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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 H<sub>2</sub>O (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 H<sub>2</sub>O

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 CH<sub>4</sub>-dominated to CO<sub>2</sub>-  
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 ( $\sigma_1$ ) 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; Ujiiie 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 $\alpha$  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 $\theta$ , with a step of 0.03°2 $\theta$  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  $\mu$ 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 CaCl<sub>2</sub> 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  $\mu$ 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 $\theta$ , with a step of 0.03°2 $\theta$  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  $\mu\text{m}$   
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), MnTiO<sub>3</sub> (Mn, Ti) and hematite (Fe). For the  
191 elemental maps, the step size and dwell time were 1  $\mu\text{m}$  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-H<sub>2</sub>O 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=Mg<sup>2+</sup>; Tschermak [Si+(Mg,Fe<sup>2+</sup>)=Al<sup>IV</sup>+Al<sup>VI</sup>] in illite and chlorite; di/trioctahedral  
201 [ $\square^{\text{VI}}$ +Al<sup>VI</sup>+Al<sup>VI</sup>=3(Fe<sup>2+</sup>,Mg)] in illite and chlorite, and pyrophyllitic [(Na,K)+Al= $\square^{\text{XII}}$ +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 [ $\square$ =H<sub>2</sub>O]  
204 substitution (see Dubacq et al., 2010). The resulting set of solid solution end-members is pyrophyllite (PrI),  
205 hydrated pyrophyllite (PrI·1H<sub>2</sub>O), 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 H<sub>2</sub>O 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  $\mu\text{m}$  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 ( $1\sigma$ ) 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  $3200\text{ cm}^{-1}$ ) and weak-hydrogen  
237 band (HBw, with the peak centered around  $3450\text{ cm}^{-1}$ ). 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 SiO<sub>2</sub> 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  $340^\circ\text{C}$ . 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  $\mu\text{m}$  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  $\mu\text{m}$  and up  
314 to 775  $\mu\text{m}$  in length when in contact with shear bands, whereas illite crystals reach 1-80  $\mu\text{m}$  in the matrix  
315 and up to 320  $\mu\text{m}$  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  $\mu\text{m}$  and 50-700  $\mu\text{m}$ , 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 SiO<sub>2</sub> 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 SiO<sub>2</sub> 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 ( $0.23 \pm 0.08$  and  $0.21 \pm 0.06$  pfu in KLB and HTM, respectively) than in higher-grade chlorite  
403 ( $0.09 \pm 0.06$  pfu and  $0.08 \pm 0.06$  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 ( $X_{clin}$   $0.24 \pm 0.01$  and  $0.21 \pm 0.03$  for the  
406 KCB and the FM, respectively), daphnite ( $X_{daph}$   $0.35 \pm 0.01$  and  $0.34 \pm 0.01$  for the KCB and the FM,  
407 respectively), and amesite ( $X_{am}$   $0.34 \pm 0.06$  and  $0.38 \pm 0.11$  for the KCB and the FM, respectively)  
408 proportions, with a low sudoite proportion ( $X_{sud}$   $0.07 \pm 0.06$  and  $0.03 \pm 0.03$  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  $21^\circ\text{C}$  and  $3.0 \pm 0.4$  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  $3.9 \pm 0.4$  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  $\text{CH}_4$ -rich fluid inclusions with a size of  
423 up to  $20 \mu\text{m}$  and negative crystal shapes. These  $\text{CH}_4$ -rich fluid inclusions are randomly oriented in the host  
424 quartz. (2) Smaller ( $<10 \mu\text{m}$ ) two-phase  $\text{H}_2\text{O}$ -rich fluid inclusions with various shapes including round,  
425 squared to irregular (Fig. 11c). The small vapor bubble is dominated by  $\text{CH}_4$  (Raimbourg et al., 2018). In  
426 zones characterized by stretched quartz, fluid inclusions (both  $\text{CH}_4$ -rich and  $\text{H}_2\text{O}$ -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  $\text{H}_2\text{O}$ -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  $\text{CO}_2$  and  $\text{CH}_4$  (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  $\sim 3.5$  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  $2.1 \pm 0.9$  wt.%  
439 NaCl eq. and  $2.1 \pm 1.1$  wt.% NaCl, respectively. Similarly, primary fluid inclusions in samples NOB\_11C and  
440 NOB\_8B of the HTM yield average salinities of  $2.2 \pm 0.9$  wt.% NaCl eq. and  $1.2 \pm 0.6$  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  $5.2 \pm 2.5$  wt.% NaCl eq.,  $2.9 \pm 0.9$  wt.% NaCl eq.,  $3.9 \pm 1.8$  wt.% NaCl  
446 eq., and  $3.5 \pm 1.4$  wt.% NaCl eq., respectively. In the FM, samples NOB\_23B, NOB\_13F and NOB\_4C yield  
447 average salinities of  $3.7 \pm 1.4$  wt.% NaCl eq.,  $3.4 \pm 1.3$  wt.% NaCl eq.,  $3.3 \pm 0.7$  wt.% NaCl eq., respectively.  
448 The salinity of secondary fluid inclusions from both localities is below 1 wt.% NaCl eq., in average  $0.5 \pm 0.3$   
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  $\sim 1.5$  to  $\sim 47\%$  and from  $\sim 1.5$  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  $\sim 150$ - $350^\circ\text{C}$ .  
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  $\text{SO}_3$  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  $\text{CH}_4$  to  $\text{CO}_2$  and  
491  $\text{H}_2\text{O}$ , 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  $70^\circ\text{C}$  (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  $260^\circ\text{C}$ ), 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  $\text{SO}_3$ ), 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  $\text{TiO}_2$  (e.g., Fig. 8), show a decrease in  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  counterbalanced by an increase  
547 in FeO, MgO,  $\text{K}_2\text{O}$  and LOI. Hence,  $\text{SiO}_2$  loss is the result of the removal of  $\text{SiO}_2$  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  $\text{SiO}_2$  or  $\text{Na}_2\text{O}$ , 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  $\text{SiO}_2$ , 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  $\text{SiO}_2$  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 SiO<sub>2</sub>. 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 SiO<sub>2</sub> by metamorphic reactions is only a secondary  
568 factor. Taken together, both sources can produce 20 to 37 g of free SiO<sub>2</sub> 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  $280^{\circ}\text{C}$  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  $\text{H}_2\text{O}$ - and  $\text{CH}_4$ -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  $250^{\circ}\text{C}$  (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<sup>-</sup> 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  $330\text{-}$   
643  $350^\circ\text{C}$  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  $\sim 13$  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  $\sim 1.3$   
649 wt.% H<sub>2</sub>O. Potentially inherited water from 10% of illite is  $\sim 0.7$  wt.% H<sub>2</sub>O, hence there is a deficit of 0.6  
650 wt.%, or 1.62 vol.% H<sub>2</sub>O. Therefore, some of the pore fluid has to provide H<sub>2</sub>O 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 H<sub>2</sub>O, the transformation of 0.5-1% of pyrite into goethite requires 0.05-0.1 wt.% H<sub>2</sub>O, 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 H<sub>2</sub>O 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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725

726 **Literature:**

727 Agard, P., Vidal, O., & Goffé, B. (2001). Interlayer and Si content of phengite in HP-LT carpholite-bearing  
728 metapelites: PHENGITE IN HP-LT METAPELITES. *Journal of Metamorphic Geology*, 19(5), 479–  
729 495. <https://doi.org/10.1046/j.0263-4929.2001.00322.x>

730 Agard, P., Goffé, B., Touret, J. L. R., & Vidal, O. (2000). Retrograde mineral and fluid evolution in high-  
731 pressure metapelites (Schistes lustrés unit, Western Alps). *Contributions to Mineralogy and*  
732 *Petrology*, 140, 296–315.

733 Ahn, J. H., & Peacor, D. R. (1985). Transmission Electron Microscopy study of diagenetic chlorite in Gulf  
734 Coast argillaceous sediments. *Clay and Clay Minerals*, 33(3), 228–236.

735 Angiboust, S., & Agard, P. (2010). Initial water budget: The key to detaching large volumes of eclogitized  
736 oceanic crust along the subduction channel? *Lithos*, 120(3–4), 453–474.

737 <https://doi.org/10.1016/j.lithos.2010.09.007>

738 Angiboust, S., Agard, P., Raimbourg, H., Yamato, P., & Huet, B. (2011). Subduction interface processes  
739 recorded by eclogite-facies shear zones (Monviso, W. Alps). *Lithos*, 127(1–2), 222–238.

740 <https://doi.org/10.1016/j.lithos.2011.09.004>

741 Angiboust, S., Pettke, T., De Hoog, J. C. M., Caron, B., & Oncken, O. (2014). Channelized Fluid Flow and  
742 Eclogite-facies Metasomatism along the Subduction Shear Zone. *Journal of Petrology*, *55*(5),  
743 883–916. <https://doi.org/10.1093/petrology/egu010>

744 Árkai, P., Faryad, S. W., Vidal, O., & Balogh, K. (2003). Very low-grade metamorphism of sedimentary  
745 rocks of the Meliata unit, Western Carpathians, Slovakia: implications of phyllosilicate  
746 characteristics. *International Journal of Earth Sciences*, *92*(1), 68–85.  
747 <https://doi.org/10.1007/s00531-002-0303-x>

748 Audet, P., & Schwartz, S. Y. (2013). Hydrologic control of forearc strength and seismicity in the Costa  
749 Rican subduction zone. *Nature Geoscience*, *6*(10), 852–855. <https://doi.org/10.1038/ngeo1927>

750 Battaglia, S. (2004). Variations in the chemical composition of illite from five geothermal fields: a  
751 possible geothermometer. *Clay Minerals*, *39*(4), 501–510.  
752 <https://doi.org/10.1180/0009855043940150>

753 Bebout, G. E. (1991). Field-Based Evidence for Devolatilization in Subduction Zones: Implications for Arc  
754 Magmatism. *Science, New Series*, *251*(4992), 413–416.

755 Bebout, G. E., Agard, P., Kobayashi, K., Moriguti, T., & Nakamura, E. (2013). Devolatilization history and  
756 trace element mobility in deeply subducted sedimentary rocks: Evidence from Western Alps  
757 HP/UHP suites. *Chemical Geology*, *342*, 1–20. <https://doi.org/10.1016/j.chemgeo.2013.01.009>

758 Bebout, G. E., Ryan, J. G., & Leeman, W. P. (1993). B–Be systematics in subduction-related metamorphic  
759 rocks: Characterization of the subducted component. *Geochimica et Cosmochimica Acta*, *57*(10),  
760 2227–2237. [https://doi.org/10.1016/0016-7037\(93\)90565-E](https://doi.org/10.1016/0016-7037(93)90565-E)

761 Becker, H., Jochum, K. P., & Carlson, R. W. (2000). Trace element fractionation during dehydration of  
762 eclogites from high-pressure terranes and the implications for element fluxes in subduction  
763 zones. *Chemical Geology*, *163*(1–4), 65–99. [https://doi.org/10.1016/S0009-2541\(99\)00071-6](https://doi.org/10.1016/S0009-2541(99)00071-6)

764 Beyssac, O., Goffé, B., Chopin, C., & Rouzaud, J. N. (2002). Raman spectra of carbonaceous material in  
765 metasediments: a new geothermometer: RAMAN SPECTROSCOPY OF CARBONACEOUS  
766 MATERIAL. *Journal of Metamorphic Geology*, 20(9), 859–871. [https://doi.org/10.1046/j.1525-  
767 1314.2002.00408.x](https://doi.org/10.1046/j.1525-1314.2002.00408.x)

768 Bodnar, R. J. (1993). Revised equation and table for determining the freezing point depression of H<sub>2</sub>O-  
769 NaCl solutions. *Geochimica et Cosmochimica Acta*, 57(3), 683–684.  
770 [https://doi.org/10.1016/0016-7037\(93\)90378-A](https://doi.org/10.1016/0016-7037(93)90378-A)

771 Boles, J. R., & Franks, S. G. (1979). Clay Diagenesis in Wilcox Sandstones of Southwest Texas:  
772 Implications of Smectite Diagenesis on Sandstone Cementation, 16.

773 Bons, P. D., Elburg, M. A., & Gomez-Rivas, E. (2012). A review of the formation of tectonic veins and their  
774 microstructures. *Journal of Structural Geology*, 43, 33–62.  
775 <https://doi.org/10.1016/j.jsg.2012.07.005>

776 Brantley, S. L., & Fisher, D. M. (1997). Segregation veins: evidence for the deformation and dewatering of  
777 a low-grade metapelite. In *Deformation-enhanced Fluid Transport in the Earth's Crust and  
778 Mantle* (pp. 267–288). Chapman & Hall, 2-6 Boundary Row, London SE1 8HN, UK.

779 Breeding, C. M., & Ague, J. J. (2002). Slab-derived fluids and quartz-vein formation in an accretionary  
780 prism, Otago Schist, New Zealand. *Geology*, 30(6), 499–502.

781 Byrne, T., & Fisher, D. M. (1990). Evidence for a Weak and Overpressured Decollement Beneath  
782 Sediment-Dominated Accretionary Prisms. *Journal of Geophysical Research*, 95(B6), 9081–9097.

783 Byrne, T. (1982). Structural evolution of coherent terranes in the Ghost Rocks Formation, Kodiak Island,  
784 Alaska. *Geological Society, London, Special Publications*, 10(1), 229–242.  
785 <https://doi.org/10.1144/GSL.SP.1982.010.01.15>

786 Byrne, T., & Fisher, D. M. (1987). Episodic growth of the Kodiak convergent margin. *Nature*, 325, 338–  
787 341.

788 Caumon, M.-C., Dubessy, J., Robert, P., & Tarantola, A. (2014). Fused-silica capillary capsules (FSCCs) as  
789 reference synthetic aqueous fluid inclusions to determine chlorinity by Raman spectroscopy.  
790 *European Journal of Mineralogy*, 25(5), 755–763. [https://doi.org/10.1127/0935-](https://doi.org/10.1127/0935-1221/2013/0025-2280)  
791 [1221/2013/0025-2280](https://doi.org/10.1127/0935-1221/2013/0025-2280)

792 Caumon, M.-C., Tarantola, A., & Mosser-Ruck, R. (2015). Raman spectra of water in fluid inclusions: I.  
793 Effect of host mineral birefringence on salinity measurement: Effect of mineral birefringence on  
794 salinity measured by Raman spectroscopy. *Journal of Raman Spectroscopy*, 46(10), 969–976.  
795 <https://doi.org/10.1002/jrs.4708>

796 Colten-Bradley, V. A. (1987). Role of pressure in smectite dehydration; Effects on geopressure and  
797 smectite- to-illite transformation. *American Association of Petroleum Geologists Bulletin*, 71,  
798 1414–1427.

799 Connelly, W. (1978). Uyak Complex, Kodiak Islands, Alaska: A Cretaceous subduction complex.  
800 *Geological Society of America Bulletin*, 89, 755–769.

801 Davis, D., Suppe, J., & Dahlen, F. A. (1983). Mechanics of fold-and-thrust belts and accretionary wedges.  
802 *Journal of Geophysical Research*, 88(B2), 1153. <https://doi.org/10.1029/JB088iB02p01153>

803 De Parseval, P., Amouric, M., Baronnet, A., Fortune, J.-P., Moine, B., & Ferret, J. (1994). HRTEM study of  
804 the chloritization of micas in the talk-chlorite deposit at Trimouns (Pyrenees, France). *Eur. J.*  
805 *Mineral*, 6, 123–132.

806 Drief, A., & Nieto, F. (2000). Chemical composition of smectites formed in clastic sediments. Implications  
807 for the smectite-illite transformation. *Clay Minerals*, 35(4), 665–678.  
808 <https://doi.org/10.1180/000985500547124>

809 Dubacq, B., Vidal, O., & De Andrade, V. (2010). Dehydration of dioctahedral aluminous phyllosilicates:  
810 thermodynamic modelling and implications for thermobarometric estimates. *Contributions to*  
811 *Mineralogy and Petrology*, 159(2), 159–174. <https://doi.org/10.1007/s00410-009-0421-6>

812 Dubessy, J., Geisler, D., Kosztolanyi, C., & Vernet, M. (1983). The determination of sulphate in fluid  
813 inclusions using the M.O.L.E. Raman microprobe. Application to a keuper halite and geochemical  
814 consequences. *Geochimica et Cosmochimica Acta*, 47(1), 1–10. [https://doi.org/10.1016-](https://doi.org/10.1016/0016-7037(83)90086-8)  
815 7037(83)90086-8

816 Elliott, T. (2003). Tracers of the slab. In J. Eiler (Ed.), *Geophysical Monograph Series* (Vol. 138, pp. 23–45).  
817 Washington, D. C.: American Geophysical Union. <https://doi.org/10.1029/138GM03>

818 Fagereng, Å., & Cooper, A. F. (2010). The metamorphic history of rocks buried, accreted and exhumed in  
819 an accretionary prism: an example from the Otago Schist, New Zealand: METAMORPHIC  
820 HISTORY OF AN ACCRETIONARY PRISM. *Journal of Metamorphic Geology*, 28(9), 935–954.  
821 <https://doi.org/10.1111/j.1525-1314.2010.00900.x>

822 Fagereng, Å., Remitti, F., & Sibson, R. H. (2011). Incrementally developed slickenfibers — Geological  
823 record of repeating low stress-drop seismic events? *Tectonophysics*, 510(3–4), 381–386.  
824 <https://doi.org/10.1016/j.tecto.2011.08.015>

825 Fagereng, Å., Diener, J. F. A., Ellis, S., & Remitti, F. (2018). Fluid-related deformation processes at the up-  
826 and downdip limits of the subduction thrust seismogenic zone: What do the rocks tell us? In  
827 Timothy Byrne, M. B. Underwood, D. Fisher, L. McNeill, D. Saffer, K. Ujiie, & A. Yamaguchi,  
828 *Geology and Tectonics of Subduction Zones: A Tribute to Gaku Kimura*. Geological Society of  
829 America. [https://doi.org/10.1130/2018.2534\(12\)](https://doi.org/10.1130/2018.2534(12))

830 Ferrill, D. A., Morris, A. P., Evans, M. A., Burkhard, M., Groshong, R. H., & Onasch, C. M. (2004). Calcite  
831 twin morphology: a low-temperature deformation geothermometer. *Journal of Structural*  
832 *Geology*, 26(8), 1521–1529. <https://doi.org/10.1016/j.jsg.2003.11.028>

833 Ferry, J. M. (1981). Petrology of graphitic sulfide-rich schists from south-central Maine: an example of  
834 desulfidation during prograde regional metamorphism. *American Mineralogist*, 66, 908–930.

835 Fisher, D. M., & Byrne, T. (1987). Structural evolution of underthrust sediments, Kodiak Islands,  
836 Alaska. *Tectonics*, 6(6), 775–793. <https://doi.org/10.1029/TC006i006p00775>

837 Fisher, D. M., & Byrne, T. (1990). The character and distribution of mineralized fractures in the Kodiak  
838 Formation, Alaska: Implications for fluid flow in an underthrust sequence. *Journal of Geophysical*  
839 *Research*, 95(B6), 9069. <https://doi.org/10.1029/JB095iB06p09069>

840 Fisher, D. M., & Brantley, S. L. (1992). Models of quartz overgrowth and vein formation: Deformation  
841 and episodic fluid flow in an ancient subduction zone. *Journal of Geophysical Research*, 97(B13),  
842 20043. <https://doi.org/10.1029/92JB01582>

843 Fisher, D. M., & Brantley, S. L. (2014). The role of silica redistribution in the evolution of slip instabilities  
844 along subduction interfaces: Constraints from the Kodiak accretionary complex, Alaska. *Journal*  
845 *of Structural Geology*, 69, 395–414. <https://doi.org/10.1016/j.jsg.2014.03.010>

846 Fisher, D. M., & Byrne, T. (1992). Strain variations in an ancient accretionary complex: Implications for  
847 forearc evolution. *Tectonics*, 11(2), 330–347. <https://doi.org/10.1029/91TC01490>

848 Fisher, D. M., Brantley, S. L., Everett, M., & Dzvonik, J. (1995). Cyclic fluid flow through a regionally  
849 extensive fracture network within the Kodiak accretionary prism. *Journal of Geophysical*  
850 *Research: Solid Earth*, 100(B7), 12881–12894. <https://doi.org/10.1029/94JB02816>

851 Frey, M. (1978). Progressive Low-Grade Metamorphism of a Black Shale Formation, Central Swiss Alps,  
852 with Special Reference to Pyrophyllite and Margarite Bearing Assemblages. *Journal of Petrology*,  
853 19(1), 95–135. <https://doi.org/10.1093/petrology/19.1.95>

854 Frey, M., Bucher, K., & Frank, E. (1980). Alpine metamorphism along the geotraverse Basel-Chiasso : a  
855 review. <https://doi.org/10.5169/SEALS-164971>

856 Goffé, B., & Chopin, C. (1986). High-pressure metamorphism in the Western Alps : zoneography of  
857 metapelites, chronology and consequences. <https://doi.org/10.5169/SEALS-50880>

858 Hacker, B. R. (2008). H<sub>2</sub>O subduction beyond arcs. *Geochemistry, Geophysics, Geosystems*, 9(3), n/a-n/a.  
859 <https://doi.org/10.1029/2007GC001707>

860 Hacker, B. R., Abers, G. A., & Peacock, S. M. (2003). Subduction factory 1. Theoretical mineralogy,  
861 densities, seismic wave speeds, and H<sub>2</sub>O contents: SUBDUCTION ZONE MINERALOGY AND  
862 PHYSICAL PROPERTIES. *Journal of Geophysical Research: Solid Earth*, 108(B1).  
863 <https://doi.org/10.1029/2001JB001127>

864 Hall, A. J. (1986). Pyrite-pyrrhotine redox reactions in nature. *Mineralogical Magazine*, 50(356), 223–  
865 229. <https://doi.org/10.1180/minmag.1986.050.356.05>

866 Herviou, C., & Bonnet, G. (2023). Paleocene-Eocene high-pressure carbonation of Western Alps  
867 serpentinites: positive feedback between deformation and CO<sub>2</sub>-CH<sub>4</sub> fluid ingression responsible  
868 for slab slicing? *Geochemistry, Geophysics, Geosystems*.

869 Herviou, C., Verlaquet, A., Agard, P., Locatelli, M., Raimbourg, H., Lefeuvre, B., & Dubacq, B. (2021).  
870 Along-dip variations of subduction fluids: The 30–80 km depth traverse of the Schistes Lustrés  
871 complex (Queyras-Monviso, W. Alps). *Lithos*, 394–395, 106168.  
872 <https://doi.org/10.1016/j.lithos.2021.106168>

873 Hower, J., Eslinger, E. V., Hower, M. E., & Perry, E. A. (1976). Mechanism of burial metamorphism of  
874 argillaceous sediment: 1. Mineralogical and chemical evidence. *Geological Society of America*  
875 *Bulletin*, 87(5), 725. [https://doi.org/10.1130/0016-7606\(1976\)87<725:MOBMOA>2.0.CO;2](https://doi.org/10.1130/0016-7606(1976)87<725:MOBMOA>2.0.CO;2)

876 Hyndman, R. D., & Wang, K. (1993). Thermal constraints on the zone of major thrust earthquake failure:  
877 The Cascadia Subduction Zone. *Journal of Geophysical Research: Solid Earth*, 98(B2), 2039–2060.  
878 <https://doi.org/10.1029/92JB02279>

879 Jarrard, R. D. (2003). Subduction fluxes of water, carbon dioxide, chlorine, and potassium: SUBDUCTION  
880 FLUXES OF WATER. *Geochemistry, Geophysics, Geosystems*, 4(5), n/a-n/a.  
881 <https://doi.org/10.1029/2002GC000392>



882 Kameda, J., Raimbourg, H., Kogure, T., & Kimura, G. (2011a). Low-grade metamorphism around the  
883 down-dip limit of seismogenic subduction zones: Example from an ancient accretionary complex  
884 in the Shimanto Belt, Japan. *Tectonophysics*, 502(3–4), 383–392.  
885 <https://doi.org/10.1016/j.tecto.2011.02.010>

886 Kameda, J., Yamaguchi, A., Saito, S., Sakuma, H., Kawamura, K., & Kimura, G. (2011b). A new source of  
887 water in seismogenic subduction zones: A SOURCE OF WATER IN SEISMOGENIC ZONE.  
888 *Geophysical Research Letters*, 38(22), n/a-n/a. <https://doi.org/10.1029/2011GL048883>

889 Kastner, M. (1981). Authigenic silicates in deep-sea sediments: formation and diagenesis. In *The oceanic*  
890 *lithosphere The sea* (C. Emiliani, Vol. 7, pp. 915–980). Wiley.

891 Kastner, M., Solomon, E. A., Harris, R. N., & Torres, M. E. (2014). Fluid Origins, Thermal Regimes, and  
892 Fluid and Solute Fluxes in the Forearc of Subduction Zones. In *Developments in Marine Geology*  
893 (Vol. 7, pp. 671–733). Elsevier. <https://doi.org/10.1016/B978-0-444-62617-2.00022-0>

894 Kawabata, K., Tanaka, H., & Kimura, G. (2007). Mass transfer and pressure solution in deformed shale of  
895 accretionary complex: Examples from the Shimanto Belt, southwestern Japan. *Journal of*  
896 *Structural Geology*, 29(4), 697–711. <https://doi.org/10.1016/j.jsg.2006.11.009>

897 van Keken, P. E., Kiefer, B., & Peacock, S. M. (2002). High-resolution models of subduction zones:  
898 Implications for mineral dehydration reactions and the transport of water into the deep mantle:  
899 HIGH-RESOLUTION MODELS OF SUBDUCTION ZONES. *Geochemistry, Geophysics, Geosystems*,  
900 3(10), 1 of 20–20 20. <https://doi.org/10.1029/2001GC000256>

901 Kominz, M. A., & Pekar, S. F. (2001). Oligocene eustasy from two-dimensional sequence stratigraphic  
902 backstripping. *Geological Society of America Bulletin*, 113(3), 291–304.  
903 [https://doi.org/10.1130/0016-7606\(2001\)113<0291:OEFTDS>2.0.CO;2](https://doi.org/10.1130/0016-7606(2001)113<0291:OEFTDS>2.0.CO;2)

904 Komninou, A., & Sverjensky, D. A. (1995). Pre-ore hydrothermal alteration in an unconformity-type  
905 uranium deposit. *Contributions to Mineralogy and Petrology*, 121(1), 99–114.  
906 <https://doi.org/10.1007/s004100050092>

907 Kondo, H., Kimura, G., Masago, H., Ohmori-Ikehara, K., Kitamura, Y., Ikesawa, E., et al. (2005).  
908 Deformation and fluid flow of a major out-of-sequence thrust located at seismogenic depth in  
909 an accretionary complex: Nobeoka Thrust in the Shimanto Belt, Kyushu, Japan: NOBEOKA  
910 THRUST, A SEISMOGENIC OST. *Tectonics*, 24(6), n/a-n/a. <https://doi.org/10.1029/2004TC001655>

911 Kontak, D. J. (2004). Analysis of evaporate mounds as a complement to fluid-inclusion thermometric  
912 data: Case studies from granitic environments in Nova Scotia and Peru. *THE CANADIAN*  
913 *MINERALOGIST*, 16.

914 Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., & Goffé, B. (2010). Evolution of the Raman  
915 spectrum of carbonaceous material in low-grade metasediments of the Glarus Alps  
916 (Switzerland): RSCM in low-grade metasediments. *Terra Nova*, 22(5), 354–360.  
917 <https://doi.org/10.1111/j.1365-3121.2010.00956.x>

918 Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E. G., & Schwartz, S. (2014).  
919 XMapTools: A MATLAB®-based program for electron microprobe X-ray image processing and  
920 geothermobarometry. *Computers & Geosciences*, 62, 227–240.  
921 <https://doi.org/10.1016/j.cageo.2013.08.010>

922 Lefeuvre, B., Agard, P., Verlaquet, A., Dubacq, B., & Plunder, A. (2020). Massive formation of lawsonite in  
923 subducted sediments from the Schistes Lustrés (W. Alps): Implications for mass transfer and  
924 decarbonation in cold subduction zones. *Lithos*, 370–371, 105629.  
925 <https://doi.org/10.1016/j.lithos.2020.105629>

926 Majzlan, J., Grevel, K.-D., & Navrotsky, A. (2003). Thermodynamics of Fe oxides: Part II. Enthalpies of  
927 formation and relative stability of goethite (a-FeOOH), lepidocrocite (g-FeOOH), and maghemite  
928 (g-Fe<sub>2</sub>O<sub>3</sub>). *American Mineralogist*, 88(5–6), 855–859. <https://doi.org/10.2138/am-2003-5-614>

929 Makvandi, S., Huang, X., Beaudoin, G., Qurt, D., Ledru, P., & Fayek, M. (2021). Trace element signatures  
930 in hematite and goethite associated with the Kiggavik–Andrew Lake structural trend U deposits  
931 (Nunavut, Canada). *Mineralium Deposita*, 56(3), 509–535. [https://doi.org/10.1007/s00126-020-](https://doi.org/10.1007/s00126-020-00980-y)  
932 00980-y

933 Masci, L., Dubacq, B., Verlaquet, A., Chopin, C., De Andrade, V., & Herviou, C. (2019). A XANES and EPMA  
934 study of Fe<sup>3+</sup> in chlorite: Importance of oxychlorite and implications for cation site distribution  
935 and thermobarometry. *American Mineralogist*, 104(3), 403–417. [https://doi.org/10.2138/am-](https://doi.org/10.2138/am-2019-6766)  
936 2019-6766

937 Moore, J. C., & Vrolijk, P. (1992). Fluids in accretionary prisms. *Reviews of Geophysics*, 30(2), 113.  
938 <https://doi.org/10.1029/92RG00201>

939 Moore, J. C., Byrne, T., Plumley, P. W., Reid, M., Gibbons, H., & Coe, R. S. (1983). Paleogene evolution of  
940 the Kodiak 266 Islands, Alaska: Consequences of ridge-trench interaction in a more southerly  
941 latitude. *Tectonics*, 2, 265–293.

942 Muffler, L. J. P., & White, D. F. (1969). Active Metamorphism of Upper Cenozoic Sediments in the Salton  
943 Sea Geothermal Field and the Salton Trough, Southeastern California. *Geological Society of*  
944 *America Bulletin*, 80, 157–182.

945 Mullis, J., Dubessy, J., Poty, B., & O’Neil, J. (1994). Fluid regimes during late stages of a continental  
946 collision: Physical, chemical, and stable isotope measurements of fluid inclusions in fissure  
947 quartz from a geotraverse through the Central Alps, Switzerland. *Geochimica et Cosmochimica*  
948 *Acta*, 58(10), 2239–2267. [https://doi.org/10.1016/0016-7037\(94\)90008-6](https://doi.org/10.1016/0016-7037(94)90008-6)

949 Muñoz-Montecinos, J., Angiboust, S., & Garcia-Casco, A. (2021). Blueschist-facies paleo-earthquakes in a  
950 serpentinite channel (Zagros suture, Iran) enlighten seismogenesis in Mariana-type subduction  
951 margins. *Earth and Planetary Science Letters*, 573, 117135.  
952 <https://doi.org/10.1016/j.epsl.2021.117135>

953 Muñoz-Montecinos, J., Angiboust, S., Garcia-Casco, A., Glodny, J., & Bebout, G. (2021). Episodic  
954 hydrofracturing and large-scale flushing along deep subduction interfaces: Implications for fluid  
955 transfer and carbon recycling (Zagros Orogen, southeastern Iran). *Chemical Geology*, 571,  
956 120173. <https://doi.org/10.1016/j.chemgeo.2021.120173>

957 Nishi, H. (1988). Structural analysis of the Shimanto Accretionary Complex, Kyushu, Japan, based on  
958 foraminiferal biostratigraphy. *Tectonics*, 7(3), 641–652.  
959 <https://doi.org/10.1029/TC007i003p00641>

960 Nishiyama, N., Ujiie, K., & Kano, M. (2021). Spatial changes in inclusion band spacing as an indicator of  
961 temporal changes in slow slip and tremor recurrence intervals. *Earth, Planets and Space*, 73(1),  
962 126. <https://doi.org/10.1186/s40623-021-01448-7>

963 Oleskevich, D. A., Hyndman, R. D., & Wang, K. (1999). The updip and downdip limits to great subduction  
964 earthquakes: Thermal and structural models of Cascadia, south Alaska, SW Japan, and Chile.  
965 *Journal of Geophysical Research: Solid Earth*, 104(B7), 14965–14991.  
966 <https://doi.org/10.1029/1999JB900060>

967 Palazzin, G., Raimbourg, H., Famin, V., Jolivet, L., Kusaba, Y., & Yamaguchi, A. (2016). Deformation  
968 processes at the down-dip limit of the seismogenic zone: The example of Shimanto accretionary  
969 complex. *Tectonophysics*, 687, 28–43. <https://doi.org/10.1016/j.tecto.2016.08.013>

970 Peacock, S. M. (1993). The importance of blueschist → eclogite dehydration reactions in subducting  
971 oceanic crust. *Geological Society of America Bulletin*, 105(5), 684–694.  
972 [https://doi.org/10.1130/0016-7606\(1993\)105<0684:TIOBED>2.3.CO;2](https://doi.org/10.1130/0016-7606(1993)105<0684:TIOBED>2.3.CO;2)

973 Penniston-Dorland, S. C., Bebout, G. E., Pogge von Strandmann, P. A. E., Elliott, T., & Sorensen, S. S.  
974 (2012). Lithium and its isotopes as tracers of subduction zone fluids and metasomatic processes:  
975 Evidence from the Catalina Schist, California, USA. *Geochimica et Cosmochimica Acta*, 77, 530–  
976 545. <https://doi.org/10.1016/j.gca.2011.10.038>

977 Perry, E. A., & Hower, J. (1970). Burial diagenesis in Gulf Coast pelitic sediments. *Clays Clay Minerals*, 18,  
978 165–177.

979 Plafker, G., Moore, J. C., Winkler, G. R., & Berg, H. (1994). Geology of the southern Alaska margin. *The*  
980 *Geology of 249 Alaska: Boulder, Colorado, Geological Society of America, Geology of North*  
981 *America*, 1, 389–449.

982 Plank, T. (2014). The Chemical Composition of Subducting Sediments. In *Treatise on Geochemistry* (pp.  
983 607–629). Elsevier. <https://doi.org/10.1016/B978-0-08-095975-7.00319-3>

984 Plunder, A., Agard, P., Dubacq, B., Chopin, C., & Bellanger, M. (2012). How continuous and precise is the  
985 record of P-T paths? Insights from combined thermobarometry and thermodynamic modelling  
986 into subduction dynamics (Schistes Lustrés, W. Alps): TOWARDS Continuous P-T PATHS? *Journal*  
987 *of Metamorphic Geology*, 30(3), 323–346. <https://doi.org/10.1111/j.1525-1314.2011.00969.x>

988 Rahn, M., Mullis, J., Erdelbrock, K., & Frey, M. (1994). Very low-grade metamorphism of the Tavayanne  
989 greywacke, Glarus Alps, Switzerland. *Journal of Metamorphic Geology*, 12(5), 625–641.  
990 <https://doi.org/10.1111/j.1525-1314.1994.tb00047.x>

991 Raimbourg, H. (2015). Fluid circulation in the depths of accretionary prisms: an example of the Shimanto  
992 Belt, Kyushu, Japan, 16.

993 Raimbourg, H., Tadahiro, S., Asuka, Y., Haruka, Y., & Kimura, G. (2009). Horizontal shortening versus  
994 vertical loading in accretionary prisms: ACCRETIONARY PRISM STRESS CONDITIONS.  
995 *Geochemistry, Geophysics, Geosystems*, 10(4), n/a-n/a. <https://doi.org/10.1029/2008GC002279>

996 Raimbourg, H., Augier, R., Famin, V., Gadenne, L., Palazzin, G., Yamaguchi, A., & Kimura, G. (2014). Long-  
997 term evolution of an accretionary prism: The case study of the Shimanto Belt, Kyushu, Japan:  
998 Long-term evolution of the Shimanto Belt. *Tectonics*, *33*(6), 936–959.  
999 <https://doi.org/10.1002/2013TC003412>

1000 Raimbourg, H., Famin, V., Palazzin, G., Yamaguchi, A., & Augier, R. (2017). Tertiary evolution of the  
1001 Shimanto belt (Japan): A large-scale collision in Early Miocene: Early Miocene Collision in  
1002 Shimanto Belt. *Tectonics*, *36*(7), 1317–1337. <https://doi.org/10.1002/2017TC004529>

1003 Raimbourg, H., Famin, V., Palazzin, G., Mayoux, M., Jolivet, L., Ramboz, C., & Yamaguchi, A. (2018). Fluid  
1004 properties and dynamics along the seismogenic plate interface. *Geosphere*, *14*(2), 469–491.  
1005 <https://doi.org/10.1130/GES01504.1>

1006 Raimbourg, H., Rajič, K., Moris-Muttoni, B., Famin, V., Palazzin, G., Fisher, D. M., et al. (2021). Quartz  
1007 vein geochemistry records deformation processes in convergent zones. *Geochemistry,*  
1008 *Geophysics, Geosystems*, *22*. <https://doi.org/10.1029/2020GC009201>

1009 Ramirez, G., Smye, A., Fisher, D. M., Hashimoto, Y., & Yamaguchi, A. (2021). Constraints on Element  
1010 Mobility During Deformation Within the Seismogenic Zone, Shimanto Belt, Japan. *Geochemistry,*  
1011 *Geophysics, Geosystems*, *22*(8). <https://doi.org/10.1029/2020GC009594>

1012 Rauchenstein-Martinek, K., Wagner, T., Wälle, M., Heinrich, C. A., & Arlt, T. (2016). Chemical evolution of  
1013 metamorphic fluids in the Central Alps, Switzerland: insight from LA-ICPMS analysis of fluid  
1014 inclusions. *Geofluids*, *16*(5), 877–908. <https://doi.org/10.1111/gfl.12194>

1015 Reynard, B. (2013). Serpentine in active subduction zones. *Lithos*, *178*, 171–185.  
1016 <https://doi.org/10.1016/j.lithos.2012.10.012>

1017 Rietveld, H. M. (1969). A profile refinement method for nuclear and magnetic structures. *Journal of*  
1018 *Applied Crystallography*, *2*(2), 65–71. <https://doi.org/10.1107/S0021889869006558>

1019 Rowe, C. D., Meneghini, F., & Moore, J. C. (2009). Fluid-rich damage zone of an ancient out-of-sequence  
1020 thrust, Kodiak Islands, Alaska: DAMAGE ZONE OF ANCIENT OOST. *Tectonics*, 28(1), n/a-n/a.  
1021 <https://doi.org/10.1029/2007TC002126>

1022 Rupke, L. (2004). Serpentine and the subduction zone water cycle. *Earth and Planetary Science Letters*,  
1023 223(1–2), 17–34. <https://doi.org/10.1016/j.epsl.2004.04.018>

1024 Saffer, D. M., & Tobin, H. J. (2011). Hydrogeology and Mechanics of Subduction Zone Forearcs: Fluid  
1025 Flow and Pore Pressure. *Annual Review of Earth and Planetary Sciences*, 39(1), 157–186.  
1026 <https://doi.org/10.1146/annurev-earth-040610-133408>

1027 Saffer, D. M., Lockner, D. A., & McKiernan, A. (2012). Effects of smectite to illite transformation on the  
1028 frictional strength and sliding stability of intact marine mudstones: FRICTION AND SMECTITE  
1029 TRANSFORMATION. *Geophysical Research Letters*, 39(11), n/a-n/a.  
1030 <https://doi.org/10.1029/2012GL051761>

1031 Saito, M. (1996). Geological Map of Japan, 1:50,000. Geol. Surv. Jpn., Shiibamura.

1032 Sakaguchi, A. (1999). Thermal maturity in the Shimanto accretionary prism, southwest Japan, with the  
1033 thermal change of the subducting slab: fluid inclusion and vitrinite reflectance study. *Earth and*  
1034 *Planetary Science Letters*, 173(1–2), 61–74. [https://doi.org/10.1016/S0012-821X\(99\)00219-8](https://doi.org/10.1016/S0012-821X(99)00219-8)

1035 Sakai et al., T. (1984). Microfossil stratigraphy of the Paleogene System in Kyushu Shimanto Belt.  
1036 *Biostratigraphy and International Correlation of the Paleogene System in Japan*, 95–112.

1037 Sample, J. C., & Fisher, D. M. (1986). Duplex accretion and underplating in an ancient accretionary prism,  
1038 Kodiak Islands, Alaska. *Geology*, 14, 160–163.

1039 Sample, J. C., & Moore, J. C. (1987). Structural style and kinematics of an underplated slate belt, Kodiak  
1040 and adjacent 260 islands, Alaska. *Geological Society of America Bulletin*, 99, 7–20.

1041 Scambelluri, M., Fiebig, J., Malaspina, N., Müntener, O., & Pettke, T. (2004). Serpentinite Subduction:  
1042 Implications for Fluid Processes and Trace-Element Recycling. *International Geology Review*,  
1043 46(7), 595–613. <https://doi.org/10.2747/0020-6814.46.7.595>

1044 Scambelluri, M., Pettke, T., & Cannà, E. (2015). Fluid-related inclusions in Alpine high-pressure  
1045 peridotite reveal trace element recycling during subduction-zone dehydration of serpentinized  
1046 mantle (Cima di Gagnone, Swiss Alps). *Earth and Planetary Science Letters*, 429, 45–59.  
1047 <https://doi.org/10.1016/j.epsl.2015.07.060>

1048 Schmidt, D., Schmidt, S. T., Mullis, J., Ferreiro Mählmann, R., & Frey, M. (1997). Very low grade  
1049 metamorphism of the Tavayanne formation of western Switzerland. *Contributions to Mineralogy  
1050 and Petrology*, 129(4), 385–403. <https://doi.org/10.1007/s004100050344>

1051 Schmidt, M. W., & Poli, S. (2014). Devolatilization During Subduction. In *Treatise on Geochemistry* (pp.  
1052 669–701). Elsevier. <https://doi.org/10.1016/B978-0-08-095975-7.00321-1>

1053 Schneider, C. A., Rasband, W. S., & Eliceiri, K. W. (2012). NIH Image to ImageJ: 25 years of image  
1054 analysis. *Nature Methods*, 9(7), 671–675. <https://doi.org/10.1038/nmeth.2089>

1055 Sharp, Z. D., & Kirschner, D. L. (1994). Quartz-calcite oxygen isotope thermometry: A calibration based  
1056 on natural isotopic variations. *Geochimica et Cosmochimica Acta*, 58(20), 4491–4501.  
1057 [https://doi.org/10.1016/0016-7037\(94\)90350-6](https://doi.org/10.1016/0016-7037(94)90350-6)

1058 Simons, K. K., Harlow, G. E., Brueckner, H. K., Goldstein, S. L., Sorensen, S. S., Hemming, N. G., &  
1059 Langmuir, C. H. (2010). Lithium isotopes in Guatemalan and Franciscan HP–LT rocks: Insights into  
1060 the role of sediment-derived fluids during subduction. *Geochimica et Cosmochimica Acta*,  
1061 74(12), 3621–3641. <https://doi.org/10.1016/j.gca.2010.02.033>

1062 Spandler, C., & Pirard, C. (2013). Element recycling from subducting slabs to arc crust: A review. *Lithos*,  
1063 170–171, 208–223. <https://doi.org/10.1016/j.lithos.2013.02.016>



1064 Spandler, C., Hermann, J., Arculus, R., & Mavrogenes, J. (2003). Redistribution of trace elements during  
1065 prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep  
1066 subduction-zone processes. *Contributions to Mineralogy and Petrology*, *146*(2), 205–222.  
1067 <https://doi.org/10.1007/s00410-003-0495-5>

1068 Spinelli, G. A. (2004). Along-strike variations in underthrust sediment dewatering on the Nicoya margin,  
1069 Costa Rica related to the updip limit of seismicity. *Geophysical Research Letters*, *31*(4), L04613.  
1070 <https://doi.org/10.1029/2003GL018863>

1071 Stern, C. R. (2011). Subduction erosion: Rates, mechanisms, and its role in arc magmatism and the  
1072 evolution of the continental crust and mantle. *Gondwana Research*, *20*(2–3), 284–308.  
1073 <https://doi.org/10.1016/j.gr.2011.03.006>

1074 Stern, R. J. (2002). SUBDUCTION ZONES: SUBDUCTION ZONES. *Reviews of Geophysics*, *40*(4), 3-1-3–38.  
1075 <https://doi.org/10.1029/2001RG000108>

1076 Sun, Q., Zhao, L., Li, N., & Liu, J. (2010). Raman spectroscopic study for the determination of Cl<sup>-</sup>  
1077 concentration (molarity scale) in aqueous solutions: Application to fluid inclusions. *Chemical*  
1078 *Geology*, *272*(1–4), 55–61. <https://doi.org/10.1016/j.chemgeo.2010.02.004>

1079 Taetz, S., John, T., Bröcker, M., & Spandler, C. (2016). Fluid–rock interaction and evolution of a high-  
1080 pressure/low-temperature vein system in eclogite from New Caledonia: insights into intraslab  
1081 fluid flow processes. *Contributions to Mineralogy and Petrology*, *171*(11), 90.  
1082 <https://doi.org/10.1007/s00410-016-1295-z>

1083 Tarantola, A., Mullis, J., Vennemann, T., Dubessy, J., & de Capitani, C. (2007). Oxidation of methane at  
1084 the CH<sub>4</sub>/H<sub>2</sub>O–(CO<sub>2</sub>) transition zone in the external part of the Central Alps, Switzerland:  
1085 Evidence from stable isotope investigations. *Chemical Geology*, *237*(3–4), 329–357.  
1086 <https://doi.org/10.1016/j.chemgeo.2006.07.007>

1087 Tarantola, A., Mullis, J., Guillaume, D., Dubessy, J., de Capitani, C., & Abdelmoula, M. (2009). Oxidation  
1088 of CH<sub>4</sub> to CO<sub>2</sub> and H<sub>2</sub>O by chloritization of detrital biotite at 270±5 °C in the external part of the  
1089 Central Alps, Switzerland. *Lithos*, *112*(3–4), 497–510.  
1090 <https://doi.org/10.1016/j.lithos.2009.04.008>

1091 Taylor, J., & Clapp, R. (1991). New Features and Advanced Applications of Siroquant: A Personal  
1092 Computer XRD Full Profile Quantitative Analysis Software Package. *Advances in X-Ray Analysis*,  
1093 *35*(A), 49–55. <https://doi.org/doi:10.1154/S037603080000865X>

1094 Teraoka, Y., & Okumura, K. (1992). Tectonic division and Cretaceous sandstone compositions of the  
1095 Northern Belt of the Shimanto Terrane, southwest Japan. *Mem. Geol. Soc. Jpn.*, *38*, 261–270.

1096 Toriumi, M., & Teruya, J. (1988). Tectono-metamorphism of the Shimanto Belt. *Modern Geology*, *12*,  
1097 303–324.

1098 Ujiie, K., Saishu, H., Fagereng, Å., Nishiyama, N., Otsubo, M., Masuyama, H., & Kagi, H. (2018). An  
1099 Explanation of Episodic Tremor and Slow Slip Constrained by Crack-Seal Veins and Viscous Shear  
1100 in Subduction Mélange. *Geophysical Research Letters*, *45*(11), 5371–5379.  
1101 <https://doi.org/10.1029/2018GL078374>

1102 Vannucchi, P. (2019). Scaly fabric and slip within fault zones. *Geosphere*, *15*(2), 342–356.  
1103 <https://doi.org/10.1130/GES01651.1>

1104 Velde, B. (1985). *Clay Minerals: a Physico-chemical Explanation of their Occurrence*. Elsevier.

1105 Vidal, O., & Parra, T. (2000). Exhumation paths of high-pressure metapelites obtained from local  
1106 equilibria for chlorite-phengite assemblages. *Geological Journal*, *35*(3–4), 139–161.  
1107 <https://doi.org/10.1002/gj.856>

1108 Vidal, O., De Andrade, V., Lewin, E., Munoz, M., Parra, T., & Pascarelli, S. (2006). P-T-deformation-  
1109 Fe<sup>3+</sup>/Fe<sup>2+</sup> mapping at the thin section scale and comparison with XANES mapping: application  
1110 to a garnet-bearing metapelite from the Sambagawa metamorphic belt (Japan): P-T-

- 1111 DEFORMATION-FE<sup>3+</sup>/FE<sup>2+</sup> MAPPING. *Journal of Metamorphic Geology*, 24(7), 669–683.  
1112 <https://doi.org/10.1111/j.1525-1314.2006.00661.x>
- 1113 Vrolijk, P., Myers, G., & Moore, J. C. (1988). Warm fluid migration along tectonic melanges in the Kodiak  
1114 Accretionary Complex, Alaska. *Journal of Geophysical Research: Solid Earth*, 93(B9), 10313–  
1115 10324. <https://doi.org/10.1029/JB093iB09p10313>
- 1116 Wang, H. (1996). Diagenesis and Metamorphism of Clay Minerals in the Helvetic Alps of Eastern  
1117 Switzerland. *Clays and Clay Minerals*, 44(1), 96–112.  
1118 <https://doi.org/10.1346/CCMN.1996.0440109>
- 1119 Yoshida, K., Hirajima, T., Ohsawa, S., Kobayashi, T., Mishima, T., & Sengen, Y. (2015). Geochemical  
1120 features and relative B–Li–Cl compositions of deep-origin fluids trapped in high-pressure  
1121 metamorphic rocks. *Lithos*, 226, 50–64. <https://doi.org/10.1016/j.lithos.2015.03.002>
- 1122 Zane, A., Sassi, A., & Guidotti, C. V. (1998). New Data On Metamorphic Chlorite As A Petrogenetic  
1123 Indicator Mineral, With Special Regard To Greenschist-Facies Rocks. *THE CANADIAN  
1124 MINERALOGIST*, 36, 713–726.

## 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 H<sub>2</sub>O Raman spectrum from fluid inclusion, decomposed into two Gaussian  
1137 bands. (b) Calculated K' value from the standard solutions with known Cl<sup>-</sup> 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 (S<sub>1</sub>) and a crenulation cleavage (S<sub>2</sub>), 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)  $(PrIH)_{Phg} = (PrI)_{Phg} + H_2O$ ; (2)  $4 Qtz - (Mg-Am)_{Chl} = 2 (PrIH)_{Phg} + 2 (Sud)_{Chl}$ ; (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.

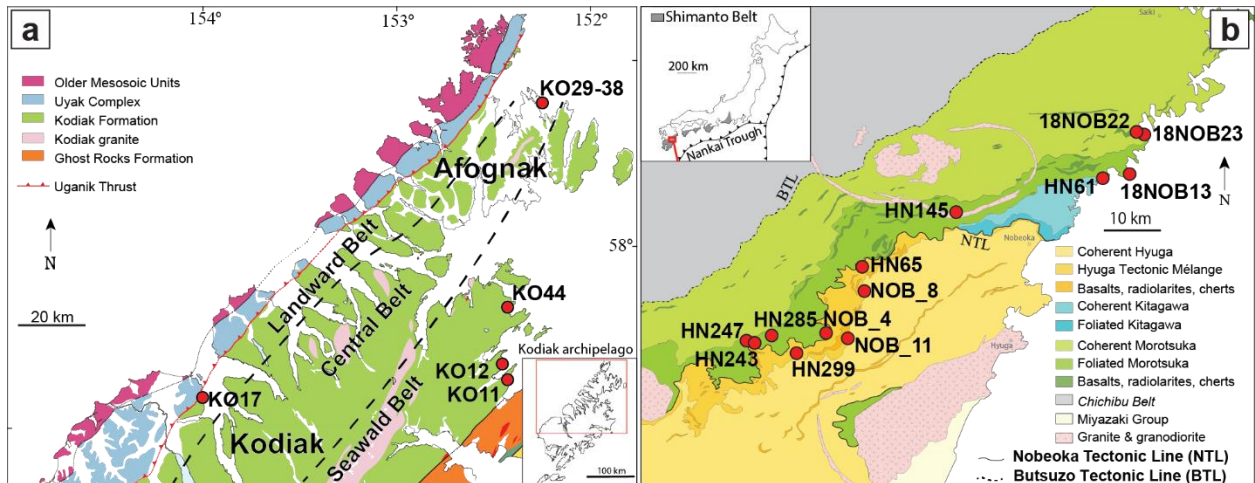
1195 Figure 13. (a) Relative proportions of Na<sub>2</sub>O, MgO, CaO, K<sub>2</sub>O, FeO, SO<sub>2</sub> and Cl in evaporate mounds from  
 1196 decrepitated fluid inclusions. Each line represents the average composition from 3-10 points analyses  
 1197 acquired by EPMA in individual evaporate mounds. (b) Ca/Na vs. K/Na binary diagram and (c) Ca/Na vs.  
 1198 SO<sub>2</sub>/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 Mélangé (Japan).

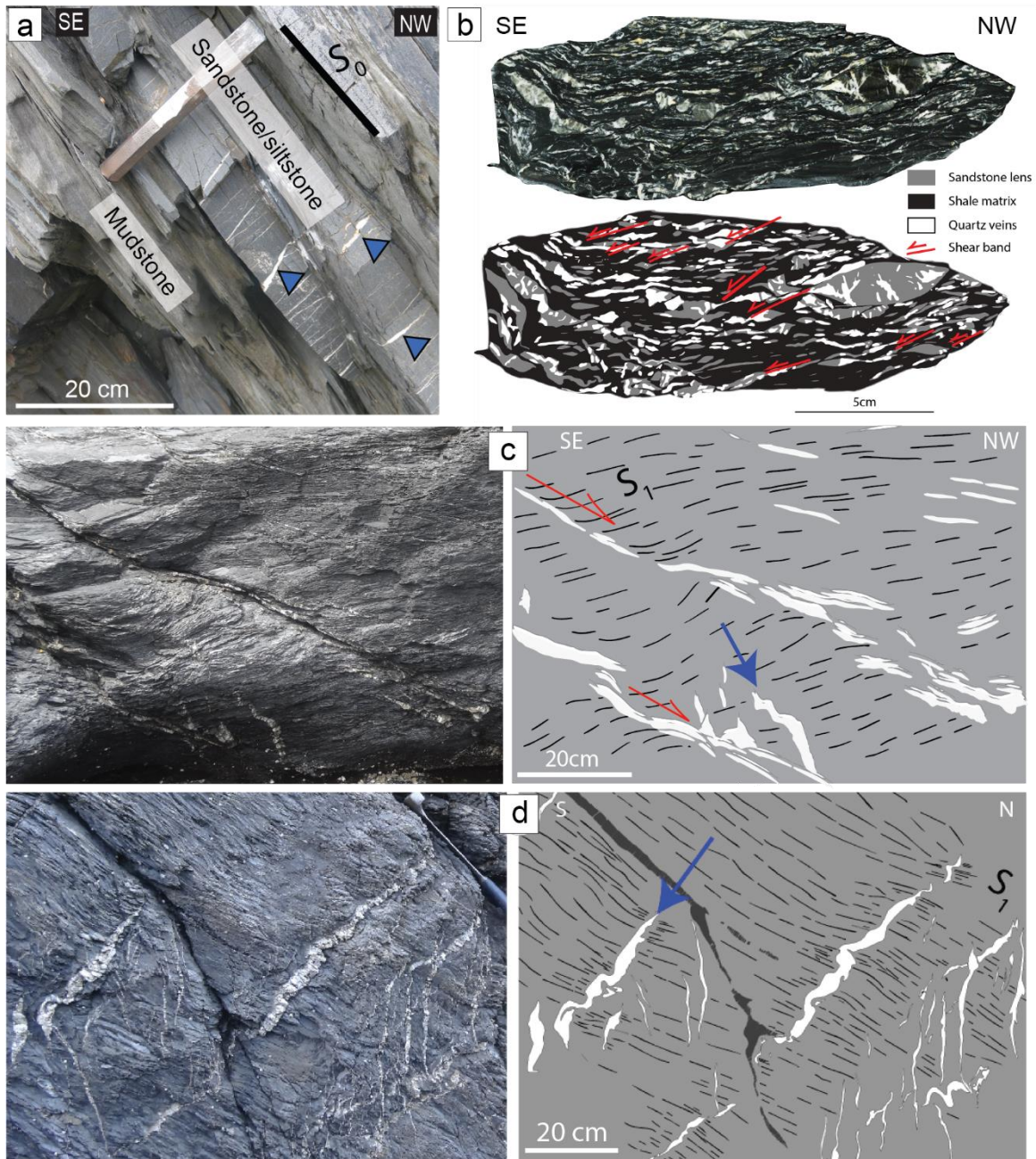
1208 Figure S2. SEM-EDS maps of evaporate mounds after the decrepitation method in (a) lower-grade quartz  
 1209 vein (Sample NOB\_11C) and (b) higher-grade quartz vein (Sample KO30D).

1210



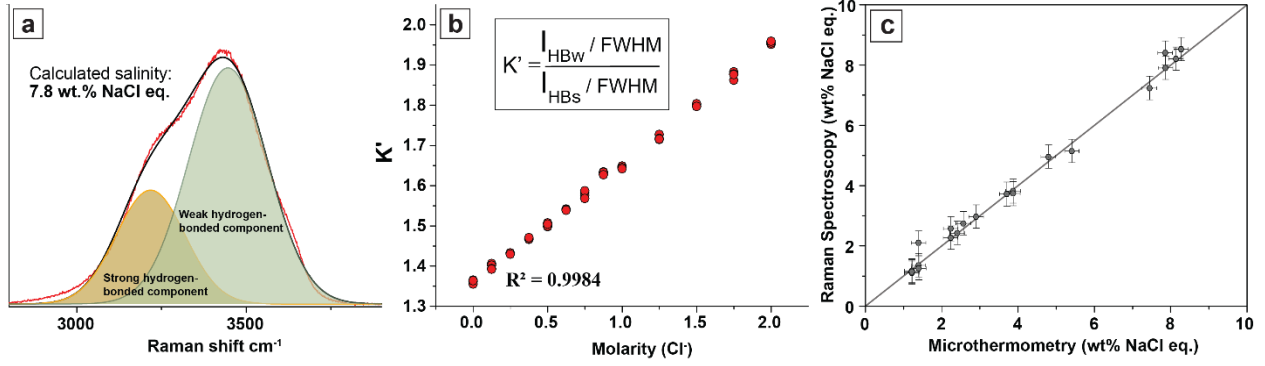
1211

1212 Figure 1.



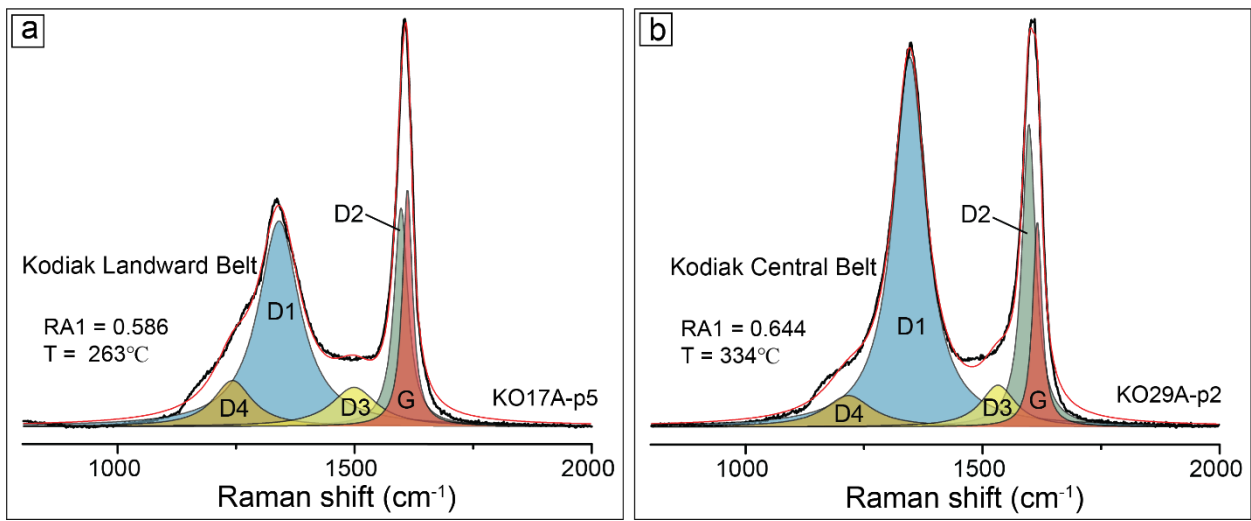
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1214 Figure 2.



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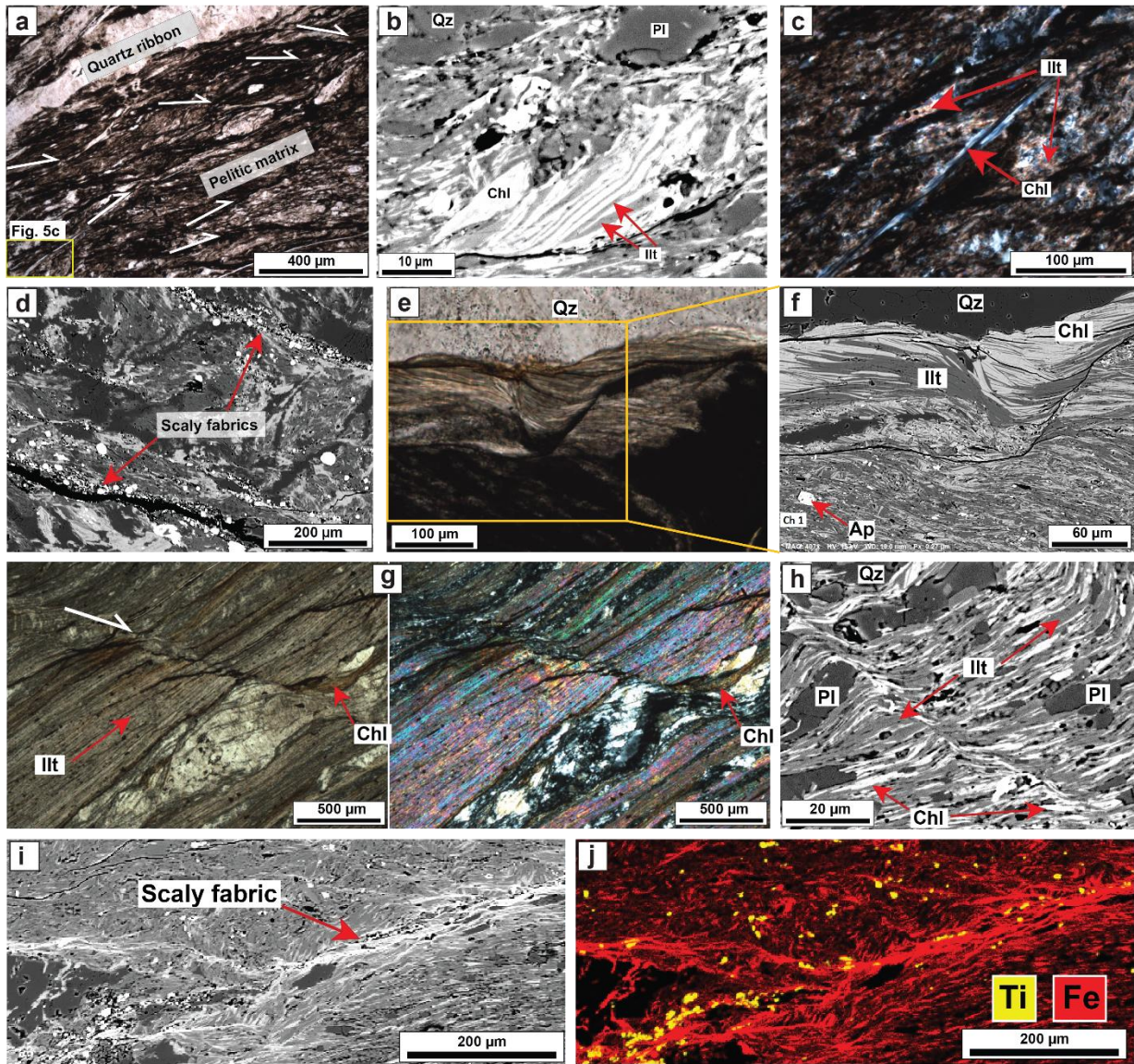
1216 Figure 3.



1217

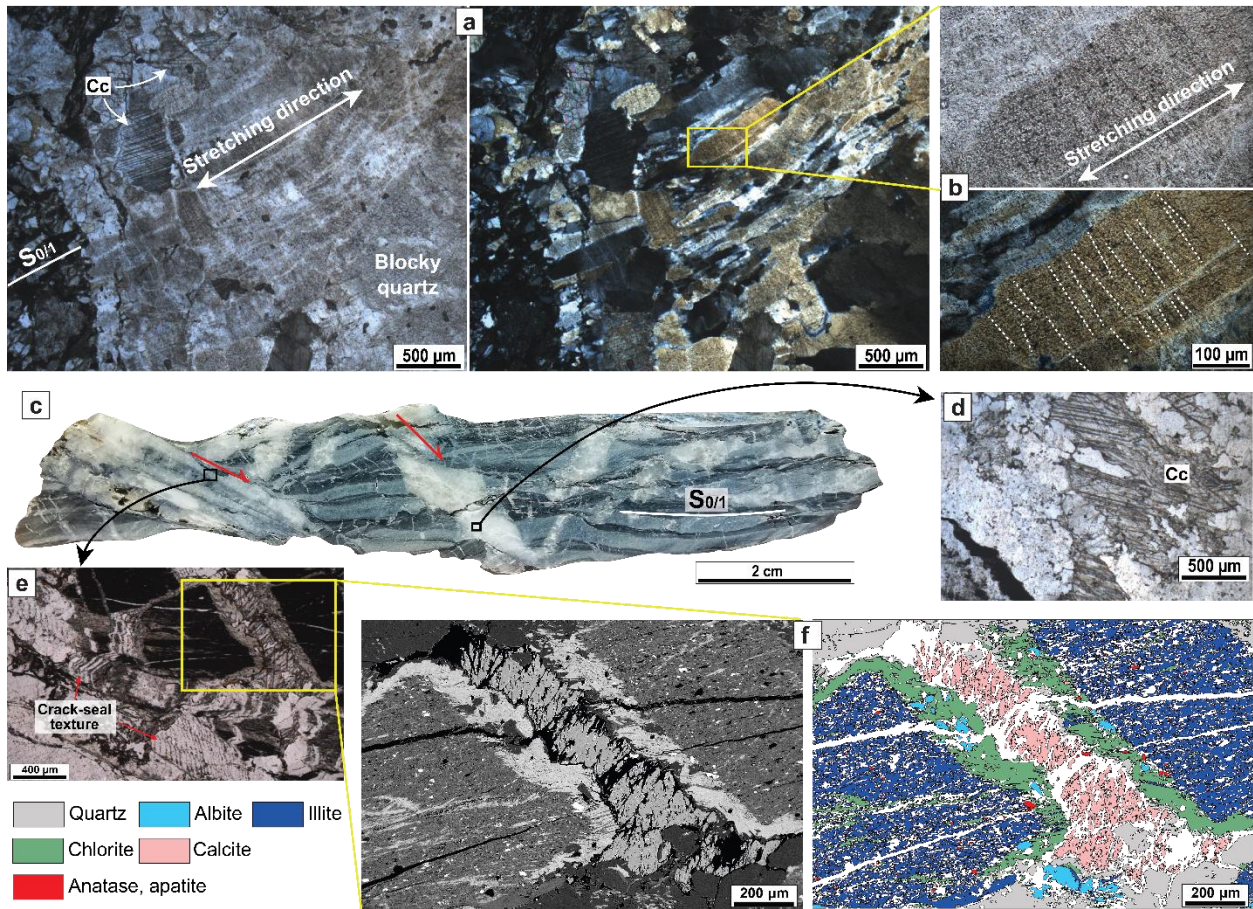
1218 Figure 4.





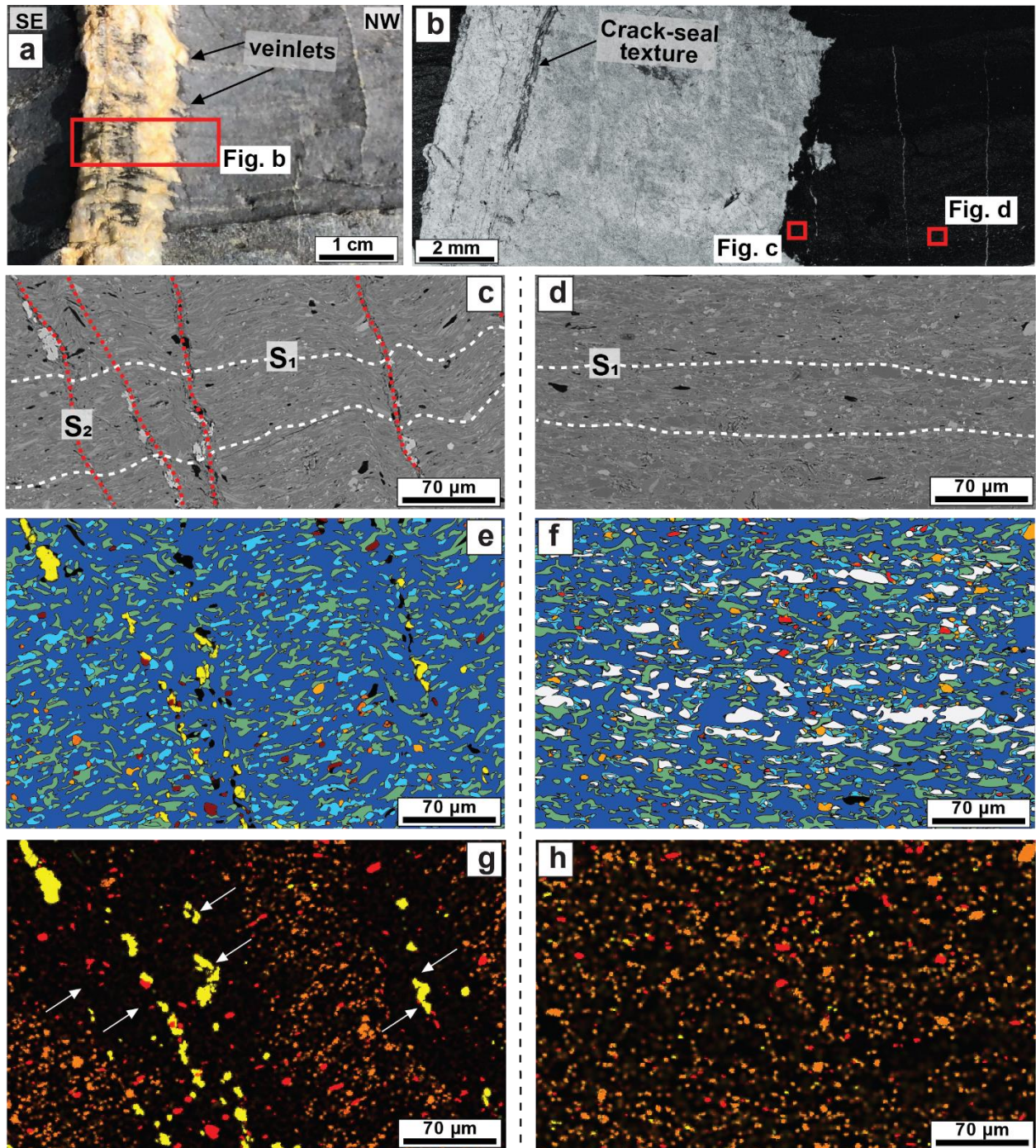
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1220 Figure 5.

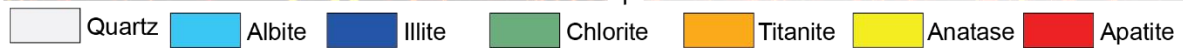


1221

1222 Figure 6.

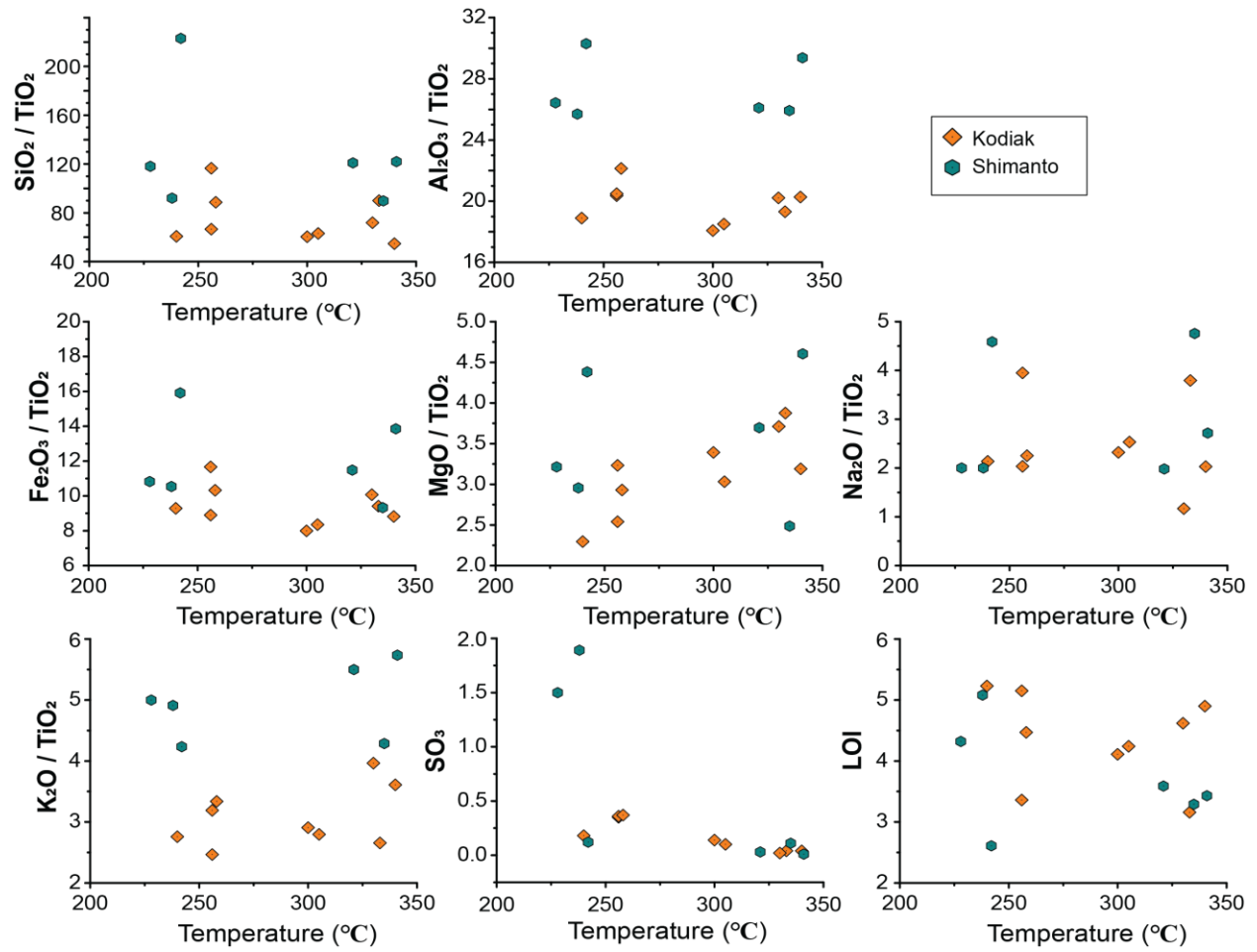


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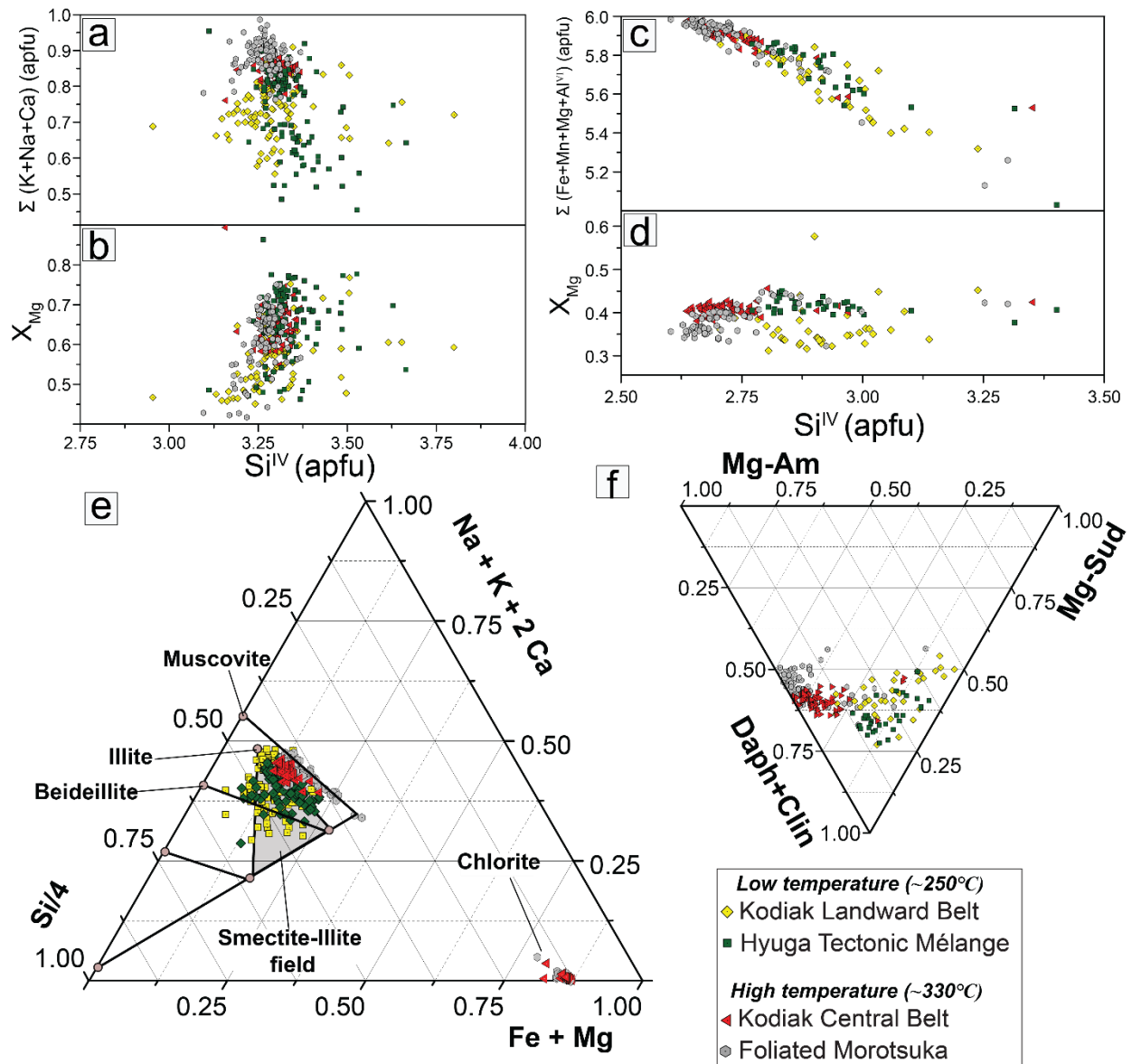
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Figure 7.



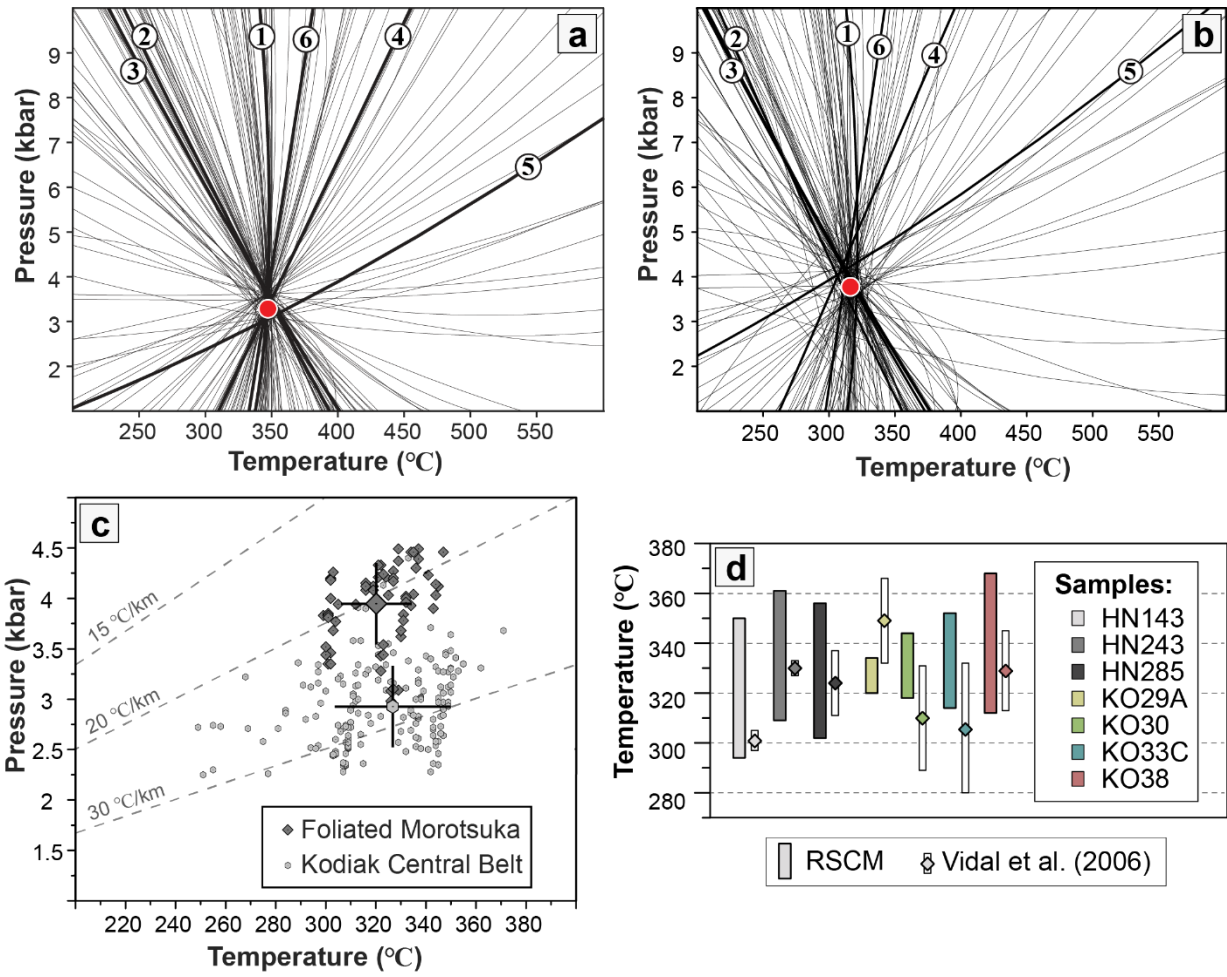
1225

1226 Figure 8.



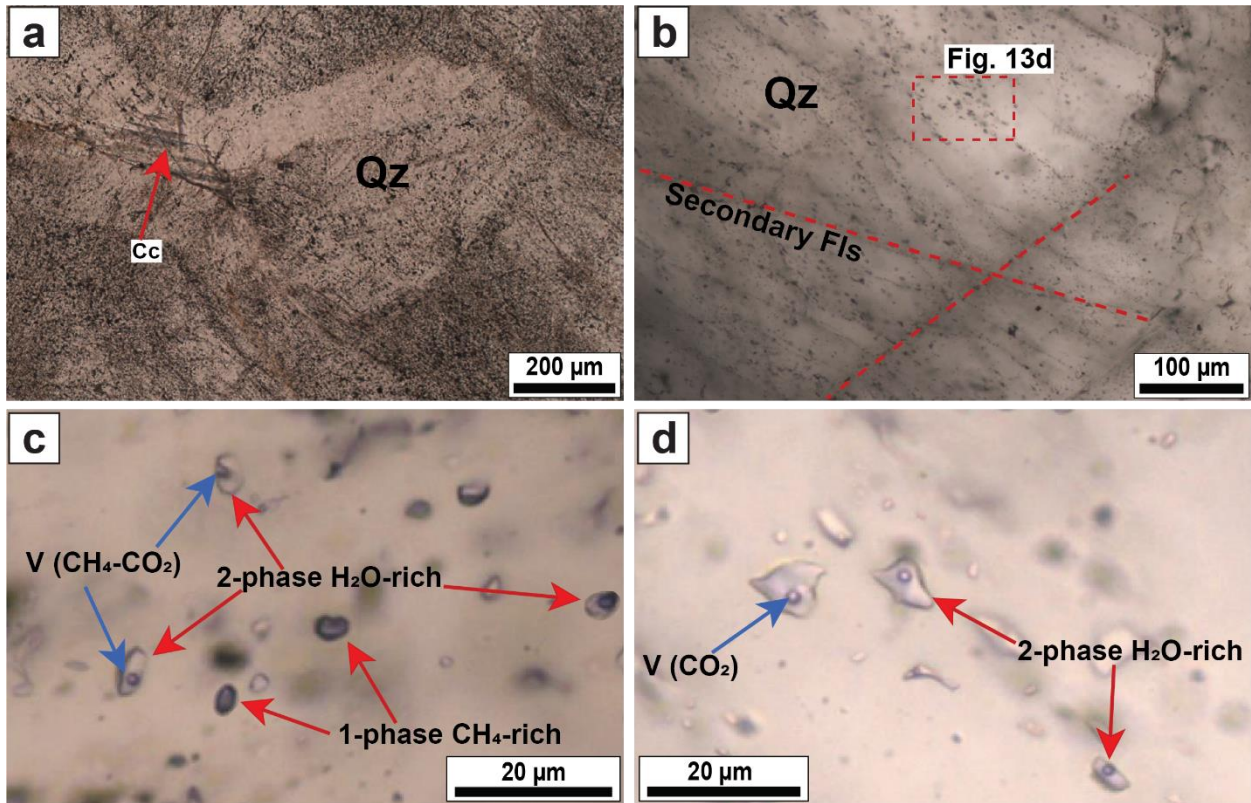
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1228 Figure 9.



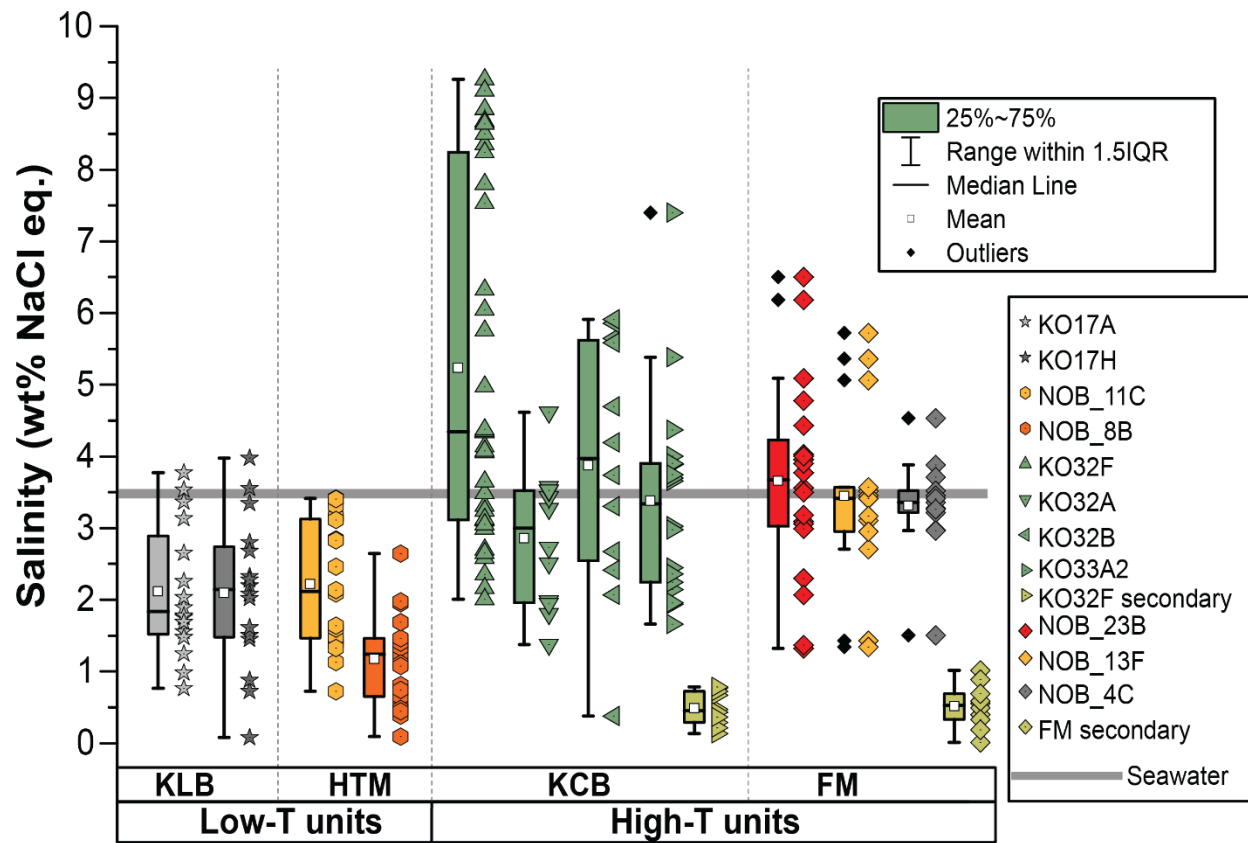
1229

1230 Figure 10.



1231

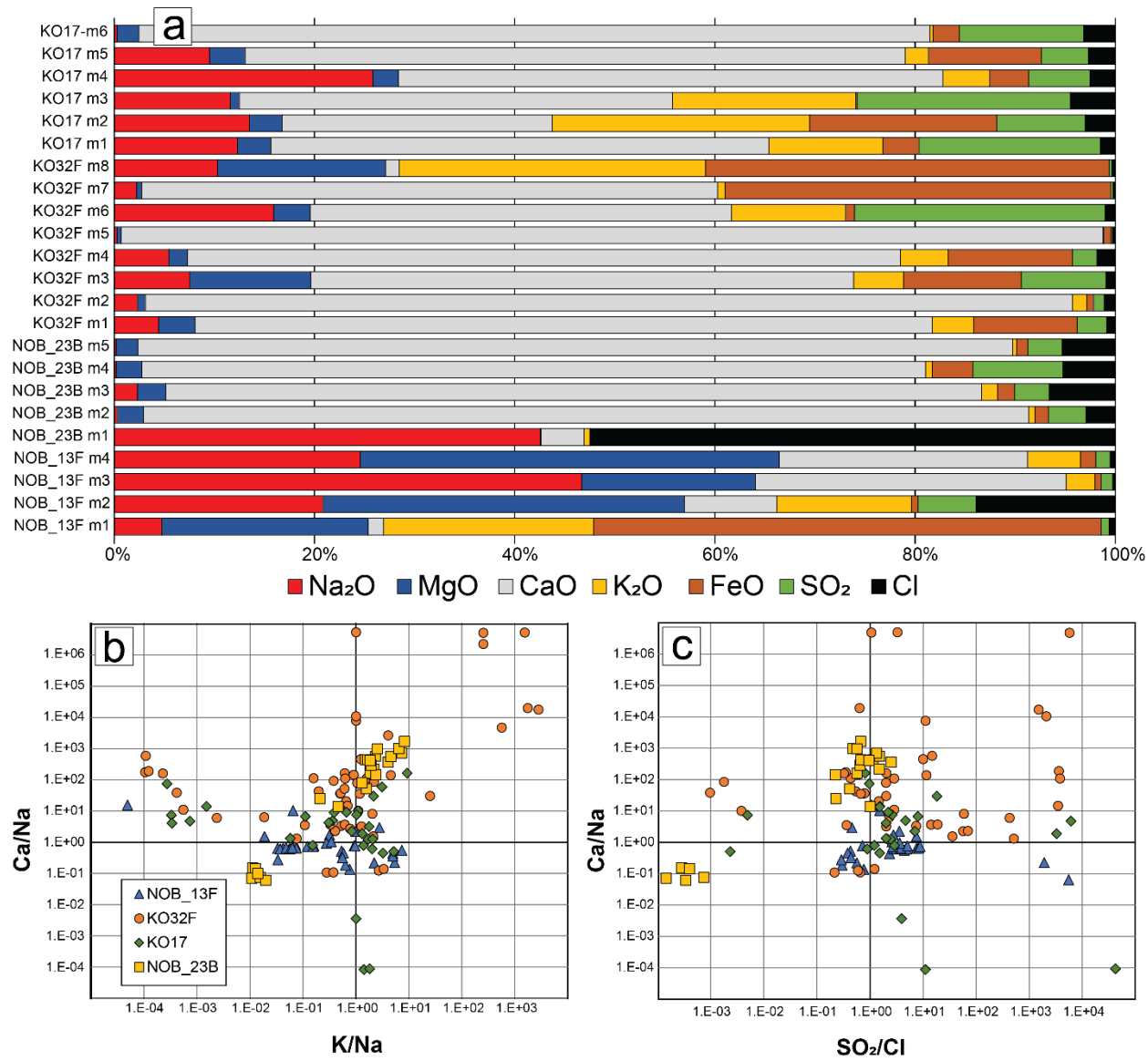
1232 Figure 11.



1233

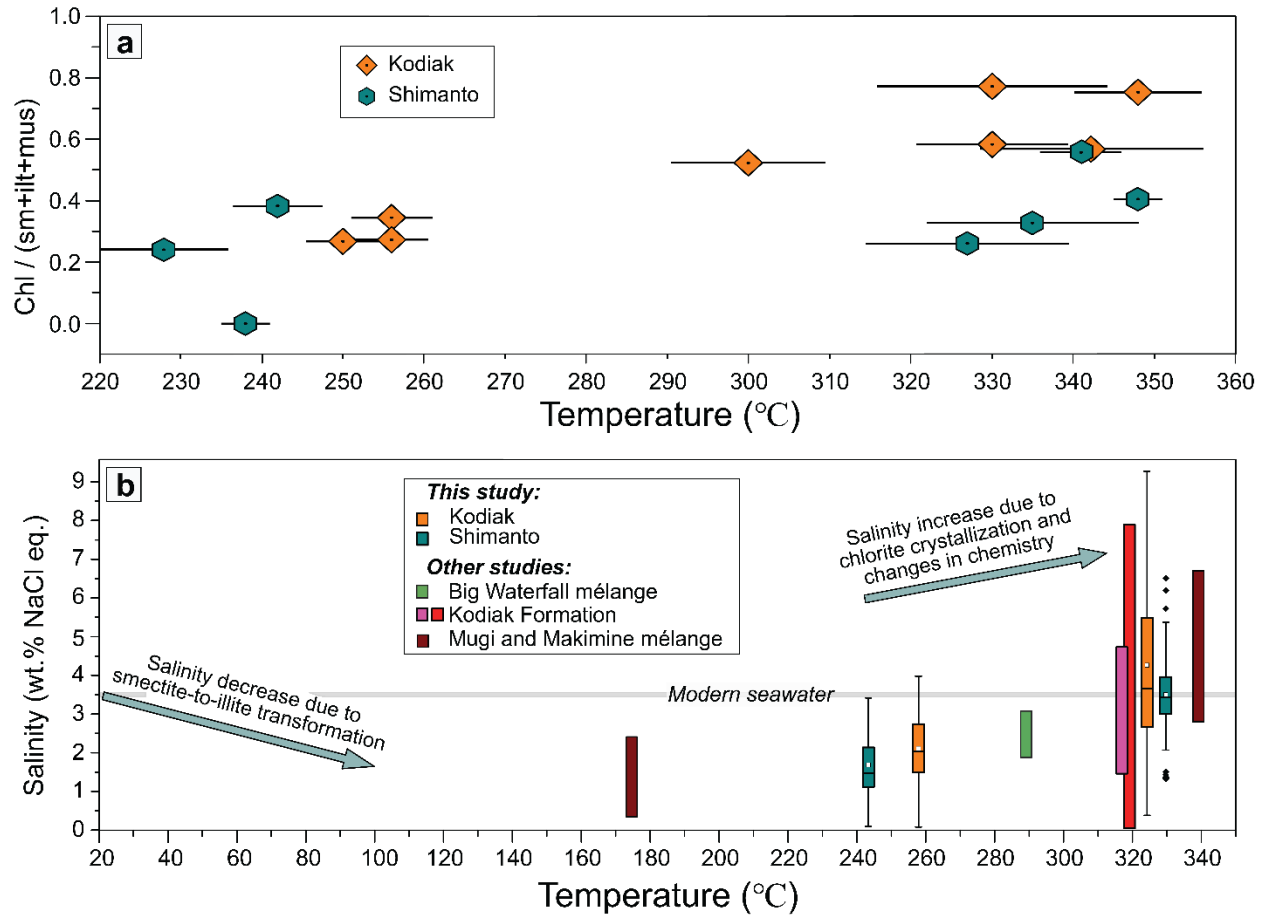
1234 Figure 12.





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: <sup>1</sup>Palazzin et al. (2016);  
 1242 <sup>2</sup>Raimbourg et al. (2018); <sup>3</sup>Raimbourg et al. (2021).

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

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

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 <sub>2</sub>	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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> O <sub>5</sub>	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 <sub>3</sub>	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
<b>Major phases</b>															
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
<b>Accessory phases</b>															
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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