage of 15 kV
257 and a dwell time of 25 ms. In addition, the chemical composition of individual evaporate crystals was
258 determined by using a Cameca SX Five electron microprobe, housed at ISTO-BRGM Orléans, that is
259 equipped with five wavelength-dispersive spectrometers (WDS). The conditions used for individual crystal
260 analyses were a 15 kV voltage, a 10 nA beam current and a 1 µm spot size. Up to 10 points were analyzed
261 in each mound. Results were recalculated by removing SiO₂ as it is recognized as from the host quartz,
262 and then normalizing the totals to 100%. However, acquired results are semi-quantitative due to
263 devolatilization and loss of certain species during the decrepitation process.

264 **4. Results**

265 **4.1. Raman Spectroscopy of carbonaceous material**

266 Peak-metamorphic temperatures obtained by RSCM are reported in Table 1 and examples of
267 deconvoluted spectra are provided in Fig. 4.

268 Temperatures for two samples from the Kodiak Landward Belt from Uyak Bay are $251 \pm 9^\circ\text{C}$ (KO17A) and
269 $240 \pm 9^\circ\text{C}$ (KO17E). Samples from the Kodiak Central Belt show narrow range of temperatures from 327
270 to 340°C . For three samples from the Kodiak Seaward Belt determined peak-temperatures are $300 \pm 19^\circ\text{C}$
271 (KO11), $348 \pm 28^\circ\text{C}$ (KO12B), and $344 \pm 16^\circ\text{C}$ (KO45C).

272 A sample HN65 from the Hyuga Tectonic Mélange has a recorded temperature of $228 \pm 16^\circ\text{C}$, whereas
273 samples from the Foliated Morotsuka (Samples 18NOB13, 18NOB22A, HN143, HN243, HN247, and
274 HN285) experienced peak-temperatures of $339 \pm 26^\circ\text{C}$. The results acquired as part of this study for
275 samples from the Shimanto Belt are consistent with previously reported RSCM results (Palazzin et al.,
276 2016; Raimbourg et al., 2017, 2018).

277 Peak temperatures obtained for higher-grade samples (from the Kodiak Central Belt and Foliated
278 Morotsuka) are around or slightly above the range of the method of Lahfid et al. (2010). However, due to
279 the presence of the D4 band and the absence of the D2 band in the Raman spectra (Fig. 4), the method of
280 Lahfid et al. (2010) is more suitable than of Beyssac et al. (2002).

281 Therefore, the Kodiak Landward Belt (KLB) and the Hyuga Tectonic Mélange (HTM) are grouped as lower-
282 grade units, whereas the Kodiak Central Belt and the Foliated Morotsuka represent higher-grade units.

283 **4.2. Microstructures and mineral petrography**

284 **4.2.1. Lower-grade units**

285 In Kodiak and the Shimanto Belt, lower-grade metapelites ($230\text{-}260^\circ\text{C}$) show three different
286 compositional and microstructural domains: pelitic matrix, quartz ribbons, and extensional veins (Fig. 5a).
287 Phyllosilicates are the most abundant phases in the matrix, with clusters of fine-grained illite (illite hereby
288 refers to minute dioctahedral aluminous phyllosilicates with composition on the muscovite-pyrophyllite
289 binary; Dubacq et al., 2010) and chlorite (Fig. 5b-c). The grain size of chlorite varies between $2.5\text{-}60\ \mu\text{m}$
290 (Fig. 5b), and increases up to $100\ \mu\text{m}$ when in contact with quartz ribbons. The grain size of illite is in the
291 range $1\text{-}24\ \mu\text{m}$ (Fig. 5b) in the matrix, whereas aggregates of illite up to $120\ \mu\text{m}$ are present close to quartz
292 ribbons. Detrital plagioclase and quartz are present in the matrix (Fig. 5b), as well as accessory phases
293 such as framboidal pyrite, calcite, apatite and Ti-oxides. The foliation (S_1) in the pelitic matrix is defined
294 by compositional layering (scaly fabrics; Ramirez et al., 2021; Vannucchi, 2019), enriched in fine-grained
295 phyllosilicates, sulfides, Ti- and Fe-oxides (Fig. 5a, 5d). Occasionally, thin shear bands composed principally

296 of elongated individual crystals of chlorite (Fig. 5c) and to a lesser extent illite and/or quartz grains, cut
297 the main foliation at low angles. These shear bands form an anastomosing network and indicate non-
298 coaxial shearing (Fig. 5a).

299 Extensional veins, commonly oriented perpendicular to the foliation, are made of blocky quartz and to a
300 lesser extent calcite (Fig. 6a). Quartz crystals in lower-grade veins occasionally display growth rims, with
301 crystal facets oriented towards the center of the vein. Occasionally quartz crystals are elongated parallel
302 to the foliation (Fig. 6b). Bulging, as a mechanism of dynamic recrystallization, is observed sparsely. Calcite
303 display characteristic undeformed twinning (Fig. 6a; Type I according to Ferrill et al., 2004). Ribbons
304 containing quartz \pm calcite \pm small flakes of chlorite are elongated parallel to the main foliation (Fig. 5a).
305 Calcite, when present, occurs as late fill of the vein and is mildly altered.

306 **4.2.2. Higher-grade units**

307 In higher-grade samples of the KCB and FM (Table 1; 330-350°C), the main mineral phases forming the
308 matrix are illite, chlorite, quartz and plagioclase. The foliation (S_1) is penetrative and underlined by
309 phyllosilicates (Fig. 5g-h), and it is locally disturbed by 5-20 μm thick shear bands containing illite, chlorite,
310 Ti-oxides, and sulfides. Whenever present, plagioclase and quartz crystals are flattened and elongated
311 parallel to the foliation (Fig. 5h). A secondary crenulation cleavage (S_2) is present only in the vicinity of
312 shear bands. The average grain size in the pelitic matrix of higher-grade samples is larger than in lower-
313 grade samples. In the KCB for instance, chlorite crystals are generally in the range of 5 to 400 μm and up
314 to 775 μm in length when in contact with shear bands, whereas illite crystals reach 1-80 μm in the matrix
315 and up to 320 μm closer to shear bands (Fig. 5e-f). In the FM, matrix illite and chlorite have significantly
316 larger grain size than in the KCB, ranging between 30-500 μm and 50-700 μm , respectively (Fig. 5f).
317 Accessory phases in the matrix are apatite, pyrite, calcite, anatase and titanite. Sulfides are locally oxidized
318 into goethite, with preserved pyrite crystal shapes. Scaly fabrics are enriched in micrometric anatase,
319 apatite and Fe-oxides (Fig. 5i-j), and occasionally act as shear planes displacing the main foliation and
320 quartz ribbons.

321 In higher-grade units, quartz ribbons are boudinaged and occasionally folded. The neck of boudins is
322 composed of illite, chlorite and elongated quartz crystals. Shear veins and Mode 1 quartz veins cutting
323 across the foliation are dominantly made of quartz and display crack-seal microstructure (Fig. 6c). Bulging
324 is recognized as a dominant mechanism of dynamic recrystallization in quartz from higher-grade veins.
325 Subgrain rotation is observed and is more prominent in the FM than in the KCB. In addition to quartz,

326 veins contain calcite, chlorite, and albite (Fig. 6e-f). Deformed calcite is characterized by curved and
327 lensoid twins (Fig. 6d; Type III according to Ferrill et al., 2004). In a few of the studied veins, clusters of
328 vermicular chlorites are sparsely distributed, as well as euhedral albite crystals (Fig. 6f).

329 Locally, mineralogical variations are observed in correspondence with the microstructures. In the matrix
330 in the contact with some shear bands, quartz and plagioclase grains are almost completely absent (Fig.
331 5e-f). Fig. 6f shows the host rock with few micrometric albite crystals, whereas larger crystals (up to 0.2
332 mm) are found in the shear band. Similar features were observed in the veins from the KCB, with veinlets
333 apparently located on one side of the main vein (Fig. 7a). On the side with veinlets, the crenulation
334 cleavage (S_2) is found close to the contact (Fig. 7c), and disappears further from the shear band (Fig. 7d).
335 The amount of quartz decreases towards the vein, and quartz is absent from the zone with crenulation
336 cleavage (Fig. 7e). Anatase also appears to be formed synchronously with crenulation cleavage (Fig. 7g),
337 as it is concentrated in crenulation cleavage planes with apatite. However, in zones where only the main
338 foliation present titanite is found (Fig. 7h).

339 **4.3. Whole-rock chemistry**

340 Whole-rock major element compositions are presented in Table 2. In samples from the Kodiak complex,
341 oxide concentrations and LOIs are in the following ranges: SiO_2 - 54.76% to 69.90%; TiO_2 - 0.60% to 1.00%;
342 Al_2O_3 - 12.22% to 20.27%; Fe_2O_3 - 6.87% to 8.82%; MgO - 1.94% to 3.29%; CaO - 0.33% to 1.28%; Na_2O -
343 0.97% to 2.77%; K_2O - 1.48% to 3.61%; SO_3 - 0.02% to 0.37%; and LOI - 3.16% to 5.23%. Major elements
344 and LOI in samples from the Shimanto Belt are in the range of: SiO_2 - 61.72% to 75.83%; TiO_2 - 0.34% to
345 0.70%; Al_2O_3 - 10.30% to 18.15%; Fe_2O_3 - 5.41% to 7.34%; MgO - 1.49% to 2.44%; CaO - 0.06% to 0.88%;
346 Na_2O - 1.11% to 3.33%; K_2O - 1.44% to 3.29%; SO_3 - 0.01% to 1.89%; and LOI - 2.61% to 5.08%.

347 No clear trend is apparent in major element compositions as a function of temperature, except for weak
348 positive correlation for K_2O , MgO and Fe_2O_3 , and strong negative correlation for SO_3 . The normalization
349 of oxides to TiO_2 (assumed as an immobile oxide) as a function of temperature of metamorphism, reveals
350 no clear trends as well (Fig. 8).

351

352 **4.4. X-Ray diffraction and phase quantification**

353 X-Ray diffraction on bulk rocks confirmed the major phases observed using optical and electronic
354 microscopy (Table 3; Fig. S1): illite, quartz, plagioclase and chlorite, and provide evidence of smectite-illite

355 mixed layers in lower-grade samples and in the higher-grade sample 18NOB23B. Accessory phases are
356 calcite and pyrite, and serpentine in three lower-grade samples and in one higher-grade sample (Sample
357 HN243). Magnesite, siderite and kaolinite are detected in individual samples (Table 3).

358 Quantitative phase proportions based on the method of Rietveld (1969) reveal that the main rock-forming
359 mineral phases of lower temperature samples (230-260°C) are illite/mica (23-48%), quartz (17-43%),
360 plagioclase (10-20%), chlorite (0-14%) and smectite-illite mixed layers (0-8%). Minor phases include
361 serpentine (detected in three samples, 1.6-3.4%) and kaolinite (only in one sample - HN64, 4%). Higher
362 temperature samples (~330-350°C) show similar proportions of main phases: illite/mica (21-42%), quartz
363 (16-34%), plagioclase (5-25%) and chlorite (15-24%). The amount of smectite-illite mixed layers in the
364 sample 18NOB23B is estimated as 1.5% and 1.8% of serpentine is estimated in the sample HN243.

365 **4.5. Mineral composition**

366 Representative analyses of illite and chlorite, as well as calculated structural formulas are listed in Table
367 S1, whereas all acquired analyses are listed in Table S2 of the Supplementary information. In all lower-
368 and higher-grade samples plagioclase is albitic ($X_{Ab} > 0.98$), with only traces of K and Ca. In contrast, K-
369 bearing phyllosilicates and chlorites show compositional variations correlated with peak-metamorphic
370 temperatures.

371 **4.5.1. K-bearing phyllosilicates**

372 More than 20 grains of mica were analyzed in the matrix of each sample. Calculation of structural formulae
373 on the basis of 11 oxygen atoms shows that analyses correspond to dioctahedral mica, which is in
374 agreement with XRD data. The sum of the interlayer cation is variable, ranging between 0.45 and 0.95 in
375 lower-grade samples, and between 0.77 and 0.95 in higher-grade samples (Fig. 9a). Values lower than 1.0
376 indicate that illite-smectite mixed layers are probably present.

377 In lower-grade samples (from KLB and HTM units), K is the dominant alkali (KLB: 0.43-0.81 apfu; HTM:
378 0.43-0.88 apfu), with secondary Na (KLB: 0.02-0.38 apfu; HTM: 0.01-0.32 apfu; Fig. 9a). Micas contain 0.27
379 vacancies pfu in average for KLB (0.09-0.44 pfu) and 0.26 pfu for HTM (0.05-0.55 pfu). Higher-grade
380 samples (from KCB and FM units) show homogenous compositions among samples (Fig. 9e). The
381 proportion of K increases in comparison with lower-grade samples (KCB: 0.74-0.89 apfu; FM: 0.74-0.96
382 apfu), whereas the amount of Na decreases (KCB: 0.01-0.04 apfu; FM: 0.01-0.06 apfu). Remaining
383 interlayer vacancies are estimated to be around 0.09-0.22 pfu for the KCB and 0.1-0.24 pfu in the case of
384 FM (Fig. 9a).

385 Octahedral sites are dominantly occupied by Al, without correlation to temperature (lower-grade: KLB av.
386 1.79 apfu, range 1.55-1.92; HTM av. 1.82 apfu, range 1.62-1.92; higher-grade: KCB av. 1.77 apfu, range
387 1.64-1.82; FM av. 1.73 apfu, range 1.54-1.81). Remaining octahedral position is occupied by Fe and Mg.
388 In KLB, Fe is more abundant than Mg (av. FeO 2.25 wt.% and av. MgO 1.6 wt.%), whereas in HTM the
389 proportion of Fe and Mg are similar (av. FeO 1.4 wt.% and av. MgO 1.45 wt.%). There is similar amount of
390 Fe and Mg in higher-grade samples (KCB: av. FeO 1.71 wt.% and av. MgO 1.73 wt.%; FM: av. FeO 2.2 wt.%
391 and av. MgO 1.9 wt.%).

392 In the tetrahedral site, there is no systematic changes in the Al-Si substitution with increasing
393 temperature. The average SiO₂ content in lower-grade samples is 49.62 wt.% (3.13-3.65 apfu) and 49.74
394 wt.% (3.11-3.67 apfu) for KLB and HTM, respectively, whereas SiO₂ in higher-grade samples shows
395 narrower concentration variations - 49.32 wt.% in average (3.24-3.37 apfu) for the KCB and 47.57 wt.% in
396 average (3.10-3.37 apfu) for the FM.

397 **4.5.2. Chlorite**

398 The structural formulae of chlorite are calculated on the basis of 14 oxygen atoms. Chlorite in lower-grade
399 samples exhibits chemical variations (Table S1 in the Supplementary information), with the magnesium
400 number (X_{Mg}) generally in the range of 0.3-0.45 (Fig. 9d). Higher-grade chlorite has similar X_{Mg} compared
401 to lower-grade chlorite but appears more homogenous. Lower-grade chlorite contain a greater number
402 of vacancies (0.23 ± 0.08 and 0.21 ± 0.06 pfu in KLB and HTM, respectively) than in higher-grade chlorite
403 (0.09 ± 0.06 pfu and 0.08 ± 0.06 pfu for KCB and FM, respectively; Fig. 9c). Tetrahedral Al increases with
404 temperature from 0.60-1.27 to 1.02-1.39.

405 All analyzed grains in higher-grade samples show high clinocllore (X_{clin} 0.24 ± 0.01 and 0.21 ± 0.03 for the
406 KCB and the FM, respectively), daphnite (X_{daph} 0.35 ± 0.01 and 0.34 ± 0.01 for the KCB and the FM,
407 respectively), and amesite (X_{am} 0.34 ± 0.06 and 0.38 ± 0.11 for the KCB and the FM, respectively)
408 proportions, with a low sudoite proportion (X_{sud} 0.07 ± 0.06 and 0.03 ± 0.03 for the KCB and the FM,
409 respectively; Fig. 9f).

410 **4.5.3. Multi-phase equilibrium model for the higher-grade units**

411 In lower-grade samples, the multi-phase equilibrium model did not permit the identification of
412 equilibrium pairs, and hence pressure-temperature conditions could not be estimated. In higher-grade
413 samples, equilibrated pairs of illite and chlorite have been identified (Fig. 10a). Fig. 10c shows the
414 pressure-temperature conditions for equilibrium of illite-chlorite pairs sampled from Fig. 9e-f. The results

415 from samples from the KCB spread over the range 250-350°C and 2-4 kbar, with a global average of $327 \pm$
416 21°C and 3.0 ± 0.4 kbar. In the FM, the results spread over the range 300-350°C and 3-4.5 kbar, with
417 average values of $320 \pm 14^\circ\text{C}$ and 3.9 ± 0.4 kbar (Fig. 10c).

418 **4.6. Fluid inclusions**

419 **4.6.1. Petrography of fluid inclusions**

420 Quartz in the veins is characterized by high abundance of fluid inclusions (Fig. 11a-b). Veins from lower-
421 grade units contain two types of primary fluid inclusions (Fig. 11c) interpreted to be the result of fluid
422 immiscibility (Raimbourg, 2015; Vrolijk et al., 1988): (1) One-phase CH_4 -rich fluid inclusions with a size of
423 up to $20 \mu\text{m}$ and negative crystal shapes. These CH_4 -rich fluid inclusions are randomly oriented in the host
424 quartz. (2) Smaller ($<10 \mu\text{m}$) two-phase H_2O -rich fluid inclusions with various shapes including round,
425 squared to irregular (Fig. 11c). The small vapor bubble is dominated by CH_4 (Raimbourg et al., 2018). In
426 zones characterized by stretched quartz, fluid inclusions (both CH_4 -rich and H_2O -rich) appearing as
427 pseudo-secondary and are commonly in fracture healing planes perpendicular to the orientation of the
428 elongation direction of quartz (Fig. 6b; Palazzin et al., 2016; Raimbourg et al., 2018).

429 In the higher-grade quartz veins, only one set of primary fluid inclusions is observed. The primary fluid
430 inclusions contain two phases and are H_2O -rich with a V/L ratio of 0.1-0.15 (Fig. 11d). A size of inclusions
431 rarely exceeds $10 \mu\text{m}$. The vapor bubble contains minor amount of CO_2 and CH_4 (Raimbourg et al., 2018).
432 Secondary fluid inclusions are common, aligned as healed fractures or trails of tiny one-phase fluid
433 inclusions without systematic orientation of trails.

434 **4.6.2. Fluid inclusion salinity**

435 The salinity of the fluid inclusions has been estimated in primary two-phase fluid inclusions and in a few
436 secondary fluid inclusions (Fig. 12). In veins formed at lower temperatures, the salinity of primary fluid
437 inclusions is often lower than ~ 3.5 wt.% NaCl eq., which is the salinity of seawater (Fig. 12). In KLB for
438 instance, primary fluid inclusions in samples: KO17A and KO17H yield average salinities of 2.1 ± 0.9 wt.%
439 NaCl eq. and 2.1 ± 1.1 wt.% NaCl, respectively. Similarly, primary fluid inclusions in samples NOB_11C and
440 NOB_8B of the HTM yield average salinities of 2.2 ± 0.9 wt.% NaCl eq. and 1.2 ± 0.6 wt.% NaCl eq.,
441 respectively. A small proportion ($<10\%$) of measured primary fluid inclusions show higher salinity than
442 seawater. On the other hand, in higher-grade veins the average salinity of primary fluid inclusions is more
443 variable and higher than in those of lower-grade veins, often exceeding the salinity of seawater (Fig. 12).
444 This is the case in the KCB, for which primary fluid inclusions in samples KO32F, KO32A, KO32B, and

445 KO33A2 yield average salinities of 5.2 ± 2.5 wt.% NaCl eq., 2.9 ± 0.9 wt.% NaCl eq., 3.9 ± 1.8 wt.% NaCl
446 eq., and 3.5 ± 1.4 wt.% NaCl eq., respectively. In the FM, samples NOB_23B, NOB_13F and NOB_4C yield
447 average salinities of 3.7 ± 1.4 wt.% NaCl eq., 3.4 ± 1.3 wt.% NaCl eq., 3.3 ± 0.7 wt.% NaCl eq., respectively.
448 The salinity of secondary fluid inclusions from both localities is below 1 wt.% NaCl eq., in average 0.5 ± 0.3
449 wt.% NaCl eq. (Fig. 12).

450 **4.6.3. Fluid inclusion chemistry**

451 SEM-EDS analyses of fluid inclusions in evaporite mounds (Fig. S2) in lower-grade veins show the presence
452 of Na, K, Ca, Mg and Fe as cations, and Cl and S as anions (Table S3; Fig. 13a). EPMA point analysis revealed
453 that the Ca/Na ratio is dominantly >1 (Fig. 13b), except for the sample NOB_13F and one evaporite mound
454 in the sample NOB_23B where NaCl is the dominant compound (Fig. 13a). The amount of Fe and Mg varies
455 between each analyzed mound (Fig. 13a), ranging from ~ 1.5 to $\sim 47\%$ and from ~ 1.5 to $\sim 42\%$, respectively.
456 As shown in Fig. 13, S and Cl are dominant anions, and the largest group of evaporite mounds ($\sim 75\%$) are
457 characterized by SO_2/Cl ratio equal or higher than 1 (Fig. 13c).

458

459 **5. Discussion**

460 **5.1. Changes in mineralogy as a function of temperature**

461 Our analyses from Kodiak and Shimanto reveal that metapelites of two studied accretionary prisms
462 underwent a similar evolution of mineral proportions with peak-metamorphic temperature. In both cases,
463 the most prominent mineral change is an increasing proportion of chlorite relative to other phyllosilicates
464 with increasing temperature (Table 3; Fig. 14a). Ramirez et al. (2021) also reported an increase in the
465 chlorite/phyllosilicates ratio with increasing temperature in metapelites of the Mugi and Makimine
466 mélanges from the Shimanto Belt, which experienced peak-metamorphic temperatures of ~ 150 - 350°C .
467 Additionally, Kameda et al. (2011a) described an increasing chlorite content from undeformed to
468 deformed metasediments of the Kitagawa Group in the Shimanto Belt, which evolved in tandem with
469 more pervasive foliation. Because both the undeformed and deformed part of the Kitagawa Group
470 experienced the same metamorphic temperatures (Kameda et al., 2011a), the crystallization of chlorite
471 must be facilitated not only by a temperature increase, but also by deformation. The same conclusion was
472 reached by Casciello et al. (2011) and Famin et al. (2021) for the transformation of smectite into illite,
473 which is enhanced in deformation microstructures within metapelites even at isothermal conditions.

474 The last important mineral reaction observed is the oxidation of pyrite. Pyrite is present in both lower-
475 and higher-grade samples. In addition, in higher-grade samples pyrite is partly or completely oxidized to
476 goethite. The main question is whether sulfide oxidation occurred during metamorphism or due to the
477 samples being exposed at the surface. Goethite is reported to be hydrothermal phase (e.g., Makvandi et
478 al., 2021), which is further supported by experimentally derived work wherein goethite is stable under
479 low to moderate pressures compatible with the metamorphic conditions of the present work (Majzlan et
480 al., 2003). The oxidation of pyrite at peak conditions is also further supported by the precipitation of Fe-
481 oxides within the scaly fabrics that formed during metamorphism (Fig. 5i-j; see also Ramirez et al., 2021).
482 Finally, sulfide oxidation is matched by a significant drop of SO_3 on whole-rock scale with increasing
483 temperature (Fig. 8). The remobilization of iron at depth by dissolution of pyrite within the fluid is also
484 attested by our analysis of the composition of the metamorphic fluid. In decrepitated mounds from the
485 higher-grade veins, S is detected qualitatively by the SEM-EDS maps as well as in EPMA point analysis, and
486 in many analyzed mounds it is predominant over chlorine (Fig. 13).

487 The progressive breakdown of pyrite in metasedimentary units is described as a result of a change in the
488 redox state of the rocks (Dubessy et al., 1983; Ferry, 1981; Frey et al., 1980; Hall, 1986). Similar
489 observations to those of the present study are reported in the external part of the Central Alps, where
490 upon temperature increase, the gas dissolved within the metamorphic fluid changed from CH_4 to CO_2 and
491 H_2O , in connection to reduction reactions in the Fe-bearing phases, biotite and pyrite (Tarantola et al.,
492 2007, 2009). Such a transition in the nature of the gas is proposed to occur at temperatures $\sim 270^\circ\text{C}$
493 (Tarantola et al., 2009), and we observed it as well in fluid inclusions from both Kodiak and Shimanto
494 (Raimbourg et al., 2018; Fig. 11).

495 As previously discussed, the main mineralogical change in the metapelites that occurred with an increase
496 in temperature is an increase in chlorite relative to other phyllosilicates (Fig. 14a). Chlorite is the dominant
497 Fe-Mg phase in the metapelites and an important question is whether the local Fe and Mg source is
498 sufficient to support the transformation of phyllosilicates into chlorite, or if an external supply of Fe and
499 Mg is needed. It is reported that diagenetic chlorite can form as a coproduct of the smectite-to-illite
500 transformation during burial at temperatures as low as 70°C (Ahn & Peacor, 1985; Drief & Nieto, 2000;
501 Hower et al., 1976; Muffler & White, 1969), or by the breakdown of smectite and kaolinite to form chlorite
502 and illite (Boles & Franks, 1979). In both of the reactions described above, illite is the predominant product
503 along with $\sim 30\%$ chlorite (Boles & Franks, 1979; Hower et al., 1976). These reactions can explain the
504 formation of chlorite in lower-grade samples from this study (below 260°C), wherein the chlorite content

534 where illite reacts with water, Fe and Mg creating chlorite and releasing Si, K and Na into the fluid. Because
535 more K is required in illite in higher-grade samples (Fig. 9a), the amount of K released during this reaction
536 is likely incorporated into remaining or newly formed illite (Eq. 1).

537 **5.2. Mass transfers**

538 Even though several mineral reactions were recognized, whole-rock chemistry (Fig. 8) revealed no
539 significant chemical variations in the pelitic matrix as a function of peak-metamorphic temperatures
540 (except for a large decrease in SO_3), therefore elements were redistributed between metamorphic
541 minerals. However, specific zones of the matrix, such as in the vicinity of the veins, are characterized by
542 changes in mineralogy that imply mass transfer at a small scale. In such zones, as presented in Fig. 6 and
543 7, the matrix in contact with veins is characterized by the absence of quartz and a lower proportion of
544 albite than in unaffected zones. Mass-balance calculations for specific zones of the higher-grade samples
545 (zones with crenulation cleavage in the contact with veins and further from veins; Table S4), presented
546 after normalization to TiO_2 (e.g., Fig. 8), show a decrease in SiO_2 and Na_2O counterbalanced by an increase
547 in FeO, MgO, K_2O and LOI. Hence, SiO_2 loss is the result of the removal of SiO_2 from the matrix and
548 preservation of other mentioned elements. This can be interpreted as a result of dissolution of quartz and
549 albite and the crystallization of chlorite and illite (e.g., Fig. 7; Fisher et al., 1995; Fisher & Brantley, 1992).
550 Other zones in the pelitic matrix where mass transfer occurred are the scaly fabrics (Fig. 5d, 5i), as they
551 are enriched in Fe- and Ti-oxides with fine-grained illite and chlorite and depleted in quartz and albite.
552 Similar observations were made in metapelites from the Shimanto Belt (Kawabata et al., 2007; Ramirez
553 et al., 2021), where the progressive formation of scaly fabrics (their abundance and depletion in mobile
554 elements) is described as being facilitated by the temperature increase in addition to deformation. For
555 the elements depleted in scaly fabrics, such as SiO_2 or Na_2O , Ramirez et al. (2021) proposed that the mass
556 transfer occurred along the planes of the scaly fabrics to the veins, where quartz and albite precipitated.
557 A similar process is observed in the present work, wherein the mass transfer occurs from the host rock in
558 the immediate vicinity of the vein towards the vein itself, which is interpreted as a site of dilation and
559 preferential precipitation by Brantley & Fisher (1997).

560 Additionally, because the two proposed reactions (Eq. 1 and Eq. 2) release SiO_2 , one can wonder whether
561 this source of silica is a major contribution to produce the quartz veins observed in the field (Fig. 2). For
562 100 g of the matrix, if 10% of the illite transformed into chlorite (with the chemical composition from
563 Table S1) approximately 3 g of SiO_2 will be released. Comparing this value with the dissolution of quartz
564 and albite observed in the matrix contacting the veins, such as in Fig. 5e and Fig. 7, the complete

565 dissolution of quartz and albite (both constituting between 10 and 20% of the rock) releases about 17 to
566 34 g of SiO₂. Therefore, most of the silica precipitated in the veins stems from the dissolved quartz and
567 albite in the host rock, whereas the production of SiO₂ by metamorphic reactions is only a secondary
568 factor. Taken together, both sources can produce 20 to 37 g of free SiO₂ in 100 g of the matrix. Thus, the
569 mass of reactive matrix is estimated as three to five times the one of crystallized veins.

570 Given the spacing between adjacent veins, it appears that local redistribution of silica is in most instances
571 sufficient to precipitate the quartz veins observed in the field without any requirement for an external
572 source of silica. The zones with noticeably different mineralogy are limited to a thickness of <2 cm from
573 the contact with the veins. Even though the length of diffuse mass transfer is difficult to trace, mass
574 balance calculations as well as textural observations, in the examined samples are consistent with mass
575 transfer being limited to a mm- to cm-scale. Unlike in examples of similar lithologies where an external
576 fluid is required, such as the Otago Schist (Breeding & Ague, 2002) or the Catalina Schist (Bebout, 1991,
577 1993; Penniston-Dorland et al., 2012), this work supports the idea of locally derived material forming the
578 veins in the Kodiak complex and the Shimanto Belt (Brantley & Fisher, 1997; Fisher et al., 1995; Ramirez
579 et al., 2021).

580

581 **5.3. P-T conditions of metamorphism**

582 Due to difficulties such as small grain size or the lack of equilibrium between newly formed phases,
583 estimating pressure-temperature conditions in low-grade metamorphic rocks is often challenging. Despite
584 these challenges, our study succeeded in estimating peak-metamorphic temperatures in the metapelites
585 from two independent techniques, RSCM and chlorite thermometry. Both techniques yield similar results
586 and confirm that chlorite formed at peak-temperatures (Fig. 10c). The illite-chlorite multi-phase
587 equilibrium model indicates that both phases are metamorphic and not inherited. Additionally, textural
588 observations are consistent with the precipitation of albite in veins at peak-metamorphic conditions,
589 because it has been observed within chlorite rims (Fig. 6f). Furthermore, newly formed chlorite and albite
590 are found at the contact with and in the crack-seal veins, which indicates that the precipitation of chlorite
591 and albite occurred contemporaneously with deformation. This confirms that the quartz in crack-seal
592 veins also crystallized at peak conditions, as inferred from structural analysis of the veins (Fisher &
593 Brantley, 2014; Raimbourg et al., 2021). Consequently, the crack-seal structures described in these veins
594 (Raimbourg et al., 2021; Ramirez et al., 2021) were also formed at temperatures ~300-350°C.

595 The RSCM temperature results in the KLB are $\sim 250^{\circ}\text{C}$, which is upper limit for homogenization
596 temperatures ($215\text{-}255^{\circ}\text{C}$) derived from fluid inclusions (Vrolijk et al., 1988). For the KCB, our estimate of
597 $2.5\text{-}3.5$ kbar, $300\text{-}340^{\circ}\text{C}$ is slightly higher than the average temperature of 280°C obtained by Brantley &
598 Fisher (1997) using $\delta^{18}\text{O}$ thermometry on quartz, mica, and chlorite (Brantley & Fisher, 1997). A possible
599 explanation to this discrepancy is that $\delta^{18}\text{O}$ thermometry is more sensitive to low-temperature re-
600 equilibration, due to intermineral oxygen diffusion (e.g., Sharp & Kirschner, 1994), than RSCM and chlorite
601 thermometry. In the case of the Shimanto Belt, our P-T estimate of $3.5\text{-}4.5$ kbar and $300\text{-}350^{\circ}\text{C}$ for the FM
602 (Fig. 10c) is consistent with Toriumi & Teruya (1988) who proposed peak-metamorphic conditions at $3\text{-}5$
603 kbar and $300\text{-}350^{\circ}\text{C}$ based on mineral assemblages in metamafic rocks from the same unit.

604 Pressure and temperature results for the KCB estimated during this study point to a geotherm that is
605 close to $30^{\circ}\text{C}/\text{km}$, which is in agreement with the previously proposed arguments for a warm geotherm
606 in the subduction zone during the Cretaceous-Paleogene (Fisher & Byrne, 1992; Sample & Moore, 1987;
607 Vrolijk et al., 1988). This geotherm is attributed to a ridge subduction less than 12 million years after the
608 accretion of thick turbiditic sequences. Based on coexisting H_2O - and CH_4 -rich fluid inclusions in
609 extensional veins, Vrolijk et al. (1988) estimated a geothermal gradient of $\sim 20\text{-}25^{\circ}\text{C}/\text{km}$ in the Uyak
610 Complex, Kodiak and Ghost Rocks Formations, and concluded that these units were buried to a depth of
611 $10\text{-}14$ km. Our geotherm estimate suggests that the KCB has been buried to a depth of $10\text{-}12$ km.
612 Furthermore, if the geothermal gradient remained constant during accretion, all of the units from the
613 Kodiak complex in this study were buried to a depth of $7\text{-}12$ km, depending on the peak-metamorphic
614 temperature.

615

616 **5.4. Effect of mineral reactions on fluid composition and the fluid budget**

617 Initially during sediment burial, compaction and cementation reduce the porosity from several tens of
618 vol.% to a few vol.% (e.g., Saffer & Tobin, 2011). Simultaneously, the pore fluid (originally seawater)
619 becomes diluted by reactions such as smectite-to-illite transformations, which release fresh water (e.g.,
620 Colten-Bradley, 1987; Kastner, 1981; Kastner et al., 2014; Moore & Vrolijk, 1992; Perry & Hower, 1970;
621 Spinelli, 2004). These transformations mostly occur in the temperature range $50\text{-}150^{\circ}\text{C}$, but may extend
622 up to 250°C (Kameda et al., 2011b; Kastner et al., 2014). In several examples of metasedimentary rocks
623 from paleo-accretionary complexes experiencing temperatures of $\sim 250^{\circ}\text{C}$, fluid inclusion salinities in syn-
624 subduction veins are lower than seawater (Herviou et al., 2021; Raimbourg et al., 2018; Fig. 12, 14b),

625 which confirms this progressive dilution of the pore fluid during burial. Raimbourg et al. (2018) point to a
626 difference in both salinities of fluid inclusions of rocks subducted to shallower and deeper than brittle-
627 plastic transition. With increasing burial, another major change in the fluid composition occurs at the
628 brittle-plastic transition at a temperature of $\sim 300\text{-}350^\circ\text{C}$ (e.g., Mullis et al., 1994; Raimbourg et al., 2018;
629 Tarantola et al., 2007, 2009). At depth below this rheological limit, pore fluid salinities, as inferred from
630 fluid inclusions in various subduction zones worldwide, become highly variable and are often higher than
631 seawater (Herviou et al., 2021; Raimbourg et al., 2018 and references therein). This increase and
632 scattering of salinities shallower than the brittle-plastic transition, from $\sim 250^\circ\text{C}$ to $300\text{-}350^\circ\text{C}$, is not
633 explained to date. To interpret the increase in salinity, two possibilities can be considered: (1) Infiltration
634 of external fluids with a high salinity; (2) Hydration reactions and uptake of low-Cl⁻ water in the minerals.
635 The increase of salinity as a result of brine infiltration has been proposed for metasedimentary units in
636 the Western Alps and explained as the infiltration of fluid from blocks of margin units containing
637 evaporites (Herviou et al., 2021). However, in the case of the Kodiak complex and the Shimanto Belt, no
638 evaporites have been reported and the majority of units are made of deep-trench sediments (Byrne, 1982;
639 Fisher & Byrne, 1987; Nishi, 1988; Sakai et al., 1984; Sample & Moore, 1987). Our fluid inclusion analyses
640 show that the salinity increase and scattering also occurs in the metapelites of Kodiak and Shimanto (Fig.
641 12). Thus, our mineralogical and chemical results allow us to propose an explanation for these salinity
642 variations. Indeed, for the pelitic rocks of the two accretionary prisms, burial between $230\text{-}260^\circ\text{C}$ and 330-
643 350°C was accompanied by an increase in chlorite proportion as previously discussed.

644 An important issue related to chlorite crystallization is that chlorite hosts more water than smectite-illite;
645 ~ 13 wt.% compared to $\sim 6\text{-}7$ wt.%, respectively (Table S2). Analyzed illite in lower-grade rocks contains
646 about 7 wt.% of water. During formation of about 10% of chlorite, it is assumed that water from illite is
647 incorporated into chlorite; however, there is still a need for additional water. In 100 g of a rock with
648 composition the same as that of sample KO38 (Table S1), 10% of newly formed chlorite contains ~ 1.3
649 wt.% H₂O. Potentially inherited water from 10% of illite is ~ 0.7 wt.% H₂O, hence there is a deficit of 0.6
650 wt.%, or 1.62 vol.% H₂O. Therefore, some of the pore fluid has to provide H₂O for chlorite crystallization
651 and as a result the salinity of pore fluid increases (Fig. 12, 14b). The amount of pore water incorporated
652 into chlorite is highly dependent upon the initial porosity and amount of illite in the metapelite protolith,
653 which explains the scattering of salinity increases toward high-T samples. This amount of water
654 incorporation by illite-to-chlorite transformation is also smaller than the variability of the initial water
655 content of metapelite, which likely, along with the amount of the carbonates in the rock, masks any
656 correlation between LOI and temperature (Fig. 8).

657 The oxidation of pyrite into goethite requires water as well. As an order of magnitude estimate, the
658 amount of initial pyrite is estimated to be roughly as 0.5-1% (Table 3). Since goethite contains ~10 wt.%
659 of crystal-bound H₂O, the transformation of 0.5-1% of pyrite into goethite requires 0.05-0.1 wt.% H₂O, or
660 0.14-0.27 vol.%. Due to low abundance of pyrite, this reaction does not significantly affect the water
661 budget. Combining the two described hydration reactions, the quantity of required fluid and the observed
662 increase in salinity (~40%), the initial pore space is estimated at 4.4-4.7 vol.% and decreases down to 2.6-
663 2.8 vol.%.

664 Beside the influence of hydration/dehydration reactions (i.e., uptake/release of H₂O from/into the pore
665 fluid), the salinity might also reflect the uptake/release of solutes out of/into the pore fluid. During this
666 study, qualitative analysis of evaporite mounds of fluid inclusions revealed the large variability in the
667 chemical composition of the pore fluid (Fig. 13). In evaporate mounds, instead of Na predominance
668 (except for one analyzed evaporite mound; 23_B mound1 in Fig. 13a), Ca is the predominant cation with
669 various amount of Na, K, Mg and Fe (Fig. 13). Additionally, S is present in equal amount to Cl or is the
670 predominant anion (Fig. 13). This enrichment is the consequence of pyrite oxidation. This is also supported
671 by iron oxides localization in shear planes and a significant decrease in S in whole-rock compositions. In a
672 similar manner, an increase of S content in the fluid inclusions along the prograde path has been described
673 in metasedimentary rocks from the Central Alps (Rauchenstein-Martinek et al., 2016), as a result of
674 prograde devolatilization reactions.

675 Another implication of our findings is that the composition of pore fluids in subducted sediments is not
676 exclusively controlled by the release or uptake of water in minerals. The chemical evolution of fluids in
677 sediments undergoing subduction is often simplified as a suite of salinity changes occurring in response
678 to the release or uptake of pure water by mineral reactions, assuming NaCl as the dominant species in
679 solution (Herviou et al. (2021) and references therein). Our study shows that other reactions, such as the
680 oxidation of pyrite, may profoundly change the composition of pore fluids, and that S may become the
681 dominant species in solution. Because S is a highly reactive species under certain redox conditions, this
682 drastic evolution in the chemistry of pore fluids may generate other reactions, for instance with
683 carbonates. Further work is required to investigate and quantify these reactions and their effect on the
684 composition of subducted fluids.

685 A final implication of our study is that the transformation of illite into chlorite and the oxidation of pyrite
686 are two reactions that transform pore water into structural water. By consuming pore fluids, these
687 hydration reactions contribute to decrease the porosity of metapelites undergoing subduction. Because

688 these reactions occur in the 250-350°C temperature range, they also strongly contribute to trapping water
689 in minerals, and thus to restrict fluid circulation in the realm of the brittle-plastic transition. As opposed
690 to large-scale circulation and infiltration of external fluids described in several exhumed blueschist and
691 eclogite facies complexes (Angiboust et al., 2011, 2014; Herviou & Bonnet, 2023; Muñoz-Montecinos,
692 Angiboust, & Garcia-Casco, 2021; Spandler & Pirard, 2013; Taetz et al., 2016), results from this study
693 support a model wherein the brittle-plastic transition is the limit between a domain of large-scale
694 circulation of external fluids below it, and a domain of small-scale transfers of local fluids above it
695 (Fagereng et al., 2018; Hyndman & Wang, 1993; Oleskevich et al., 1999; Raimbourg et al., 2018).

696 **6. Conclusions**

697 The present results show well-identified mineral equilibrium in higher-grade samples (at temperatures
698 >300°C), whereas at lower-grade equilibrium is not achieved (at temperatures <300°C). Chlorite
699 thermometry revealed similar temperature of crystallization as RSCM, consistent with the occurrence of
700 mineral reactions at peak-metamorphic conditions.

701 Our study shows that during prograde metamorphism of subducted metapelites, in the range of 230-
702 260°C to 330-350°C, the major mineralogical change is an increase in chlorite/illite ratio as a result of illite-
703 to-chlorite transformation. Other reactions include the oxidation of pyrite into goethite and dissolution
704 of titanite and precipitation of anatase.

705 The bulk composition of the rock is not significantly modified at a temperature range from 230-260°C to
706 330-350°C, which suggests limited mass transfer. Local mass transport is nevertheless observed in the
707 vicinity of veins that formed at peak conditions. There, the matrix is depleted in quartz and albite, which
708 is counterbalanced by their precipitation in the veins. The growth of phyllosilicates is enhanced in the
709 vicinity of the veins. Textural observations point to all reactions occurring during the main deformation
710 event.

711 The salinity of fluid inclusions in quartz veins that experienced 230-260°C is consistently lower than that
712 of seawater, as a result of freshening of the fluid from smectite-to-illite transformation. At higher
713 temperatures the salinity is closer or higher to the seawater. Crystallization of chlorite is a possible
714 explanation for this salinity increase as chlorite requires additional water.

715 Observed mineral reactions, such as illite-to-chlorite transformation, affect the water budget in subducted
716 sediments along the seismogenic zone where the pore fluid is transformed into crystal-bound water,
717 potentially influencing the proportion of pore fluid and consequently pore fluid pressure.

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1125 **FIGURE CAPTIONS**

1126 Figure 1. Geological map of (a) the Kodiak accretionary complex, Alaska, and (b) the Shimanto Belt on
1127 Kyushu, Japan, with the locations of samples used in this study.

1128 Figure 2. Field pictures of metasediments and veins used in this study from the Kodiak accretionary
1129 complex (a and c) and from the Shimanto Belt (b and d). (a) Mode 1 quartz veins in coherent portion of
1130 the Kodiak Landward Belt (Alaska). Note that veins are restricted to sandstone/siltstone layers and absent
1131 in mudstone. (b) Photograph of a polished rock slab from the Hyuga Tectonic Mélange (Shimanto Belt,
1132 Japan). Quartz veins are located in the sandstone lenses in strongly sheared shales. (c) Top-to-the-NW
1133 shear veins in shale-dominated zone cutting across the foliation S_1 , Kodiak Central Belt. (d) Example of en
1134 echelon vein arrays in shale-rich zone of the Foliated Morotsuka (Shimanto Belt, Japan). Blue arrows point
1135 to the sampled veins, whereas red arrows indicate shear bands and displacement directions.

1136 Figure 3. (a) Example of a H₂O Raman spectrum from fluid inclusion, decomposed into two Gaussian
1137 bands. (b) Calculated K' value from the standard solutions with known Cl⁻ molarity. (c) Salinity of 22 fluid
1138 inclusions estimated by Raman spectroscopy and microthermometry, showing the good agreement
1139 between the two independent measurements.

1140 Figure 4. Representative Raman spectra of carbonaceous material from (a) the Kodiak Landward Belt and
1141 (b) the Kodiak Central Belt. The spectra were deconvoluted following the method of Lahfid et al. (2010).

1142 Figure 5. Main microstructures and mineral phases in lower- and higher-grade samples of the Kodiak
1143 accretionary complex and the Shimanto Belt: (a) Photomicrograph of intercalated quartz ribbons and
1144 pelitic matrix rich in fine-grained phyllosilicates, plagioclase and quartz (Sample HN299C, Shimanto). (b)
1145 SEM-BSE image showing intertwined illite and chlorite (sample KO17E, Kodiak). (c) Photomicrograph
1146 (cross-polarized view) of chlorite shear band at low angle to the main foliation (Sample HN299A,
1147 Shimanto). (d) SEM-BSE image of a pelitic matrix with scaly fabrics enriched in Ti-oxides and sulfides
1148 (Sample HN299A, Shimanto). (e) Photomicrograph and (f) SEM-BSE image of the contact between a shear
1149 vein and the surrounding matrix. Note the rim of increasing crystal size in the matrix in immediate contact
1150 with the vein compared to the host rock further away (sample KO38, Kodiak). (g) Optical photomicrograph
1151 (left: plain-polarized view; right: cross-polarized view) of illite+chlorite layers separated by scaly fabrics
1152 (Sample HN285, Shimanto). (h) BSE image of strongly foliated metapelite with the alignment of plagioclase
1153 and quartz parallel to the foliation (Sample HN247, Shimanto). (i) SEM-BSE image and (j) A mask image of
1154 EDS Ti and Fe maps of a shear zone enriched in titanium and iron (Sample HN145, Shimanto).
1155 Abbreviations: Qz – quartz; Pl – plagioclase; Chl – chlorite; Ill – illite; Ap – apatite.

1156 Figure 6. Characteristic vein textures in lower- and higher-grade samples: (a) A Mode-1 quartz-calcite vein
1157 with blocky and elongated quartz. (b) Elongated quartz with trails of pseudo-secondary fluid inclusions
1158 perpendicular to the stretching direction. (c) A sample slab with two extensional shear veins (Sample
1159 KO33C, Kodiak). (d) Deformed calcite in shear vein. (e) A part of shear vein characterized by crack-seal
1160 texture. (f) SEM-BSE image (left) and mask image (right) of an extensional vein connected to a shear vein
1161 from (c), showing chlorite rim along the contact between vein and matrix. Note albite crystals in the vein
1162 and its absence in the matrix.

1163 Figure 7. (a) A field photo of an example of quartz vein with veinlets only on the northwestern side (Site
1164 KO30, Kodiak). (b) Scan of the thin section from the vein of Fig. 7a. (c) SEM-BSE image of the host rock
1165 closer to the vein characterized by the presence of a foliation (S₁) and a crenulation cleavage (S₂), whereas

1166 away from the vein (d) only the foliation (S_1) is present. (e-f) Mask images of (c-d). Note that away from
1167 the vein quartz is still present in the host rock, whereas closer to the vein it is completely absent. (g-h)
1168 Mask images of Ti- and Ca- bearing phases: titanite, anatase and apatite. In zones showing crenulation
1169 cleavage, titanite is partly dissolved and anatase precipitates as indicated by white arrows, whereas
1170 titanite is still present in the host rock away from the vein.

1171 Figure 8. Major and minor element results analyzed by X-ray fluorescence normalized by TiO_2 versus
1172 peak-metamorphic temperature. SO_3 and LOI are plotted without normalization.

1173 Figure 9. Chemical composition of illite and chlorite: Si^{IV} (apfu) in illite versus (a) total alkali (apfu) and (b)
1174 magnesium number (X_{Mg}). Si apfu in chlorite versus (c) sum at octahedral position and (d) magnesium
1175 number ($X_{Mg} = Mg^{2+}/(Fe^{2+}+Mg^{2+})$). (e) Composition of phyllosilicates shown in ternary diagram $Si/4 -$
1176 $(Na+K+2Ca) - (Mg+Fe^{2+})$ according to Velde (1985). (f) Composition of chlorite in amesite (Am) – sudoite
1177 (Sud) – clinocllore+daphnite (Clin+Daph) ternary diagram.

1178 Figure 10. Examples of illite-chlorite equilibrium calculations in samples from (a) the Kodiak Central Belt
1179 (KO38, Kodiak) and (b) the Foliated Morotsuka (HN285, Shimanto). Bold lines represent independent
1180 reactions: (1) $(PrI)_{Phg} = (PrI)_{Chl} + H_2O$; (2) $4 Qtz - (Mg-Am)_{Chl} = 2 (PrI)_{Phg} + 2 (Sud)_{Chl}$; (3) $- 2 (Mg-Cel)_{Phg} +$
1181 $15 Qtz + 2 (Ms)_{Phg} = 4 (PrI)_{Phg} + (Sud)_{Chl}$; (4) $- 5 (Mg-Cel)_{Phg} + (Clin)_{Chl} = (Fe-Am)_{Chl} + 4 (Fe-Cel)_{Phg} + (Ms)_{Phg}$; (5)
1182 $- 4 (Mg-Cel)_{Phg} + 4 (Daph)_{Chl} = 5 (Fe-Am)_{Chl} + (Mg-Am)_{Chl} + 4 (Ms)_{Phg}$; (6) $4 (Mg-Cel)_{Phg} + (Daph)_{Chl} = 5 (Fe-$
1183 $Cel)_{Phg} - (Mg-Am)_{Chl} + (Ms)_{Phg}$. (c) Pressure-temperature results from each of equilibrated illite-chlorite pair.
1184 (d) Comparison of the peak-metamorphic temperatures inferred from RSCM and the chlorite
1185 thermometry using the method by Vidal et al. (2006).

1186 Figure 11. (a) Quartz with high fluid inclusion density from the Kodiak Landward Belt (Sample KO17H). (b)
1187 Quartz from higher-grade shear vein from the Kodiak Central Belt (Sample KO32F). Dashed lines represent
1188 trails of secondary fluid inclusions. (c) Two types of coexisting fluid inclusions in lower-grade veins: One-
1189 phase CH_4 and two-phase H_2O -rich with CH_4-CO_2 vapor bubble (Kodiak Landward Belt, sample KO17H). (d)
1190 two-phase H_2O rich fluid inclusions from quartz vein in the Kodiak Central Belt. Vapor bubble is composed
1191 of CO_2 .

1192 Figure 12. Box plots of estimated salinities of primary fluid inclusions and to a lesser extent of secondary
1193 inclusions in all the studied samples. Points next to each box plot correspond to the salinity of individual
1194 fluid inclusions in a given sample.

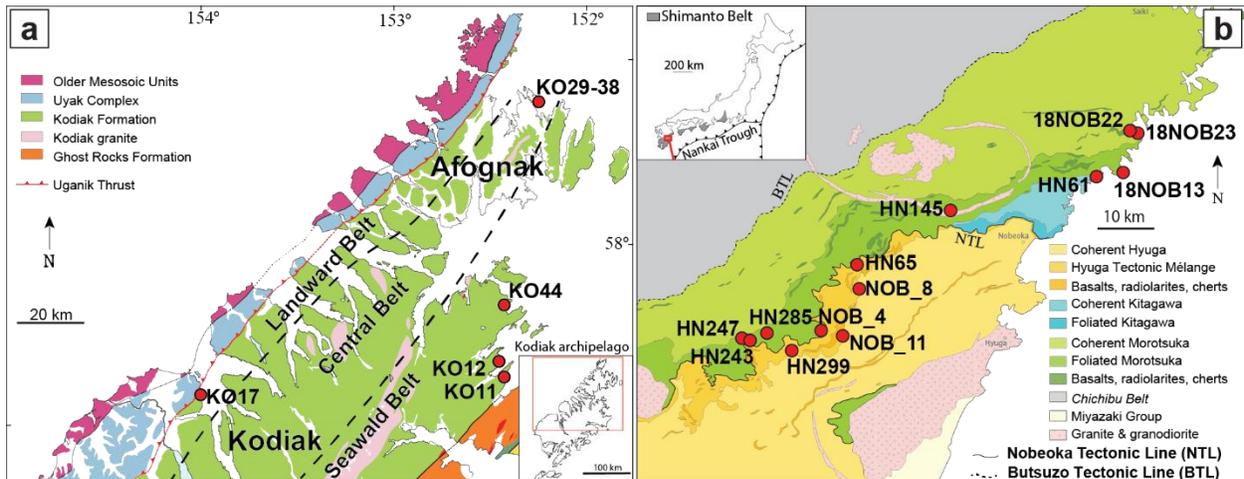
1195 Figure 13. (a) Relative proportions of Na₂O, MgO, CaO, K₂O, FeO, SO₂ and Cl in evaporate mounds from
 1196 decrepitated fluid inclusions. Each line represents the average composition from 3-10 points analyses
 1197 acquired by EPMA in individual evaporate mounds. (b) Ca/Na vs. K/Na binary diagram and (c) Ca/Na vs.
 1198 SO₂/Cl binary diagram of each individual point analysis in all examined evaporate mounds.

1199 Figure 14. (a) The chlorite / (smectite + illite + muscovite) ratios based on XRD results. Note that for both
 1200 localities there is an increase of the proportion of chlorite as a function of temperature. (b) Box plots of
 1201 fluid inclusion salinities in quartz veins from this study as well as from previous studies concerning salinity
 1202 in the Kodiak accretionary complex and the Shimanto Belt in Japan. Compilation of literature: Big Waterfall
 1203 mélangé, Kodiak (Rowe et al., 2009); Kodiak Formation, Alaska: pink – Afognak transect, red – Kodiak
 1204 transect (Brantley & Fisher, 1997); Mugi mélangé (Sakaguchi, 1999); Makimine mélangé (Nishiyama et al.,
 1205 2021).

1206 Figure S1. X-ray diffraction patterns of samples from the Kodiak Formation (Alaska), the Foliated
 1207 Morotsuka, and the Hyuga Tectonic Mélange (Japan).

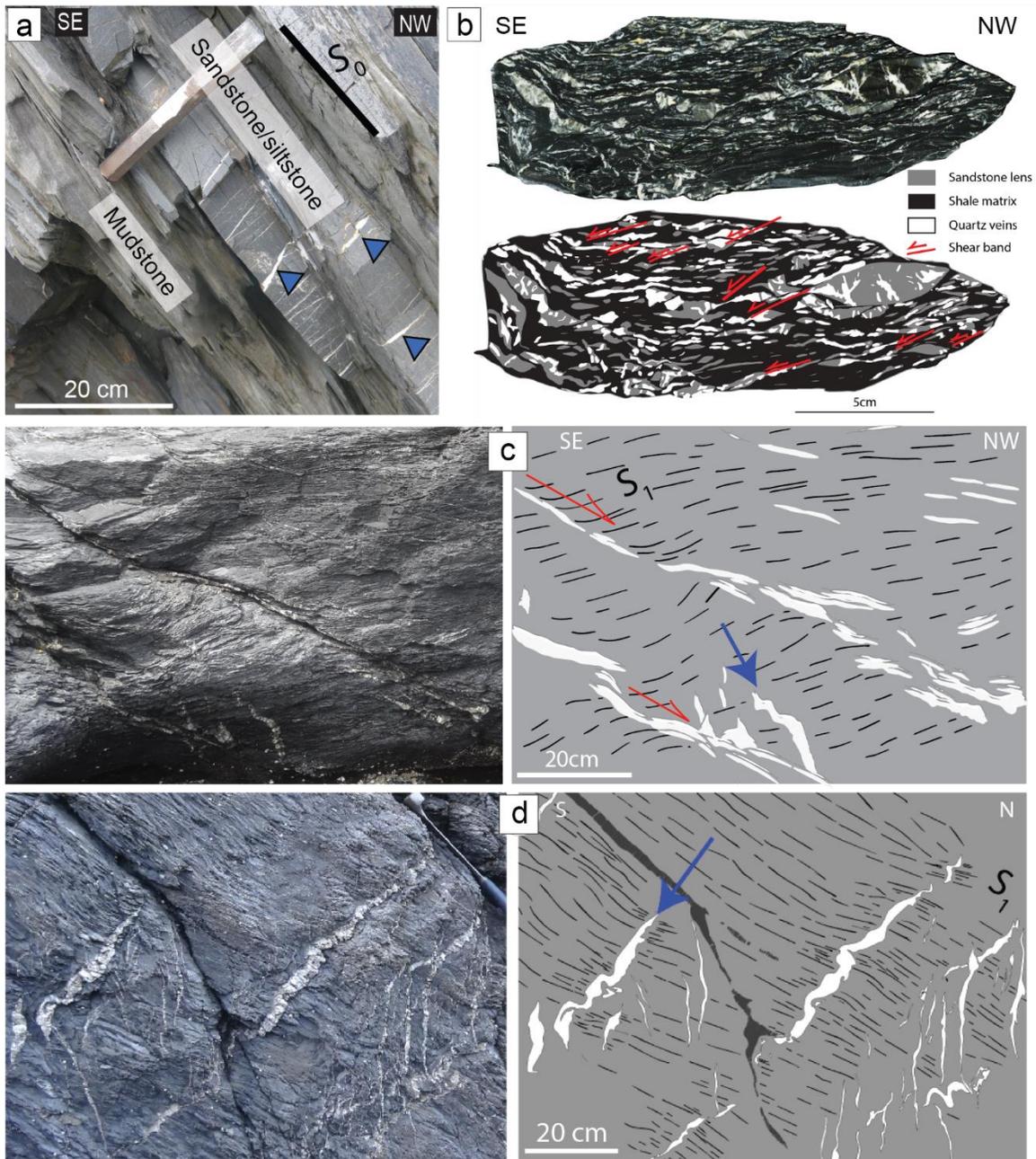
1208 Figure S2. SEM-EDS maps of evaporate mounds after the decrepitation method in (a) lower-grade quartz
 1209 vein (Sample NOB_11C) and (b) higher-grade quartz vein (Sample KO30D).

1210



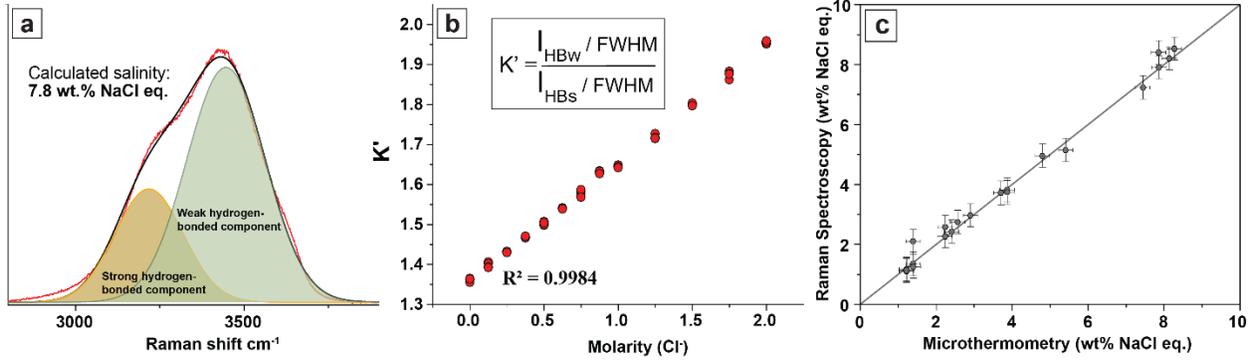
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1212 Figure 1.



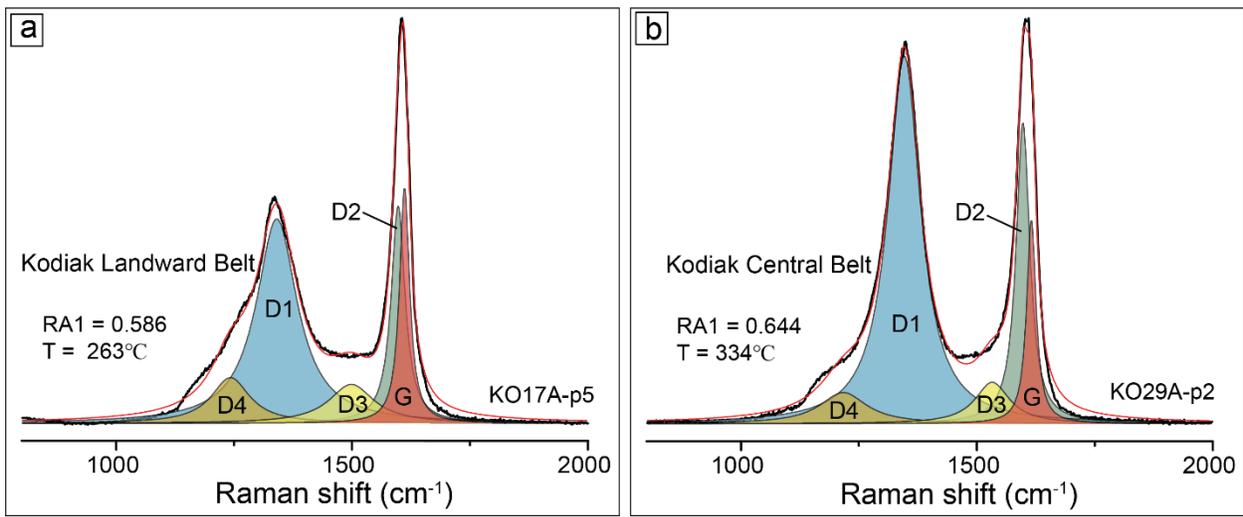
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1214 Figure 2.



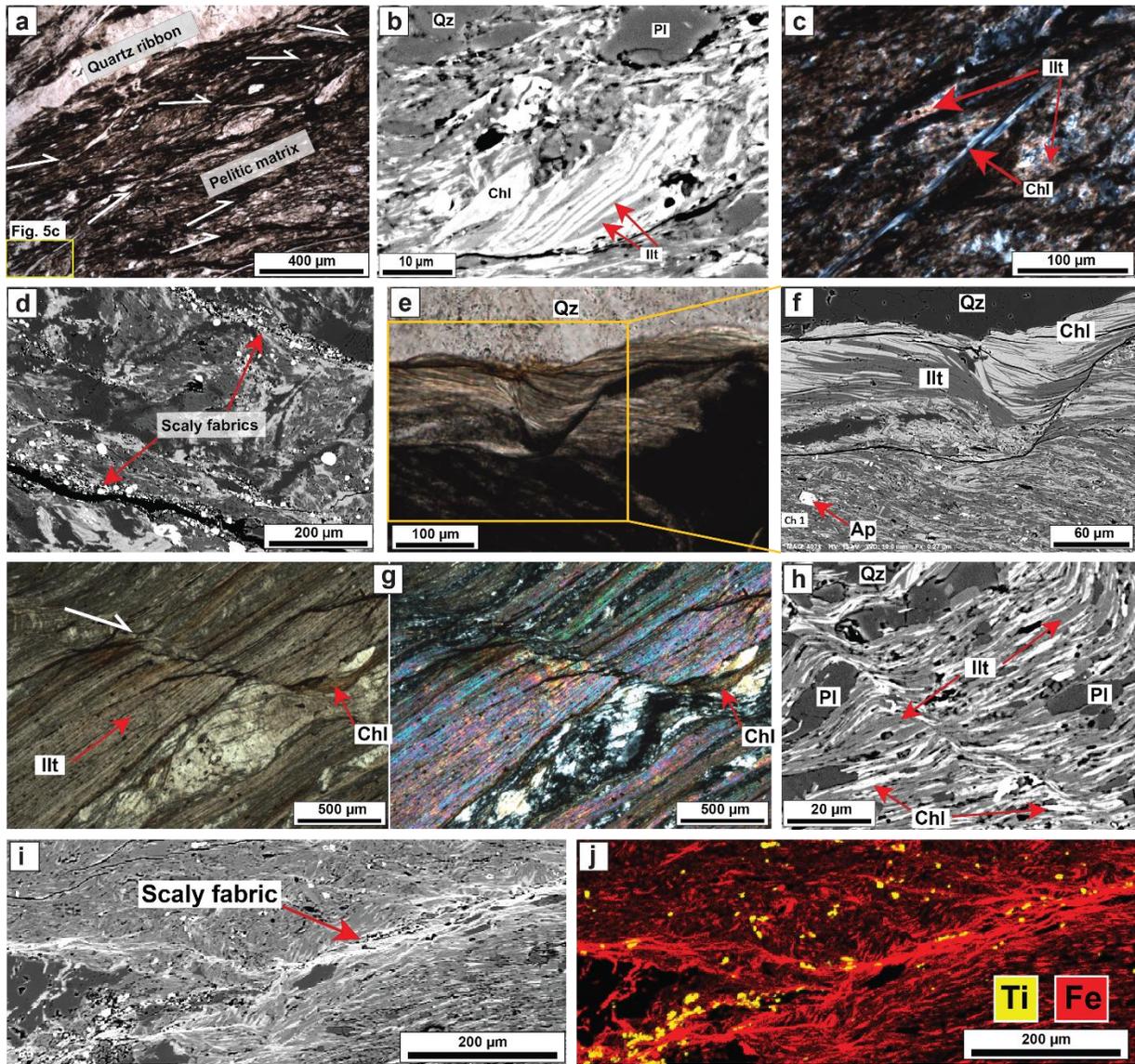
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1216 Figure 3.



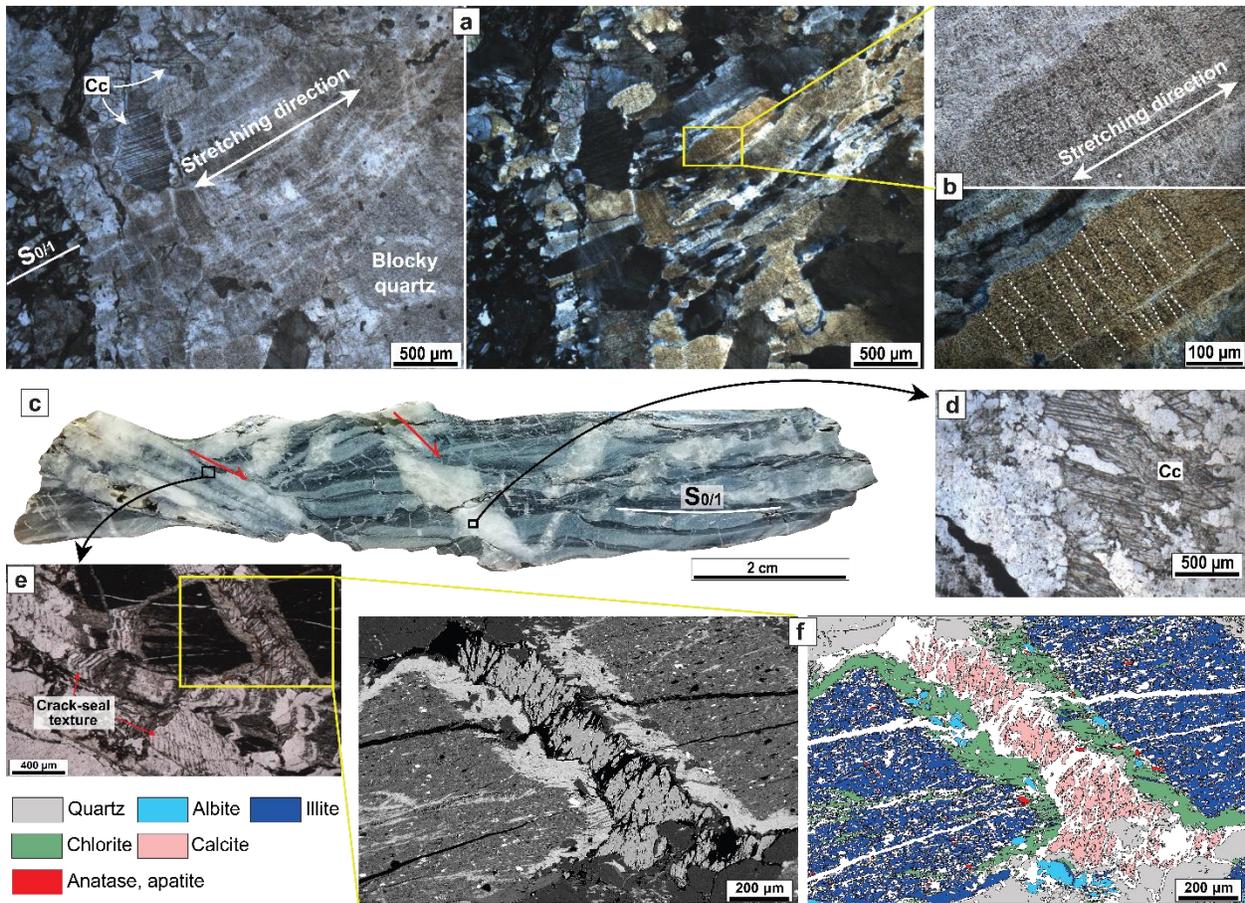
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1218 Figure 4.



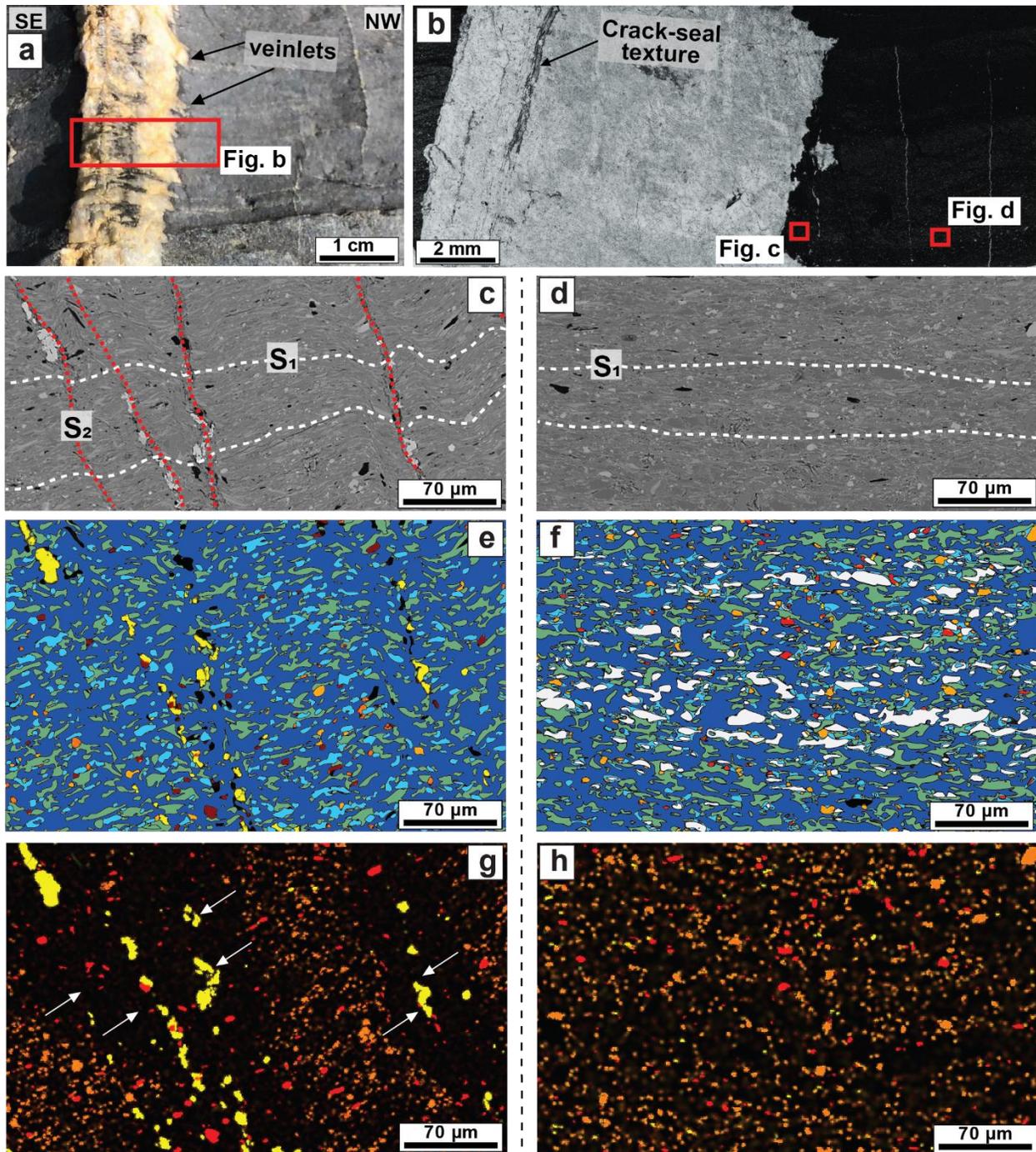
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1220 Figure 5.



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1222 Figure 6.

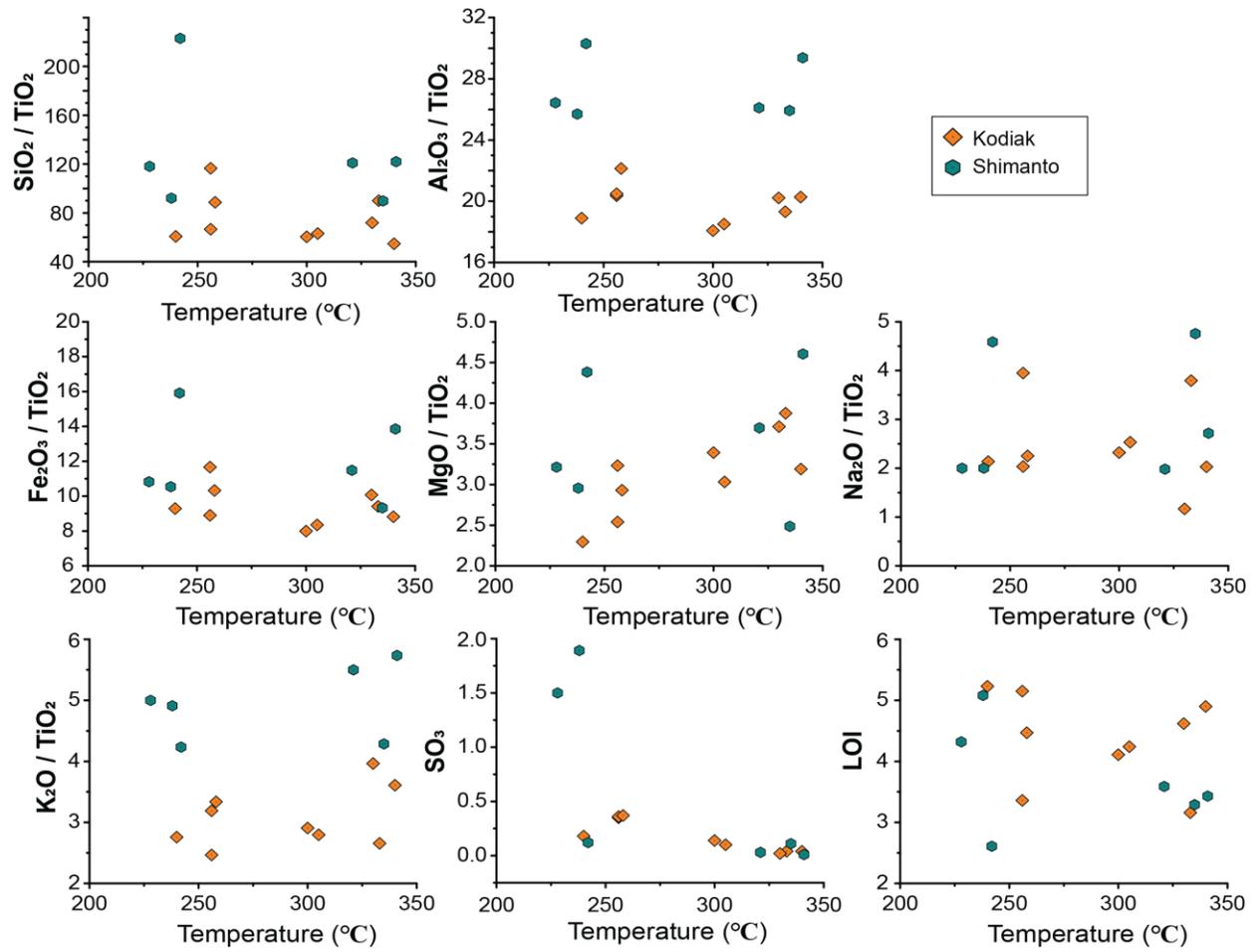


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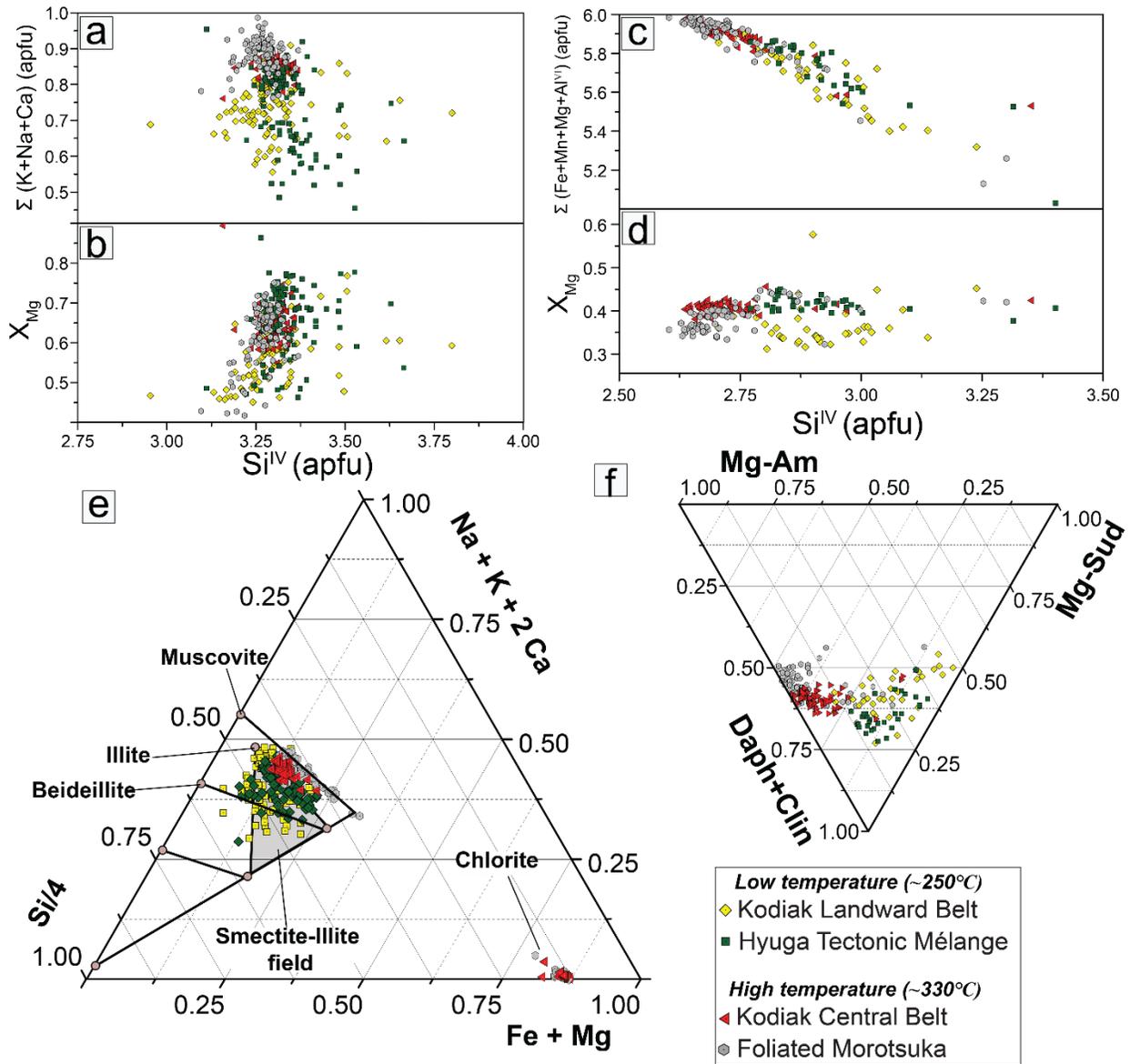
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Figure 7.



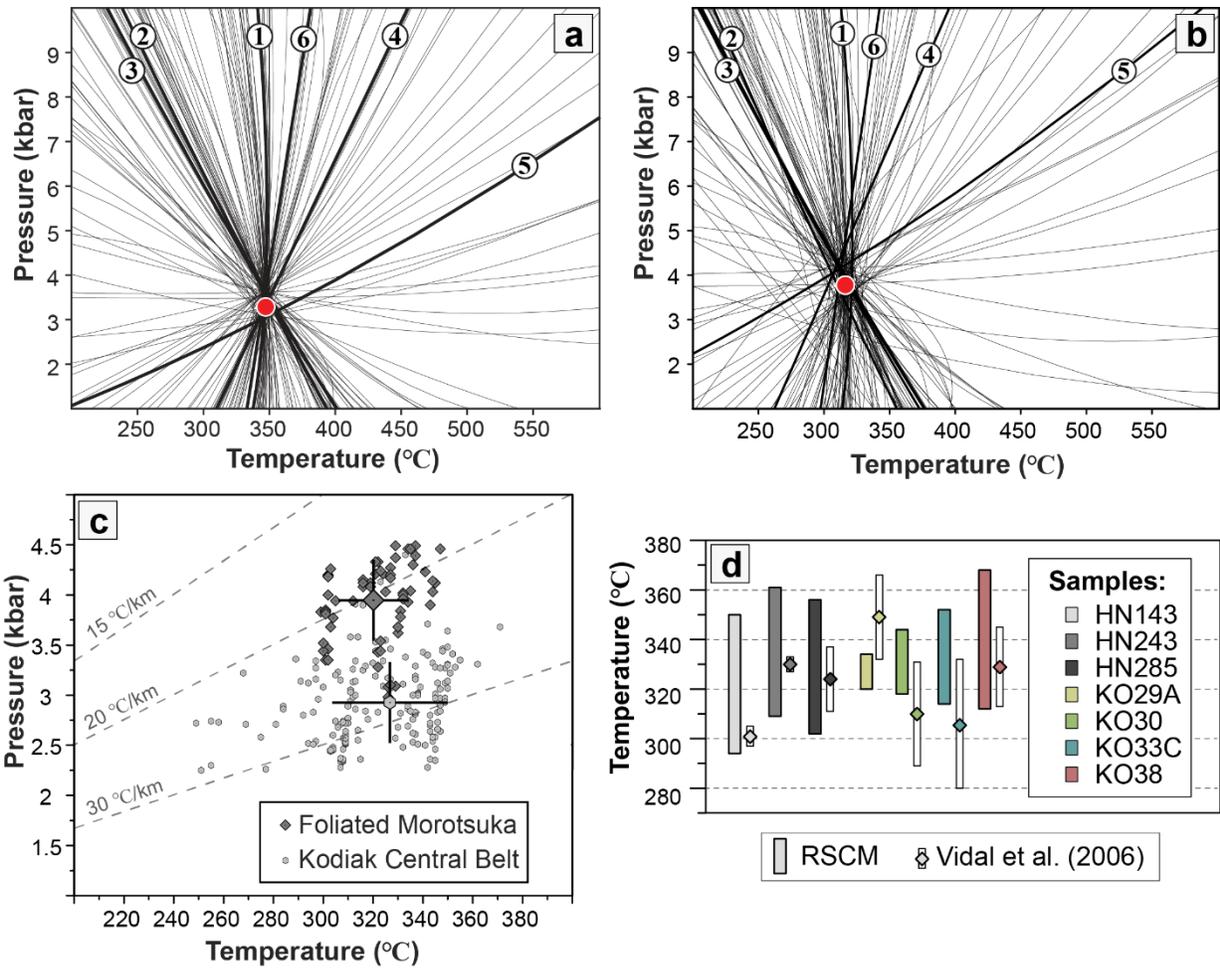
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1226 Figure 8.



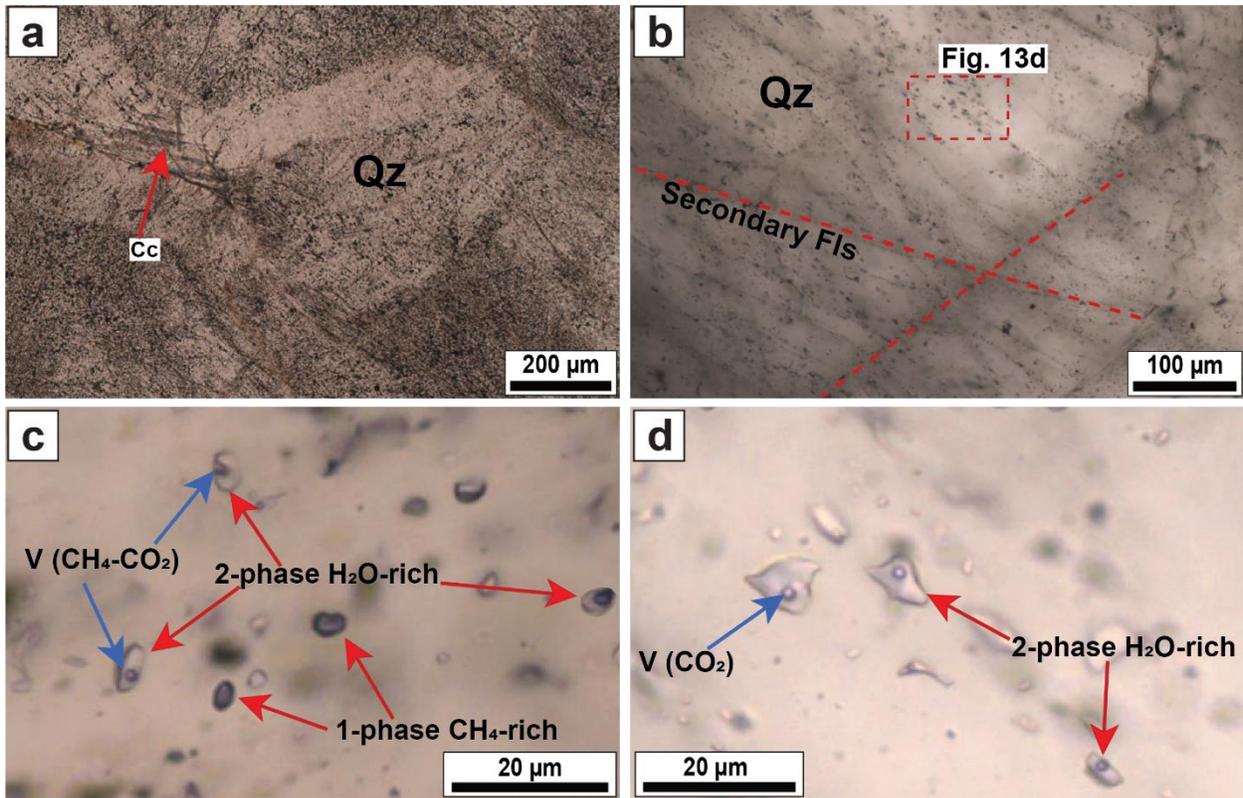
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1228 Figure 9.



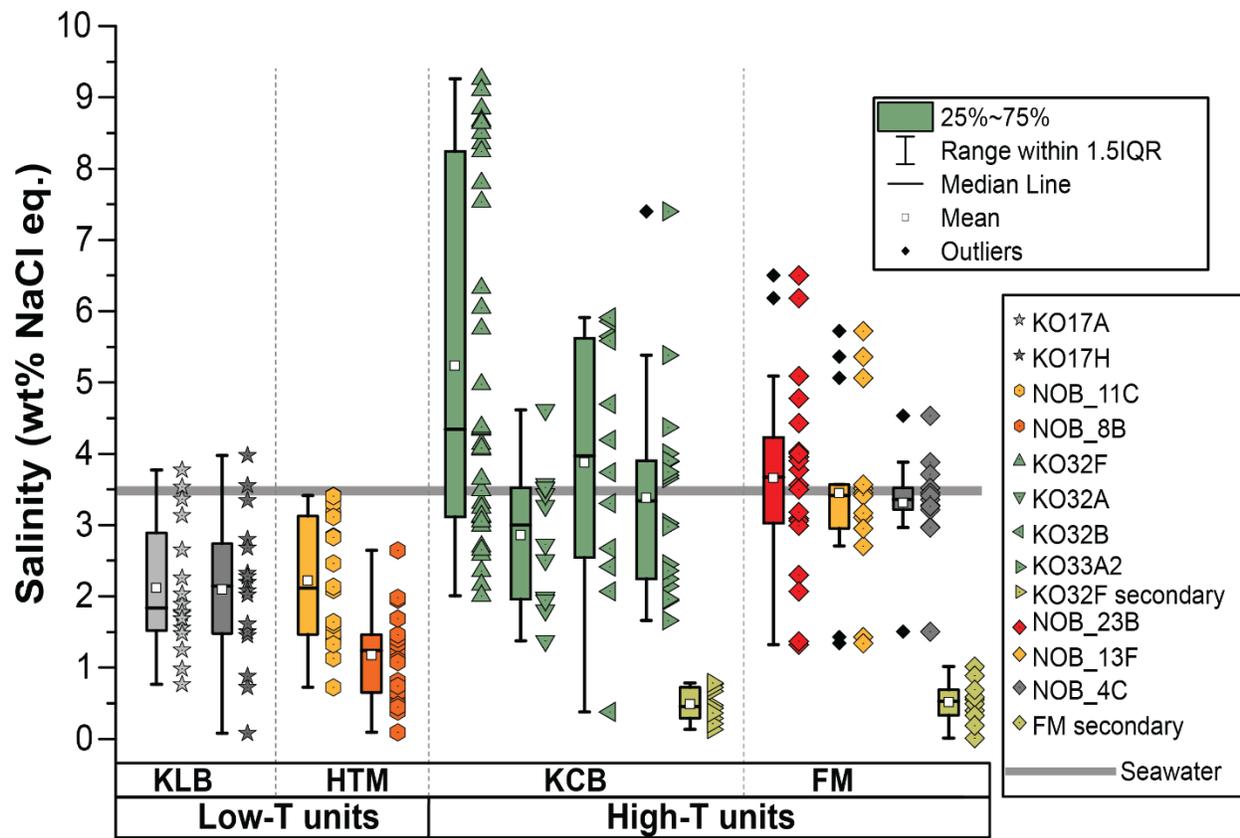
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1230 Figure 10.



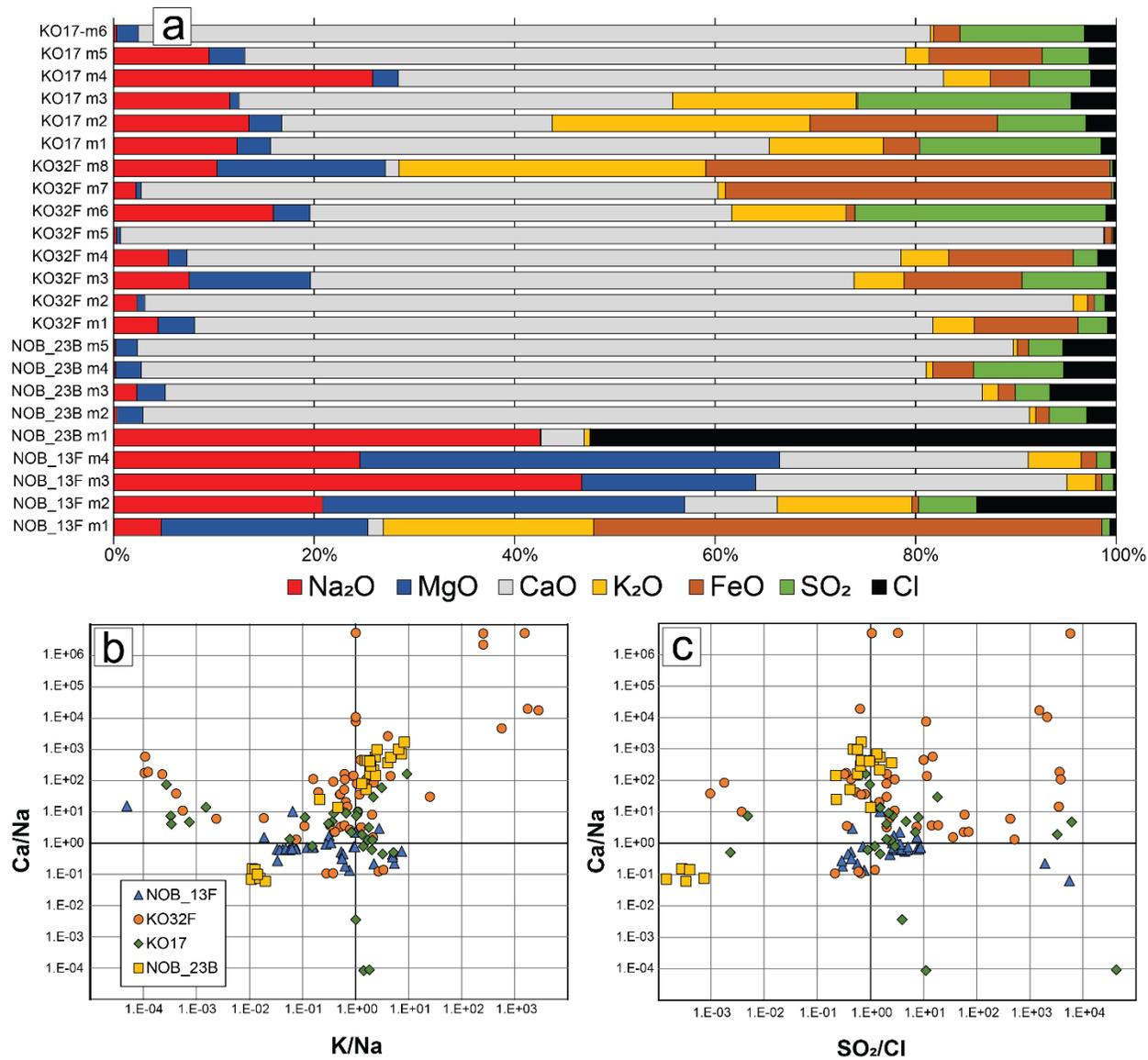
1231

1232 Figure 11.



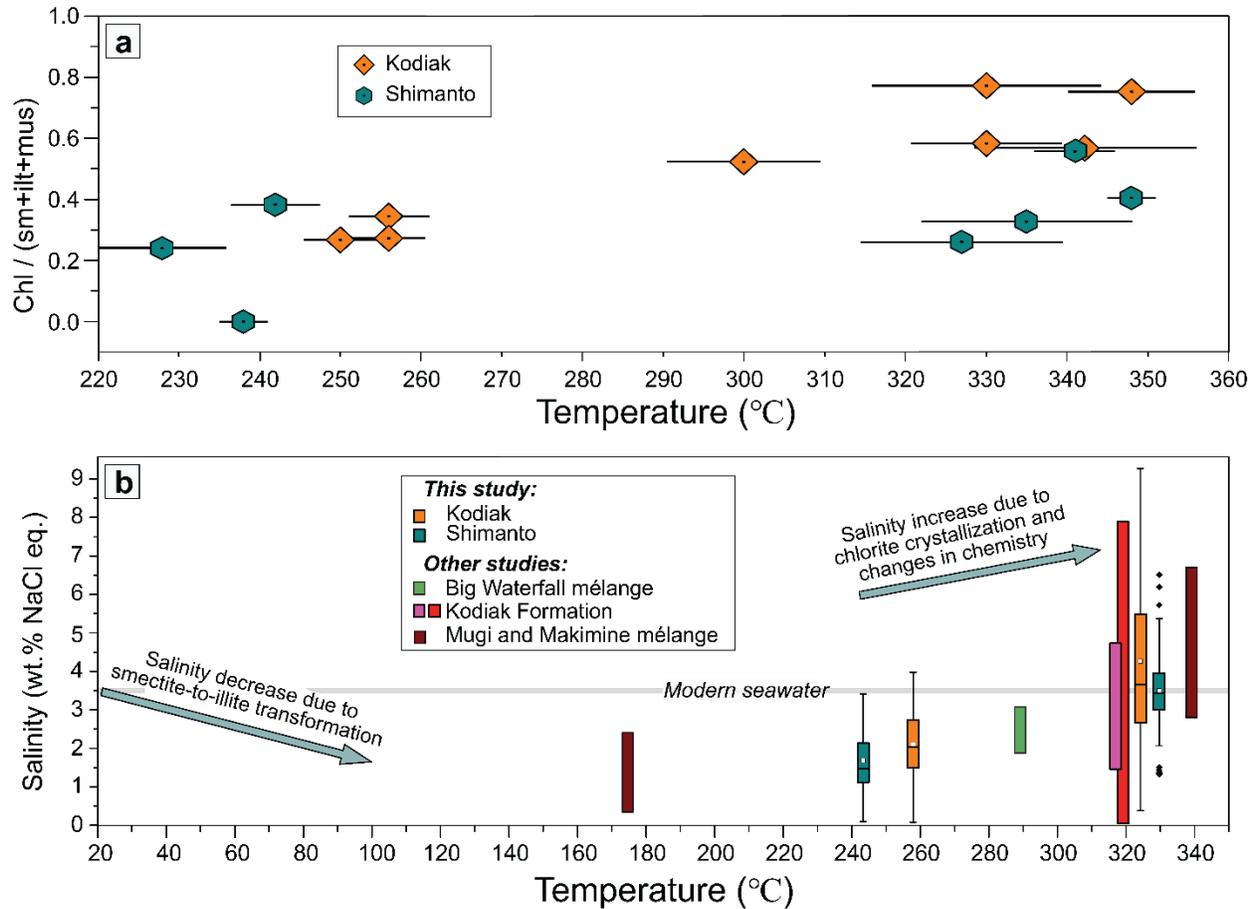
1233

1234 Figure 12.



1235

1236 Figure 13.



1237

1238 Figure 14.

1239 **TABLES**

1240 Table 1. Sample locations and pressure-temperature estimates based on Raman Spectroscopy of
 1241 Carbonaceous Material and multi-phase equilibrium model. Literature references: ¹Palazzin et al. (2016);
 1242 ²Raimbourg et al. (2018); ³Raimbourg et al. (2021).

| | Sample | Longitude | Latitude | RSCM | | Multi-phase equilibrium | | | | Ref. |
|---------------|---------------|-----------|----------|------------|----|-------------------------|----|------------|-----|------------|
| | | | | T (°C) | SD | T (°C) | SD | P (kbar) | SD | |
| Kodiak | Landward Belt | | | | | | | | | |
| | KO17A | -153.9843 | 57.6094 | 251 | 09 | | | | | This study |
| | KO17B | -153.9843 | 57.5093 | 256 | 10 | | | | | This study |
| | KO17E | -153.9841 | 57.6119 | 240 | 09 | | | | | This study |
| Central Belt | KO29A | -152.218 | 58.3774 | 327 | 07 | 349 | 17 | 3.5 | 0.8 | This study |
| | KO30 | -152.2228 | 58.3542 | 331 | 13 | 310 | 21 | 3.1 | 0.4 | This study |
| | KO32A | -152.245 | 58.3893 | 330 | 16 | | | | | This study |
| | KO32F | -152.245 | 58.3893 | 330 | 16 | | | | | This study |
| | KO33C | -152.2568 | 58.3576 | 333 | 19 | 306 | 26 | 2.9 | 0.3 | This study |
| | KO36A | -152.2586 | 58.3661 | 330 | 29 | | | | | This study |

| | | | | | | | | | | |
|-------------------------------|----------|-----------|------------|------------|------------|------------|----------|------------|-------------------------|--------------|
| Seaward Belt | KO38 | -152.2865 | 58.3889 | 340 | 28 | 329 | 16 | 3.0 | 0.4 | This study |
| | KO11 | -152.4386 | 57.6516 | 300 | 19 | | | | | This study |
| | KO12B | -152.4764 | 57.6875 | 348 | 28 | | | | | This study |
| | KO45C | -152.4385 | 57.8393 | 344 | 16 | | | | | This study |
| Shimanto Belt | | | | | | | | | | |
| <i>Hyuga Tectonic Mélange</i> | HN65 | 131.4036 | 32.5452 | 240 | 06 | | | | | ¹ |
| | HN85 | 131.3148 | 32.4287 | 242 | 11 | | | | | This study |
| Foliated Morotsuka | HN299 | 131.279 | 32.4033 | 228 | 16 | | | | | This study |
| | 18NOB13 | 131.5433 | 32.7211 | 323 | 19 | | | | | This study |
| | 18NOB22A | 131.8556 | 32.7552 | 349 | 06 | | | | | This study |
| | 18NOB23 | 131.8786 | 32.7614 | 338 | 10 | | | | | ³ |
| | HN61 | 131.8559 | 32.7202 | 348 | 06 | | | | | ² |
| | HN143 | 131.5583 | 32.6137 | 322 | 28 | 301 | 04 | 3.9 | 0.3 | This study |
| | HN243 | 131.2075 | 32.4094 | 335 | 26 | 330 | 03 | 3.7 | 0.4 | This study |
| HN247 | 131.2026 | 32.3095 | 327 | 33 | | | | | This study | |
| HN285 | 131.2392 | 32.4200 | 329 | 27 | 324 | 13 | 4 | 0.4 | This study ¹ | |

1243

1244 Table 2. Major element compositions of metapelites expressed in wt.% from the Kodiak accretionary
 1245 complex and the Shimanto Belt of Japan.

| Sample | Kodiak Landward Belt | | | | Central Belt | | | Seaward Belt | | Hyuga Tectonic Mélange | | | Foliated Morotsuka | | |
|--------------------------------|----------------------|-------|-------|-------|--------------|-------|-------|--------------|-------|------------------------|--------|--------|--------------------|-------|--------|
| | KO17B | KO17C | KO17D | KO17E | KO33A | KO36A | KO38 | KO11C | KO43C | HN64 | HN85 | HN299 | NOB_23B | HN145 | HN243 |
| SiO ₂ | 69.9 | 59.23 | 62.98 | 57.67 | 65.7 | 59.69 | 54.76 | 58.53 | 59.32 | 61.72 | 75.83 | 66.14 | 64.65 | 67.69 | 62.89 |
| TiO ₂ | 0.60 | 0.89 | 0.71 | 0.95 | 0.73 | 0.83 | 1.00 | 0.97 | 0.94 | 0.67 | 0.34 | 0.56 | 0.53 | 0.56 | 0.70 |
| Al ₂ O ₃ | 12.22 | 18.24 | 15.72 | 17.95 | 14.1 | 16.78 | 20.27 | 17.54 | 17.40 | 17.22 | 10.3 | 14.80 | 15.57 | 14.62 | 18.15 |
| Cr ₂ O ₃ | 0.04 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 | 0.01 |
| Fe ₂ O ₃ | 7.00 | 7.92 | 7.33 | 8.82 | 6.87 | 8.36 | 8.82 | 7.76 | 7.85 | 7.06 | 5.41 | 6.06 | 7.34 | 6.43 | 6.53 |
| MnO | 0.04 | 0.08 | 0.10 | 0.12 | 0.09 | 0.11 | 0.11 | 0.10 | 0.13 | 0.07 | 0.15 | 0.07 | 0.35 | 0.08 | 0.13 |
| MgO | 1.94 | 2.26 | 2.08 | 2.18 | 2.83 | 3.08 | 3.19 | 3.29 | 2.85 | 1.98 | 1.49 | 1.80 | 2.44 | 2.07 | 1.74 |
| CaO | 0.33 | 0.79 | 0.88 | 1.20 | 1.00 | 0.96 | 0.99 | 1.28 | 1.18 | 0.74 | 0.62 | 0.88 | 0.86 | 0.06 | 0.07 |
| Na ₂ O | 2.37 | 1.81 | 1.60 | 2.03 | 2.77 | 0.97 | 2.03 | 2.25 | 2.38 | 1.34 | 1.56 | 1.12 | 1.44 | 1.11 | 3.33 |
| K ₂ O | 1.48 | 2.84 | 2.37 | 2.62 | 1.94 | 3.29 | 3.61 | 2.82 | 2.63 | 3.29 | 1.44 | 2.80 | 3.04 | 3.08 | 3.00 |
| P ₂ O ₅ | 0.16 | 0.26 | 0.22 | 0.28 | 0.22 | 0.25 | 0.27 | 0.44 | 0.36 | 0.10 | 0.08 | 0.09 | 0.09 | 0.07 | 0.11 |
| SO ₃ | 0.35 | 0.36 | 0.37 | 0.18 | 0.04 | 0.02 | 0.04 | 0.14 | 0.10 | 1.89 | 0.12 | 1.50 | 0.01 | 0.03 | 0.11 |
| SrO | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.02 | 0.01 | 0.02 | 0.03 | 0.02 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 |
| BaO | 0.05 | 0.11 | 0.08 | 0.10 | 0.12 | 0.14 | 0.15 | 0.11 | 0.12 | 0.07 | 0.03 | 0.06 | 0.05 | 0.06 | 0.06 |
| LOI | 3.36 | 5.15 | 4.47 | 5.23 | 3.16 | 4.62 | 4.90 | 4.11 | 4.24 | 5.08 | 2.61 | 4.32 | 3.43 | 3.59 | 3.29 |
| Total | 99.96 | 100.1 | 99.05 | 99.53 | 99.72 | 99.24 | 100.3 | 99.51 | 99.7 | 101.35 | 100.05 | 100.35 | 99.97 | 99.59 | 100.20 |

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1247 Table 3. Mineral phase proportions based on X-Ray Diffraction patterns using the Rietveld method
 1248 (Rietveld, 1969). I/S stands for smectite-illite mixed layers.

| Formation | Landward Belt | | | Central Belt | | | Seaward Belt | | HTM | | | Foliated Morotsuka | | | |
|-------------------------|---------------|-------|-------|--------------|-------|------|--------------|-------|-------|------|------|--------------------|------|-------|-------|
| Sample | KO17B | KO17C | KO17E | KO33A | KO36A | KO38 | KO45C | KO11C | HN299 | HN64 | HN85 | 23B | 61 | HN243 | HN246 |
| Major phases | | | | | | | | | | | | | | | |
| Illite/muscovite | 23.2 | 42.1 | 47.6 | 21 | 40.7 | 42.4 | 25.5 | 36.5 | 42.4 | 39.3 | 36.4 | 38.6 | 38.1 | 31.1 | 31.2 |
| Chlorite | 8.0 | 11.5 | 12.7 | 16.2 | 23.7 | 24.1 | 19.2 | 19.1 | 10.2 | 0.0 | 13.9 | 21.6 | 15.4 | 10.2 | 8.1 |
| I/S | 1.8 | 2.6 | 4.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.5 | 2.3 | 1.4 | 0.9 | 0.0 | 0.0 | 0.0 |
| Quartz | 43.1 | 27 | 17.3 | 34.2 | 25.7 | 15.8 | 29.4 | 22.7 | 27.7 | 32.9 | 35.1 | 23.9 | 25.2 | 30 | 30.0 |
| Plagioclase | 19.5 | 13.1 | 16.2 | 25.2 | 5.2 | 16.0 | 22.2 | 17.7 | 10.1 | 13.3 | 12.6 | 11.5 | 20.2 | 26.3 | 26 |
| K feldspar | 0.0 | 0.0 | 0.0 | 3.3 | 4.7 | 1.7 | 2.4 | 3.8 | 0.0 | 0.0 | 0.0 | 2.4 | 0.0 | 2.3 | 2.2 |
| Phyllosilicates | 33 | 56.2 | 64.3 | 37.2 | 64.4 | 66.5 | 44.7 | 55.6 | 57.1 | 41.6 | 51.7 | 61.1 | 53.5 | 41.3 | 39.3 |
| Chl / (Chl+mus) | 24.2 | 20.5 | 19.8 | 43.5 | 36.8 | 36.2 | 43.0 | 34.4 | 17.9 | 0.0 | 26.9 | 35.4 | 28.8 | 24.7 | 20.6 |
| I/S / phs | 5.5 | 4.6 | 6.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.9 | 5.5 | 2.7 | 1.5 | 0.0 | 0.0 | 0.0 |
| Accessory phases | | | | | | | | | | | | | | | |
| Calcite | 0.9 | | 0.6 | | | | 1.2 | | 0.5 | <0.5 | <0.5 | 0.9 | | | |
| Magnesite | | | | | | | | | | | | | 0.8 | | |
| Serpentine | 3.4 | 2.8 | | | | | | | 1.6 | | | | | 1.8 | |
| Pyrite | <0.5 | 0.9 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 1.5 | 0.9 | <0.5 | | | <0.5 | <0.5 |
| Dolomite | | | | | | | | | 1.1 | 1 | | | | | |
| Siderite | | | | | | | | | | 6.1 | | | | | |
| Kaolinite | | | | | | | | | | 4 | | | | | |

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