

Manuscript Number:

Title: Use of fracture filling mineral assemblages for characterizing the formation process of an accretionary complex: an example from the Shimanto Belt southern Kyushu, Japan

Article Type: Full Length Article

Keywords: Fracture fillings, assemblage, accretionary complex, formation process

Corresponding Author: Prof. Hidekazu Yoshida, Dr

Corresponding Author's Institution: Nagoya University

First Author: Takuya Ono, Ms

Order of Authors: Takuya Ono, Ms; Hidekazu Yoshida, Dr; Metcalfe Richard, Dr

Abstract: Various kinds of fracture filling minerals and secondary minerals in the wall rocks of fractures were formed by fluid-rock interaction during the development of mélangé in an accretionary complex. Each mineral formed under favourable geological conditions and can be used to estimate the conditions of accretion and formation of the mélangé. Petrographic observations, mineralogical and geochemical analyses were made on fracture fillings and secondary minerals from boreholes of ca. 140 metres depth, in the Paleogene Shimanto Belt of Kyushu, Japan. Results revealed that the secondary minerals were formed in five-stages distinguished by the sequential textural relationships of the minerals and the interpreted environment of mineral formation. Filling mineral assemblages show that the studied rock formation has been subducted to a depth of several km and the temperature reached was ca. 200 - 300°C. After the subduction, the rock formation uplifted and surface acidic water penetrated up to 80 metres beneath the present ground surface. The acid water dissolved calcite fracture fillings to form the present groundwater flow-paths which allowed recent wall rock alteration to occur. The results shown here imply that filling mineral assemblages can be an effective tool to evaluate the environmental changes during and after accretionary complex formation.

20151210

Journal of Structural Geology

Dear Editor,

Here we submit a paper, entitled '**Use of fracture filling mineral assemblages for characterizing the formation process of an accretionary complex: an example from the Shimanto Belt southern Kyushu, Japan**' by Ono, Yoshida and Metcalfe with eleven figures and two tables.

This paper is the first one trying to show the usefulness of fracture fillings from deep core materials developed in the accretionary complex in order to understand the geological conditions of complex formation widely distributed in Japan as well as the feature of presently still acting as flow-paths influencing on the hydrological and engineering point of view.

I would be very grateful if you could please give this submission your consideration for publication in Structural geology.

Yours sincerely,

H. Yoshida

[dora@num.nagoya-u.ac.jp](mailto:dora@num.nagoya-u.ac.jp)

Nagoya University Museum/Graduate School of Environmental Studies  
Nagoya, Aichi, Japan

## Highlights

- A method using fracture fillings for understanding geological condition is proposed.
- Fracture filling assemblages are effective index for estimating the conditions.
- This method can be used for the evaluation of deep geological environment.

Journal of Structural Geology (Ono et al.)

**Use of fracture filling mineral assemblages for characterizing the  
formation process of an accretionary complex: an example from the  
Shimanto Belt southern Kyushu, Japan**

Takuya Ono<sup>1</sup>, Hidekazu Yoshida<sup>2\*</sup> & Richard Metcalfe<sup>3</sup>

1) Japan Atomic Energy Agency, Ibaraki, Tokai, Japan

2) Material Research Section, Nagoya University, University Museum, Chikusa, Nagoya, Japan

\*corresponding author

3) Quintessa Limited, The Hub, Henley-on-Thames, Oxfordshire, UK



## 21 **1. Introduction**

22 Accretionary complexes containing rock formations known as *mélange* are widely  
23 distributed in Japan. Understanding the process of complex formation is crucial to reveal the  
24 tectonic setting and geological evolution of the Japanese archipelago because more than 60%  
25 of the area of geology in Japan can describe as accretionary complex. The facies of *mélange*  
26 also has a quite complex structure with various kind of sedimentary rocks mixed in the  
27 different sedimentary conditions. In order to therefore understand the accretion conditions  
28 during terrane development distributed within Japan, various methodology estimationg the P-  
29 T conditions of complex development have been applied. As an example, a previously used  
30 methodology involved studying altered minerals in the rock matrices and fault zones that  
31 formed under relatively high P-T conditions (e.g. [Tsuji-mori, 2010](#); [Yamaguchi et al., 2011](#);  
32 [Charvet, 2013](#)). Another approach has been to determine the temperature of circulating fluid  
33 using fluid inclusions in secondary quartz veins in the rock matrices (e.g. [Sakaguchi, 1999](#);  
34 [Hashimoto et al., 2002](#)). These methodologies, however, are limited to interpreting the  
35 evolution of relatively high P-T conditions during the development of an accretionary  
36 complex.

37 On the other hand, there are various kinds of fracture filling minerals and secondary  
38 minerals developed along fractures in the *mélange* facies. It is known that these minerals are  
39 formed from pore water squeezed from sediments during accretionary complex formation  
40 (e.g. [Moore and Vrolijk, 1992](#)). These fluids migrated under high pressure along grain  
41 boundaries and/or fractures developed in the rock. The various kinds of secondary minerals  
42 and the fracture-filling mineral assemblages record the conditions of mineral formation, and  
43 potentially can be used to trace the detailed P-T path during accretionary complex formation.

44 Fracture filling minerals sampled from deep bore holes drilled in crystalline rocks in Japan  
45 have been used to determine the past conditions of fluid migration and mineral formation in

46 the Japanese orogenic field (e.g. [Yoshida et al., 2005](#); [Yoshida et al., 2008](#); [Nishimoto et al.,](#)  
47 [2008](#); [Nishimoto and Yoshida, 2011](#); [Ishibashi et al., 2014](#)). The methodology involved  
48 identifying the minerals present in the various fracture-filling and wall-rock mineral  
49 assemblages and studying morphological relationships between the minerals. These studies  
50 have shown how the sequential order of mineral fillings and morphological relationships trace  
51 different stages of fluid circulation in crystalline host rocks and reveal the sealing process of  
52 flow-paths ([Yoshida, 2012](#); [Yoshida et al., 2013](#)).

53 The study presented here aims firstly to demonstrate a methodology for evaluating the  
54 history of fluid flow through fractures in accretionary sedimentary rocks by using secondary-  
55 and fracture-filling minerals. The methodology is demonstrated by examining one of the  
56 major mélanges in an accretionary complex of the Shimanto belt of western Japan. This is the  
57 first time that this methodology has been used to determine the detailed conditions of fluid  
58 circulation during accretion and to evaluate how long the flow-paths remained open before  
59 their eventual sealing by precipitated minerals.

60 The methodology and the kinds of information obtained are expected to be transferable to  
61 site characterization for a variety of underground facilities. For example, should a deep un-  
62 weathered geological environment within the orogenic field of Japan be selected to site a  
63 repository for the disposal of nuclear waste, the methodology could be applied to evaluate the  
64 long-term stability of the host rock ([NUMO, 2011](#); [Committee for Geological Stability](#)  
65 [Research, 2011](#)).

66

67

## 68 **2. Studied materials and methodology**

69 The study was carried out on the Hyuga Group, a member of the Shimanto accretionary  
70 complex, which is distributed in the southern part of the island of Kyushu. The Hyuga Group

71 is mainly composed of bedded sandstone and sandstone-rich alternating beds of sandstone and  
72 mudstone (Figures 1a, b). Such alternating sediments are a typical feature of the Shimanto  
73 belt throughout the south-eastern part of Japan. The age of the sediments has been estimated  
74 from radiolarian fossils to range from the middle Eocene to early Oligocene (Kimura et al.,  
75 1991; JGS, 2010;). The formation is composed mainly of calcareous, greyish turbidity  
76 sequences generally dipping northwards at 30° with a strike of N55°E N. The original  
77 sedimentary textures are generally well preserved (Figure 2).

78 Within the studied area along the north-south trending Omaru river, five boreholes were  
79 drilled into the Shimanto sequences along an east-west line. The purpose of the boreholes was  
80 to characterize the detailed geological structure of the basement and weathering conditions, in  
81 order to determine the suitability of a proposed dam construction site. The study reported in  
82 this paper used core specimens from the five boreholes (named Core A to E; Figure 3) in  
83 order to characterize the spatial distribution of geological features with increasing depth  
84 below the ground surface, namely fracture distribution, alteration characteristics and the  
85 mineralogy of fracture fillings.

86 The deepest borehole 'A' reaches to 140 metres depth from the surface. Although some  
87 small fraction of the cores was lost after excavation, almost all core samples are well  
88 preserved (total recovery is about 97 %) and enable us to clarify the distribution of fractures  
89 and the occurrence of filling minerals without alteration or physical damage after exposure  
90 (Figure 4). In particular, penetration of a redox front from the ground surface can be clearly  
91 identified by the distribution of Fe-oxyhydroxide, the limits of which are marked by colour  
92 changes from reddish (oxidized rock) to grayish (reduced rock) (e.g. Akagawa et al., 2006;  
93 Yamamoto et al., 2013). The zone distinguished with Fe-oxyhydroxide occurs throughout  
94 almost the entire core or along fractures described in this paper as occurring in the shallower  
95 part of the rock sequence. This shallower part is distributed roughly parallel to the surface



96 topography, but below the present groundwater table (Figure 3b). This is clear evidence of  
97 oxidized and/or acidic surface water infiltrating and reacting with the initially reduced greyish  
98 rocks which form the deeper part of the formation. These deeper rocks have primary fresh  
99 minerals without evidence of alteration by water infiltrating from the present ground surface  
100 (Yoshida and Yamamoto, 2014). The low temperature geochemical processes that influenced  
101 the host rock alteration can also be identified by using the morphological relationships and the  
102 mineralogical assemblages of fracture filling minerals as described below.

103

## 104 **2.1 Fracture description**

105 Initially the presence or absence of minerals on fracture surfaces was used to distinguish  
106 between fractures developed naturally and those developed artificially during drilling or after  
107 excavation. During the analysis, more than 3000 fractures (total 3168) were examined (Table  
108 1). Fractures that developed naturally are characterized by fillings of euhedral crystals. On the  
109 other hand, open fractures without any fracture fillings and with the fracture surfaces  
110 exposing of fresh and clear quartz and feldspar crystal surface are readily distinguishable and  
111 formed synthetically during or after drilling or after exposure by drying and/or wetting. Such  
112 synthetically formed fractures (total 80) were excluded from the analysis of structural features  
113 that act presently as flow-paths in the *mélange* host rock.

114 Naturally formed fractures (3088) with fillings were then classified according to whether:  
115 1) the fracture is totally sealed by filling minerals; or 2) the fracture is only partially filled by  
116 euhedral crystals and has interconnected macroscopic (visible with the naked eye) open pore  
117 space. Fractures of the first type cannot presently be acting as pathways for significant fluid  
118 movement. In contrast, fractures of the second type might act as pathways for present fluid  
119 migration. Based on the macroscopic observation of fracture fillings, the presence of euhedral  
120 crystals shows that fluids have circulated after the fracture was formed and that crystals grew

121 on the surfaces of the wall rock without being damaged subsequently by crushing or shearing  
122 movements. Although any given borehole shows only the conditions at a particular a point on  
123 a given fracture plane, based on the large number of fracture observations it is possible to  
124 understand at least the general characteristics of the flow-path geometry developed in the  
125 mélangé formation.

126 Fractures within the oxidized zone that developed from the ground surface (i.e. the  
127 shallower part of the studied rock sequence) and their mineral fillings have also been  
128 characterized. The fractures within this zone have Fe-oxyhydroxides within and around them.  
129 These fractures are used to determine the extent of oxidizing meteoric water penetration, as in  
130 studies of crystalline rocks at several other sites in Japan (e.g. [Yoshida et al., 2013](#); [Yamamoto  
131 et al., 2013](#); [Yoshida and Yamamoto, 2014](#)). Fractures formed artificially within the oxidized  
132 zone do not contain any Fe-oxyhydroxides or other filling or lining minerals, and therefore are  
133 readily distinguished from the natural fractures distributed in the zone.

134

## 135 **2.2 Morphological observations, mineralogy and geochemical characteristics**

136 In order to analyze the morphological and structural inter-relationships among the mineral  
137 infills in the fractures, thin-sections of wall rocks and infilling minerals were prepared and  
138 optical microscopic observations were carried out. Rock thin-sections were made vertically  
139 across the fracture plane and filling minerals to clarify the textural relationships among them.

140 Core specimens with fillings were impregnated by epoxy resin to prevent destruction of the  
141 micro pores distributed in and around the fillings by cutting. This impregnation was necessary  
142 because the fracture fillings are quite fragile and softer than the wall rock. The impregnated  
143 specimens were thereafter carefully sliced and polished to use for optical microscopy and also  
144 for observations by scanning electron microscopy (SEM). Wavelength-dispersive x-ray  
145 (WDX) analyses were also carried out to produce chemical maps of the thin sections and

146 thereby support the optical microscopic observations. For these SEM-WDX analyses, the thin  
147 sections observed under an optical microscope were coated with carbon by means of an ion-  
148 spattering apparatus. The WDX analyses of the coated thin sections were performed at  
149 Nagoya University Museum by using a S-3400N (Hitachi High Technologies Co. Ltd.)  
150 instrument, operated with an accelerating voltage of 15 kV.

151 The mineralogy of the filling minerals was determined by using X-ray diffraction (XRD).  
152 Firstly, targeted minerals were shaved from fractures using a micro-drill under an optical  
153 microscope. The shaved minerals were powdered with a mortar and a pestle. The powdered  
154 samples were then painted onto a slide glass and analyzed. The analyses were performed by a  
155 RAD-2C (Rigaku Co. Ltd.) instrument at Nagoya University Museum, with operating  
156 conditions as follows: Cu tube, Ni filter, 40 kV tube voltage, 20 mA tube current, and a  
157 scanning rate of 1 °/min.

158 The geochemical compositions of the mineral fillings were also analyzed by X-ray  
159 fluorescence (XRF), including ignition loss measurement, to determine the relationship  
160 between the spatial distribution of the oxidized zone and chemical composition changes in the  
161 host rock. The analyses were conducted on host rock samples a few-centimetres across and  
162 also on samples of mineral fillings extracted from the naturally opened fractures. Each sample  
163 was crushed by stamp mill and put through a sieve of 115 mesh, to produce a powder for  
164 analysis. Then, 0.5 g of powdered sample was mixed with 5.0 g lithium tetraborate and fused  
165 to produce glass beads for XRF analyses. The XRF analyses were performed by an SXF-120  
166 instrument (Shimadzu Co. Ltd. at Graduate school of environmental studies of Nagoya  
167 University) with Rh tube, 40 kV tube voltage, and 70 mA tube current. Reference rock  
168 samples produced by the National Institute of Advanced Industrial Science and Technology  
169 (AIST) ([Yamamoto and Morishita, 1999](#)) were also used to calibrate the instrument. For the  
170 ignition loss test, the powdered samples were heated by muffle furnace at 950 °C for 3 hours.

## 171 **3. Results**

### 172 **3.1. Fracture and oxidized zone distribution**

173 Observations on the rock cores show that fracture frequencies vary little within the  
174 alternating sandstones and mudstones of the formation. As shown in Table 1, the average of  
175 fractures frequency identified by core observation including all sealed and open one is about  
176 7/m through all cores from A to E (Figures 3 and 4). This finding suggests that the mechanical  
177 deformation occurred after lithification when the rocks had developed similar mechanical  
178 properties..

179 Open fractures are mainly identified in the shallower part, while sealed ones are distributed  
180 mainly in the deeper part (Figure 3). Open fractures of the shallower part are closely  
181 associated with Fe-oxyhydroxides that occur within the oxidized zone that occurs  
182 immediately beneath the ground surface. The maximum depth of this oxidized zone, as  
183 recognized by the deepest occurrence of Fe-oxhydroxides, reaches up to 78 metres (Core-A),  
184 72 metres (Core-B) and 76 metres (Core-E). The core observations show that the base of the  
185 oxidized zone is almost concordant with the sedimentary layers probably due to groundwater  
186 flow along the topography and occurs deeper than present groundwater table (Figure 3b).

187 The chemical compositions of core-E sandstone specimens from the shallower part, as  
188 measured by XRF, show that slight movement of redox sensitive elements (e.g. Fe and Mn)  
189 and pH sensitive elements (e.g. Ca) has occurred (Table 2, Figure 5). In particular, Ca has  
190 been leached intensively at depths up to about 40 metres below the surface. This finding  
191 strongly suggests that surface water has reached at least this depth by flowing through the  
192 fracture network (Figure 5a). Due to this surface water penetration, carbonate rich fracture or  
193 pore filling minerals have been dissolved and the resulting pore spaces have remained open in  
194 the upper part of the studied rock sequence (Figure 5b). As the water was relatively oxidizing,  
195 Fe-oxyhydroxides were precipitated in and around the pore spaces. The relatively acidic water

196 also resulted in the formation of smectite. Microscopic observations of mineral textures  
197 confirm that the Fe-oxyhydroxides and smectite were formed during the last stage of fracture  
198 evolution (Figures 5c, d).

199 A comparison of fracture fillings between the deeper un-oxidized zone and shallower  
200 oxidized zone in the same fracture clearly show that dissolution of the calcite filling  
201 accompanied oxidation of the rock (Figures 5e, f). The detailed process of oxidized zone  
202 formation and the reaction with the fillings are discussed following section.

203

### 204 **3.2. Fracture fillings of deeper part**

205 Fractures distributed deeper than the oxidized zone are almost sealed and less than 10% of  
206 the fractures without Fe-oxyhydroxides remain open. In other words, almost 90% of fractures  
207 observed in the cores are sealed without any evidence of functioning of groundwater flow.  
208 The minerals and mineral textures identified in each fracture in the deeper, unoxidized part of  
209 the studied rock sequence are shown in Figure 6. Fractures (Figures 6a - c) have various  
210 sealing minerals, primarily ankerite, siderite and quartz. Fractures having open pore space  
211 lined by quartz and ankerite are also identified and are possibly able to conduct water (Figures  
212 6 d - f).

213 First of all, siderite is only identified as a mineral fill in pore spaces formed during ductile  
214 deformation (Figure 6a). Ankerite is sometimes associated with the siderite in ductile  
215 deformation structures (Figure 6b). It is presumed that the fractures formed when much of the  
216 rock matrix was still able to deform plastically. Other minerals are seen only within the pore  
217 spaces of fractures formed by brittle deformation, after the lithification of the sediments due  
218 to high-pressure compaction during accretion. The different mineral fillings in different kinds  
219 of fracture clearly enable a distinction to be made between different stages of fracturing and  
220 mineral formation under different conditions.

221 The minerals observed in each fracture basically grew from both walls of the fracture until  
222 they met at the centre of the fracture, thereby occluding almost all the open space. Although  
223 almost 90 % of the fractures are sealed by calcite, the remaining 10% or so of the voids  
224 volume in the fractures remained open and was able to conduct fluids.

225 Fine network texture veins of siderite and ankerite , without euhedral crystals, formed  
226 penetrating the muddy fine layers. The morphology of veins with uneven boundaries between  
227 the vein and the host rock matrices show that the fillings formed before the matrix was fully  
228 consolidated (Figures 7a, b). On the other hand, within the open space of fractures that formed  
229 within consolidated rock quartz crystals (Figures 8a, b) grew on the wall rock directly. In  
230 these cases, sometimes euhedral ankerite (Figures 8c, d) and fibrous siderite cover the quartz  
231 crystals. Calcite crystals formed on these fillings (Figures 8e, f) showing and is not  
232 overgrown by any later minerals; this calcite represents the latest stage of mineralisation  
233 (Figures 7c, d). The euhedral form of the calcite is a quite specific feature readily identified  
234 by SEM observations, suggesting the pore space and/or opened fractures are still acting as  
235 flow-paths for ground water movement, as is also known in the case of deep crystalline rocks  
236 distributed in Japan (e.g. [Yoshida et al., 2013](#)).

237 Illite is seen in the wall rocks along fractures filled by un-deformed quartz (Figure 7e) and  
238 feldspar grains (Figure 7f). This implies that the illite was formed during the circulation of  
239 hydrothermal fluids and simultaneously the fluids precipitated the quartz crystals on the pore  
240 surfaces of the fracture.

241

242

## 243 **4. Discussion**

### 244 **4.1. Formation stage of filling and alteration minerals**

245 The morphological and textural relationships of fracture fillings and secondary minerals in  
246 the rock matrices, suggest that the following stages of mineralisation occurred during the  
247 development of the accretionary complex and the subsequent uplift of the rock.

248

#### 249 **Stage I**

250 Stage I is characterized by siderite and ankerite fillings in pore space that formed during  
251 the ductile deformation of unconsolidated sediment (Figures 7a, b). Pores filled with these  
252 minerals without forming crystal texture with a restricted distribution in mudstone layers and  
253 do not cut across the sedimentary structure. These pores show pinch-and-swell structures, and  
254 composite planar fabrics with the Y surfaces parallel to sedimentary structures (Figures 6a, b).  
255 Also almost no alteration occurs along the margins of the matrix pores that are filled with  
256 ankerite and siderite. This observation suggests that the pore fillings are authigenic and  
257 formed concordantly with the ductile pore geometry, probably soon after the sediments  
258 subducted, but before their consolidation.

259 The fluid involved in the formation of siderite and ankerite in Stage I is interpreted to have  
260 been enriched in Ca and Mg, and probably was expelled from the muddy layers due to  
261 squeezing during accretion, as suggested by the structures shown in Figures 6a, b. Moreover,  
262 the fracture with a pinch-and-swell structure and Y-P fabrics suggests that the fracturing  
263 progressed by layer-parallel shearing (e.g. [Kano and Murata, 1998](#); [Ben et al., 2002](#)). Such  
264 ductile deformation resulting in the pinch-and-swell structures also show that the rock body  
265 was still unconsolidated and had relatively high porosity during the early stage of the  
266 accretion process. This interpretation is also supported by the quartz grains in the rock  
267 matrices showing no deformation (Figures 7e).

268 It is known that siderite is generally formed during diagenesis under reducing conditions at  
269 temperatures less than about 100 °C (e.g. [Mohamed et al., 2006](#)). [Kondo et al. \(2005\)](#) has also

270 been reported that, based on fluid inclusion measurements, sheared ankerite in fractures  
271 around shear zones or thrust zones in the Shimanto Belt within the same area of Kyushu is  
272 estimated to have formed at a temperature of 100 – 250 °C.

273

## 274 **Stage II**

275 Stage II is characterized by quartz fillings within the porosity of fractures developed under  
276 conditions of relatively high pressure and high temperature (Ohira et al., 2010). This quartz  
277 typically forms euhedral columnar crystals that cover the fracture surfaces (Figures 8a, b).  
278 Fractures with this type of quartz commonly have planar fracture surfaces and cut  
279 sedimentary layers at high angles (Figures 6c, d). Within the rock matrices along the same  
280 fractures, illite was formed in and around feldspar grain boundaries (Figure 7f), probably due  
281 to the circulation of relatively high temperature hydrothermal fluids.

282 The planar shape fractures with quartz fillings developed in Stage-II cross-cut the  
283 sedimentary layers that were deformed in Stage-I (Figures 6c, d), thereby showing that the  
284 Stage II fractures formed after the had sediments completely solidified. In particular, euhedral  
285 crystals on the planar fracture surfaces indicate that fracturing developed open pore space  
286 sufficient for mineral growth (e.g. Nicholas and Paul, 2001). These features suggest that the  
287 fractures formed after the stress had started to decrease, probably due to unloading during  
288 uplift of the consolidated sediments.

289 Based on measurements of homogenisation temperatures on fluid inclusions within the  
290 euhedral quartz it has been estimated that the geothermal fluids from which the quartz  
291 precipitated had temperatures in the range 80 – 300 °C (e.g. Muramatsu, 1987; Ohira et al.,  
292 2010). XRD analyses on illite in samples from the altered zone around the fractures with  
293 quartz fillings (Figures 9a, b) and the mode of occurrence of the illitized plagioclase, are quite  
294 similar to illitized plagioclase formed along flow-paths within crystalline rock by geothermal



295 activity (Nishimoto and Yoshida, 2010). The illite in such situations is most likely to have  
296 formed within the temperature range 200 – 300 °C (e.g. White and Hedenquist, 1995).  
297 Stage-II is therefore interpreted to have formed later than Stage I, at relatively high pressure  
298 and temperature, during uplift that accompanied the accretion process after maximum depths  
299 had been attained.

300

### 301 **Stage III**

302 Stage III is characterized by ankerite crystals with euhedral rhombic shapes, which are in  
303 contrast to the microcrystalline ankerite crystals identified in Stage-I. Since the euhedral  
304 ankerite crystals cover the Stage-II columnar quartz (Figures 8c, d), the stage clearly post-  
305 dates Stage I and II. Fractures formed in Stage-III have form a network and/or branching  
306 structure and cut the fractures formed in Stage-II (Figures 6e, f). However, there is almost no  
307 alteration identified along the fractures, suggesting that the geothermal fluids from which the  
308 Stage III ankerite precipitated had lower temperatures than those of the geothermal fluids that  
309 formed the Stage II mineralisation.

310 The mode of occurrence of the branching fractures, the fillings of which contain fine  
311 fragments of wall rock, suggest that the pore fluid pressure was still relatively high during  
312 fracturing and mineral filling formation, probably close to lithostatic pressure, (e.g. Yoshida et  
313 al., 2013). Fractures with euhedral Mg-rich carbonates have been reported from  
314 hydrothermally altered limestone and their formation temperature has been estimated to have  
315 been between 100 – 280 °C (Tritlla et al., 2001; Chen et al., 2004; Luczaj et al., 2006). Saller  
316 (1984) has also reported Mg-rich carbonate precipitations from modern Pacific Ocean water  
317 at deeper than 1,000 metres depth with relatively high temperature condition.

318 As the sediments had already consolidated by the time that Stage III mineralisation formed,  
319 the source of the Mg that became incorporated into this mineralisation was unlikely to have

320 been water squeezed from the rock matrix. It is more likely that the Mg was supplied by  
321 another process. One possibility is that, during stage III, during continuing uplifting, seawater  
322 might have penetrated through the open fractures and provided the Mg that became  
323 incorporated into the Stage III fracture-filling minerals.

324

#### 325 **Stage IV**

326 This stage is characterized calcite that seals up to ca. 90% of the pore-space that remained  
327 in the fractures following the fracturing and mineralisation of Stages I ~ III. The calcite in this  
328 stage typically shows euhedral shapes (Figures 8e, f) and covers or develops on the quartz and  
329 ankerite fillings formed in Stage-II and Stage-III respectively (Figures 7c, d). Such a textural  
330 relationship is also shown by WDX analysis (Figure 10) and suggests that the calcite of Stage  
331 IV post-dates the other stages and healed the remaining fracture porosity.

332 Fracture-filling and diagenetic calcite from various locations was estimated to have formed  
333 over a wide range of temperature, between 60 – 240 °C (e.g. [Muramatsu, 1987](#); [Sakaguchi,](#)  
334 [1999](#); [Blyth et al., 2000](#)). However, there is no major alteration developed in the wall-rocks of  
335 fractures adjacent to Stage IV mineralisation, implying that this mineralisation formed  
336 towards the lower end of this temperature range. Without groundwater chemistry data, it is  
337 rather difficult to estimate the origin of the Ca and the fluids from which the Stage IV calcite  
338 circulated. However, calcite is a common fracture-filling mineral along pathways for present  
339 groundwater flow identified at depths of up to 1,000 metres in granitic rocks studied in  
340 underground facilities excavated in central Japan (e.g. [Yoshida et al., 2013](#); [Ishibashi et al.,](#)  
341 [2014](#)). Indeed these previous studies have revealed that the calcite mineralisation can be used  
342 as an indicator of flow-paths presently conducting groundwater circulation.

343 The detailed observations identified various shapes of calcite crystals in the Stage IV  
344 mineralisation. It is possible that these morphological changes reflect changes in pore water

345 salinity caused by mixing between old seawater and more recent, fresh meteoric water; more  
346 elongate crystals tend to precipitate from more saline water (e.g. [Iwatsuki et al. 2002](#)).  
347 Possibly the source of the Ca in the calcite of stage IV was seawater that infiltrated the  
348 formation during uplift.

349

#### 350 **Stage V**

351 Stage V is characterized by Fe-oxyhydroxides that coat fracture surfaces. Fractures  
352 showing this stage of mineralisation are developed dominantly within the shallower part of  
353 the studied sequence (i.e. the oxidized zone). In particular, Fe-oxyhydroxides occur in  
354 fractures from which calcite fillings have been dissolved, probably due to the penetration of  
355 relatively acidic, fresh meteoric water ([Yamamoto et al., 2013](#); Figures 5e, f). Microscopic  
356 observations on rock samples from the oxidized zone also show that plagioclase has altered to  
357 smectite, again consistent with the penetration of meteoric water (Figure 5d).

358 Stage V is therefore interpreted as the final stage of fracture mineralisation, that formed  
359 after the sedimentary formation had approached the ground surface, or after exposure at the  
360 ground surface. The Fe-oxyhydroxides could have been formed as a consequence of the pH  
361 increase that would have occurred as the acidic meteoric water dissolved calcite and reacted  
362 with feldspar to form smectite. This redox reaction developed the oxidized zone recognized  
363 from the distribution of Fe-oxyhydroxides along fractures at depths of up to several tens of  
364 metres beneath the ground surface, as shown in a cross section through this site (see Figure 3).  
365 The temperature of smectite formation in other sedimentary sequences has been estimated to  
366 have been lower than 100 °C (e.g. [White and Hedenquist, 1995](#)). Formation of fracture-lining  
367 Fe-oxyhydroxides and related smectite alteration of granitic rock under near-surface  
368 conditions was also investigated along water conducting fractures in a fault zone in granitic  
369 rock (e.g. [Nagatomo and Yoshida, 2009](#)).

370 The mineralisation stages developed during accretion of the Hyuga Group and their  
371 estimated conditions of formation are summarized in Figure 11. Based on the filling mineral  
372 assemblages and the deformation features of the fractures, it is suggested that the accretion  
373 depth of the Hyuga Group was shallower than reported for the same Shimanto complex  
374 further to the east, in the Kii area of central Japan (e.g. [Hashimoto et al., 2002](#)). Filling  
375 minerals seen in the Kii area are epidote and chlorite, which indicate that mineralisation in the  
376 Kii area occurred under higher formation temperatures and/or pressures than the fracture-  
377 filling minerals of the study area considered in this paper. These differences also support the  
378 use of mineral assemblages to distinguish how the same accretionary complex subducted  
379 under different geological conditions.

380

#### 381 **4.2. Redox front development from the ground surface**

382 The characteristics of fracture fillings in the shallower part of the studied rock sequence  
383 (i.e. the oxidized zone) show that meteoric water has penetrated along fractures and reacted  
384 with the calcareous sandstone wall rocks to a depth of at least 80 metres beneath the present  
385 ground surface. Microscopic features of the fracture mineralisation reveal that the calcite  
386 filling formed in Stage IV has been almost totally dissolved and Fe-oxyhydroxides have  
387 formed on the surfaces exposed by the loss of calcite. The calcite dissolution developed flow-  
388 paths which facilitated circulation of meteoric water, penetrating from the ground surface.  
389 This is the first time for a melange sequence that original fluid flow paths have been  
390 distinguished from secondary ones formed as a result of meteoric water penetration. Such a  
391 distinction should be taken into account for understanding the suitable depth of facility  
392 allocation when undertaking hydrological and geotechnical investigations for siting of any  
393 relevant underground facility used e.g. for radioactive waste disposal in Japan.

394 The behaviour of Ca, Mn and Fe in the fractured rocks, as measured by the XRF analyses,  
395 imply that the infiltrating water was acidic but not of such low pH that it could not be  
396 buffered to more alkaline pH by water / rock reactions, causing fixation of Fe as Fe-  
397 oxyhydroxide. The source of such acidic water could have been pore water in soils covering  
398 the basement rock. Soils in general tend to be rich in organic acid, due to decomposition of  
399 organic materials (Küsel et al., 2002; Petrunic et al., 2005).

400 The characteristics of the oxidized zone in the shallower part of the studied rock sequence  
401 is quite similar to oxidized zones in crystalline rocks, which are interpreted to have been  
402 controlled by the pH-buffering effect of water / rock reactions (Yamamoto et al., 2013). These  
403 studies of crystalline rocks concluded that the source of the Fe fixed in the Fe-oxyhydroxides  
404 was the overlying soils, based on the observation that Fe has been gained by the oxidized  
405 zone in the granitic rock. However, in the case of the Shimanto, XRF data for the calcareous  
406 sedimentary rocks show almost no Fe accumulation in the oxidized zone. This shows that any  
407 Fe dissolved from the soil or near-surface rock-forming minerals probably precipitated soon  
408 just after dissolution and did not migrate far. Such differences between the cases of crystalline  
409 rocks and the Shimanto sedimentary rocks are explained by the relatively high potential for  
410 pH buffering of the Hyuga Group. This relatively high buffering capacity is provided by the  
411 high abundance of carbonate cement in the fractures and sedimentary matrices. Such  
412 differences in buffering capacity are important considerations when assessing the potential  
413 barrier function of the geological environment surrounding underground waste disposal  
414 facilities, for example for the disposal of nuclear wastes.

415

416

417

418

419 **5. Conclusion**

420 The modes of occurrence, mineralogical assemblages and geochemistry revealed that  
421 fracture filling minerals in the studied Hyuga Group mélangé were formed in five-stages, each  
422 one distinguished by the sequential textural relationships of the minerals and the interpreted  
423 environment of mineral formation. Stage I: fibrous siderite and ankerite precipitated in a  
424 muddy matrix formed before sediment consolidation; Stage II: euhedral quartz precipitated  
425 from high-temperature hydrothermal fluids circulating within the open pore space of fractures  
426 and at the same time the fluids altered plagioclase in the wall rocks; Stage III: euhedral  
427 ankerite grew on minerals formed in Stage II; Stage IV: euhedral calcite growth was caused  
428 by meteoric water penetration and sealed most of the fractures up to ca. 90%; Stage V: calcite  
429 dissolved and Fe-oxyhydroxides precipitated due to infiltration of acidic meteoric water that  
430 percolated through organic rich soil. The dissolution front reaches a depth of about 70 metres  
431 below the present ground surface. Within the five stages, the mineralogical assemblages  
432 suggest that Stage-II was developed under the highest temperature conditions, ca. 200 –  
433 300 °C, during the period when the rock mass was buried to depths of at least several km. The  
434 results shown here imply that the use of mineral assemblages formed in fractures can be an  
435 effective tool to evaluate the collision processes and the environmental changes during  
436 accretionary complex formation. The observations can also be used to develop a predictive  
437 model for the present spatial distribution features of the rock mass that may conduct flowing  
438 groundwater. Such a predictive model is important for developing various kinds of  
439 underground facilities, such as waste repositories.

440

441

442

443

444 **Acknowledgments**

445 We are grateful to Dr. Y. Nishizono and Mr. A. Oshima of West Japan Engineering  
446 Consultants, Inc. for their helpful sample preparation and advices over all of this study. We  
447 also thank to Prof. M. Takeuchi, Prof. K. Yamamoto, Lecturer Dr. Y. Asahara of Nagoya  
448 University for their discussion and support on geochemical analysis during the research.  
449 Ms.M. Nozaki, Mr. S. Yogo of the Nagoya University Museum and Dr. S. Nishimoto of  
450 Nagoya City Science Museum for their technical supports and advice during observations and  
451 analysis.

452

453

454 **Captions**

455 **Figure 1** Index map of the distribution of Shimanto accretionary complex and studies site (a).

456 Geological map around the dam site along Omaru river (b) modified after [Kimura et](#)  
457 [al. \(1991\)](#).

458 **Figure 2** Sandstone hosted formation of Hyuga group occurred in the dam site. Well layered  
459 formation (a) and mudstone rick part (b).

460

461 **Figure 3** Detailed surface geology with location of bore hole drillings (a). Geological cross  
462 section along the boreholes (b). Red coloured zone of shallower part identified as  
463 oxidized zone with open fractures and blue coloured deeper part characterized by  
464 the sealed fractures.

465

466 **Figure 4** Occurrence of the core specimens drilled at the dam site (Core-B) from the surface  
467 to depth of 75 metres. Shallower part is identical with the reddish colour by ferric  
468 iron precipitation due to surface acidic water penetration.

469

470 **Figure 5** Depth profile of major elements according the XRF data shown in Table 2 (a). The  
471 feature of  $\text{CaCO}_3$  dissolution at the oxidation front (b). Photomicrograph shows the  
472 Fe-oxyhydroxides precipitation in and around the  $\text{CaCO}_3$  dissolved fractures (c, d)  
473 and the  $\text{CaCO}_3$  filled pores and dissolved pores due to acidic surface water  
474 penetration cross the reaction front (e, f).

475

476 **Figure 6** Occurrences of fracture fillings of different stages identified in the host rock.  
477 Siderite and ankerite veins in muddy layers without cutting sedimentary layers  
478 (Stage-I) (a,b). Quartz vein cut sedimentary structure showing brittle fracturing after  
479 consolidation of sediments (Stage-II) (c,d). Ankerite with euhedral crystal filling  
480 identified in the opened brittle formed fracture (Stage-III) (e, f).

481

482 **Figure 7** Photomicrograph of optical microscope (cross) of veins and matrix. Siderite and  
483 ankerite fillings within the host-rock sedimentary layer without clear boundary  
484 between fillings and matrix suggesting still unconsolidated facies remained the veins  
485 were formed recognized as Stage-I (a, b). Illite precipitated within micro-pores in  
486 the matrix probably due to high temperature fluid circulation defined as Stage-II (e,  
487 f). Occurrence of carbonate ( $\text{CaCO}_3$ ) clearly showing the latest stage filled all  
488 previously formed fillings as Stage-IV (c, d).

489

490 **Figure 8** SEM micrographs of fillings identified in the opened fractures. Euhedral quartz  
491 formed identified in the opened fractures of Stage-II (a, b). Euhedral ankerite  
492 covering on euhedral quartz of Stage-II identified as the Stage-III (c, d). Various



493 shape of calcite crystals forming on the fillings previously formed as defined as  
494 Stage-IV (e, f).

495

496 **Figure 9** XRD patterns of unaltered host rock and hydrothermally altered host rock (a) and  
497 the filling of calcite and without calcite comparing cross the acidic water penetration  
498 in the same fracture (b).

499

500 **Figure 10** Micrograph of SEM (a) and WDX mappings (b ~ d) of Ca, Fe and Mg cross the  
501 fillings clearly showing the compositional differences of filling and precipitated  
502 order distinguishable the each Stage.

503

504 **Figure 11** Summarised configuration of accretionary complex forming constructed by using  
505 secondary fracture filling minerals assemblage and the conditions estimated in each  
506 Stage.

507 **Table 1** Fracture frequencies (number of fractures identified: 3168) of all drilled cores (A - E)  
508 and showing the depth of shallower part identified by reddish coloured by Fe-  
509 oxyhydroxides.

510

511 **Table 2** XRF data of host rock taken from deepest drilled Core-E from the surface to the  
512 depth of 115.8 metres.

513

514

515 **References**

516 Akagawa, F., Yoshida, H., Yogo, S., Yamamoto, K., 2006. Redox front formation in fractured  
517 crystalline rock: an analogue of matrix diffusion in an oxidizing front along water-  
518 conducting fractures. *Geochemistry: Exploration, Environment, Analysis*, 6, 49–56.

519 Ben, D. G., Cees, W. P., Martin, H., 2002. Boudinage classification: end-member boudin  
520 types and modified boudin structures. *Journal of Structural Geology*, 26, 739–763.

521 Blyth, A., Frapé, S., Blomqvist, R., Nissinen, P., 2000. Assessing the past thermal and  
522 chemical history of fluids in crystalline rock by combining fluid inclusion and isotopic  
523 investigations of fracture calcite. *Applied Geochemistry*, 15, 1417–1437.

524 Charvet, J., 2013. Late Paleozoic-Mesozoic tectonic evolution of SW Japan: A review –  
525 reappraisal of the accretionary orogeny and revalidation of the collisional model. *Journal*  
526 *of Asian Earth Science*, 72, 88–101.

527 Chen, D., Qing, H., Yang, C., 2004. Multistage hydrothermal dolomites in the Middle  
528 Devonian (Givetian) carbonates from the Guilin area, South China. *Sedimentology*, 51,  
529 1029–1051.

530 Committee for Geological Stability Research, 2011. Geological Leaflet 4, Japanese Island-arc  
531 and Geosphere Stability. The Geological Society of Japan, No.4.

532 Hashimoto, Y., Enjoji, M., Sakaguchi, A., Kimura, G., 2002. P-T conditions of cataclastic  
533 deformation associated with underplating: An examples from the Cretaceous Shimanto  
534 complex, Kii Peninsula, SW Japan. *Earth Planets Space*, 54, 1133–1138.

535 Ishibashi, M., Ando, T., Sasao, E., Yuguchi, T., Nishimoto, S., Yoshida, H., 2014.  
536 Characterization of water conducting fracture and their long-term behavior in deep  
537 crystalline rock: a case study of the Toki Granite. *Journal of the Japan Society of*  
538 *Engineering Geology*. 55, 156–165.

539 Iwatsuki, T., Satake, R., Metcalfe, H., Yoshida, H., Hama, K., 2002. Isotopic and  
540 morphological features of fracture calcite from granitic rocks of the Tono area, Japan: a  
541 promising paleohydrogeological tool. *Applied Geochemistry*, 17, 1241–1257.

542 JGS (The Geological Society of Japan), 2010, *Nihon chihou chishitsu shi* [Local Geology of  
543 Japan] 8, The Kyushu and Okinawa Area. Asakura Shoten, Tokyo.

544 Kano, K., Murata, A., 1998. *Kouzou chishitsu gaku* [Structural geology]. Asakura Shoten,  
545 Tokyo.

546 Kimura, K., Iwaya, T., Mimura, K., Sato, Y., Sato, T., Suzuki, Y., Sakamaki, Y., 1991.  
547 Geology of the Osuzuyama District (with Geological Sheet Map at 1:50,000). Geological  
548 Survey of Japan, Tsukuba.

549 Kondo, H., Kimura, G., Masago, H., Ohmori-Ikehara, K., Kitamura, Y., Ikesawa, E.,  
550 Sakaguchi, A., Yamaguchi, A., Okamoto, S., 2005. Deformation and fluid flow of a major  
551 out-of-sequence thrust located at seismogenic depth in an accretionary complex: Nobeoka  
552 Thrust in the Shimanto Belt, Kyushu, Japan. *Tectonics*, 24, TC6008.

553 Küsel, K., Wagner, C., Trinkwalter, T., Gössner, A. S., Bäumler, R., Drake, H. L., 2002.  
554 Microbial reduction of Fe(III) and turnover of acetate in Hawaiian soils. *FEMS*  
555 *Microbiology Ecology*, 40, 73–81.

556 Luczaj, J. A., Harrison III, W. B., Williams, N. S., 2006. Fractured hydrothermal dolomite  
557 reservoirs in the Devonian Dundee Formation of the central Michigan Basin. *AAPG*  
558 *Bulletin*, 90, 1787–1801.

559 Mohamed, A. K. E., Howri, M., Sadoon, M., Ihsan, A. A., George, A., 2006. Distribution of  
560 diagenetic alterations in fluvial and paralic deposits within sequence stratigraphic  
561 framework: Evidence from the Petrohan Terrigenous Group and the Svidol Formation,  
562 Lower Triassic, NW Bulgaria. *Sedimentary Geology*, 190, 299–321.

563 Moore, J. C., Vrolijk, P., 1992. Fluids in accretionary prisms. *Reviews of Geophysics*, 30,  
564 113–135.

565 Muramatsu, Y., 1987. Distributions, paragenesis and fluid inclusions of hydrothermal  
566 minerals in the Kakkonda geothermal field, Northeastern Japan. *Journal of mineralogy,*  
567 *petrology and economic geology*, 82, 216–229.

568 Nagatomo, A., Yoshida, H., 2009. Analysis of the geological history of the active Atera Fault,  
569 central Japan, based on fault and fracture systems and infilling minerals. *Journal of*  
570 *geological society of Japan*, 115, 512–527.

571 Nicholas, H. S. O., Paul, D. B., 2001. Mechanisms of fluid flow and fluid-rock interaction in  
572 fossil metamorphic hydrothermal systems inferred from vein-wallrock patterns, geometry  
573 and microstructure. *Geofluids*, 1, 137–162.

574 Nishimoto, S., Ukai, E., Amano, K., Yoshida, H., 2008. Analysis of alteration process of deep  
575 granitic rock – A case study of Toki granitic rock-. *Journal of Engineering Geology of*  
576 *Japan*, **49**, 94-104.

577 Nishimoto, S., Yoshida, H., 2010. Hydrothermal alteration of deep fractured granite: Effects  
578 of dissolution and precipitation. *Lithos*, 115, 153–162.

579 Nuclear Waste Management Organization of Japan (NUMO), 2011. Safety analysis of  
580 Nuclear waste disposal, NUMO-TR-11-01.

581 Ohira, H., Nagai, R., Nishizaka, R., Takeuchi K., 2010. Fluid inclusion and thermal history of  
582 the Izumiyama pottery stone deposit, Arita district, Saga Prefecture. *Fission track news*  
583 *letter*, 23, 4–6.

584 Petrunic, B. M., MacQuarrie, K. T. B., Al, T. A., 2005. Reductive dissolution of Mn oxides in  
585 river-recharged aquifers: a laboratory column study. *Journal of Hydrology*, 20, 163–181.

586 Sakaguchi, A., 1999. Thermal maturity in the Shimanto accretionary prism, southwest Japan,  
587 with the thermal change of the subducting slab: fluid inclusion and vitrinite reflectance  
588 study. *Earth and Planetary Science Letters*, 173, 61–74.

589 Saller, A. H., 1984. Petrologic and geochemical constraints on the origin of subsurface  
590 dolomite, Enewetak Atoll: An example of dolomitization by normal seawater. *Geology*, 12,  
591 217–220.

592 Tritlla, J., Cardellach, E., Sharp, Z. D., 2001. Origin of vein hydrothermal carbonates in  
593 Triassic limestones of the Espdán Ranges (Iberian Chain, E Spain). *Chemical Geology*,  
594 172, 291–305.

595 Tsujimori, T., 2010. Paleozoic subduction-related metamorphism in Japan: new insights and  
596 perspectives. *Journal of Geography*, 119, 294–312.

597 White, N. C., Hedenquist, J. W., 1995. Epithermal gold deposits: styles, characteristics and  
598 exploration. Published in *SEG Newsletter*, 23, 9–13.

599 Yamaguchi, A., Cox, F. Stephan, Kimura, G., Okamoto, S. 2011. Dynamic changes in fluid  
600 redox state associated with episodic fault rupture along a megasplay fault in a subduction  
601 zone. *Earth and Planetary Science Letters*, 302, 369–377.

602 Yamamoto, K., Yoshida, H., Akagawa, F., Nishimoto, S., Metcalfe, R., 2013. Redox front  
603 penetration in the fractured Toki Granite, central Japan: An analogue for redox reactions  
604 and redox buffering in fractured crystalline host rocks for repositories of long-lived  
605 radioactive waste. *Applied Geochemistry*, 35, 75–87.

606 Yoshida, H., Takeuchi, M., Metcalfe, R., 2005. Long-term stability of flow-path structure in  
607 crystalline rocks distributed in an orogenic belt, Japan. *Engineering Geology*, **78**, 275–284.

608 Yoshida, H., Nishimoto, S., Cho, A., Yamamoto, K., Katsuta, N., 2008. Alteration of  
609 subsurface granitic rock in Okayama area, Japan, *Journal of Engineering Geology of*  
610 *Japan*, **49**, 256–265.

611 Yoshida, H., 2012. Fluid Conducting Fractures and Their Long-term Behavior in Crystalline  
612 Rocks: Present Understanding and Future Perspectives. *Journal of Geography*, **121**, 68-95.

613 Yoshida, H., Metcalfe, R., Ishibashi, M., Minami, M., 2013. Long-term stability of fracture  
614 systems and their behavior as flow paths in uplifting granitic rocks from the Japanese  
615 orogenic field. *Geofluids*, 13, 45–55.

616 Yoshida, H., Yamamoto, K., 2014. Fe oxyhydroxides in underground geological environments  
617 and high-level radioactive waste disposal: Analysis of influence on nuclide migration  
618 scenarios. *Journal of Geological Society of Japan*, 120, 327–343.

619

Figure 1

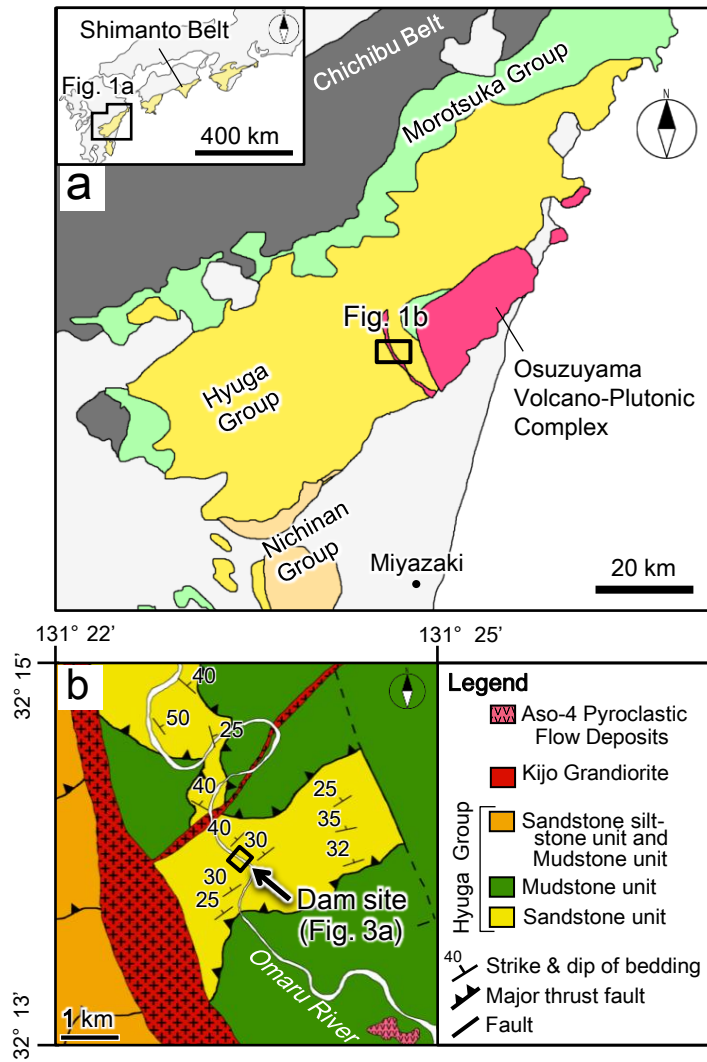


Figure 1

Figure 2

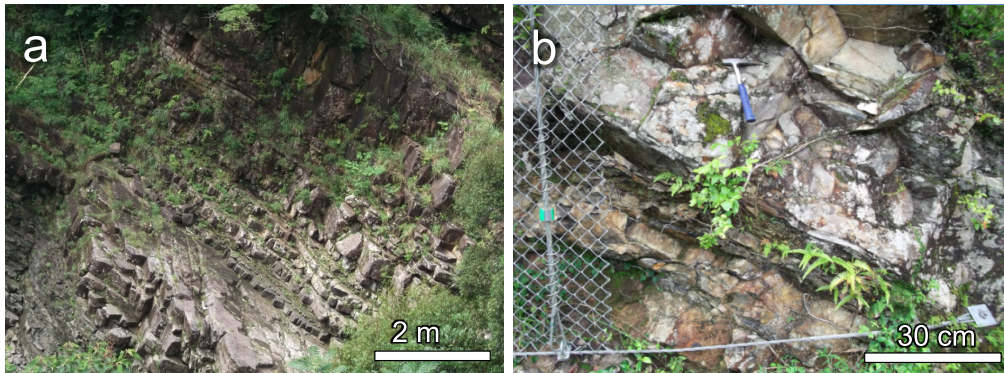


Figure 2



Figure 3

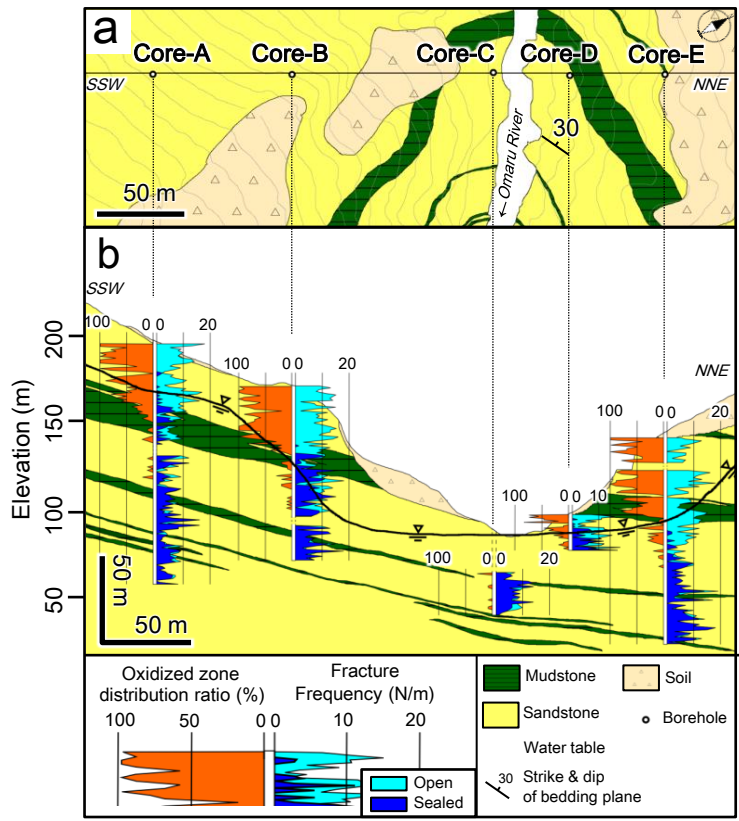


Figure 3

Figure 4

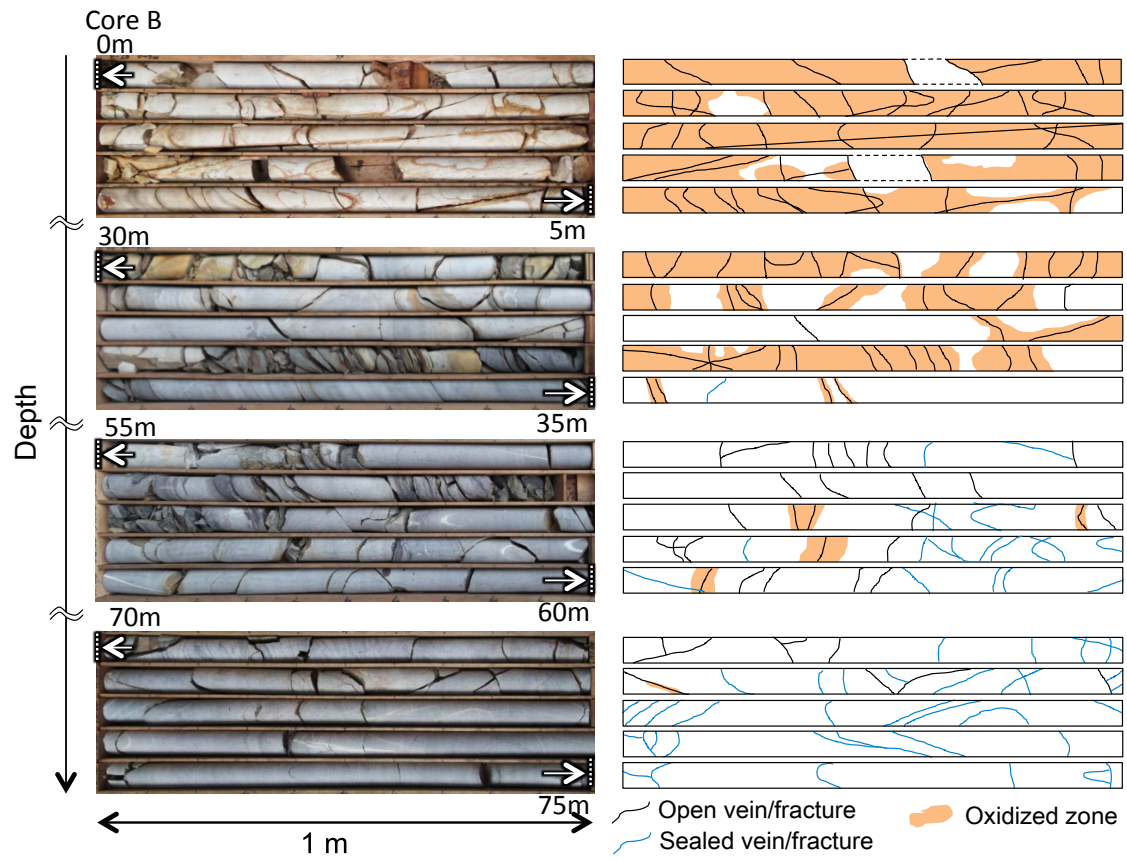


Figure 4

Figure 5

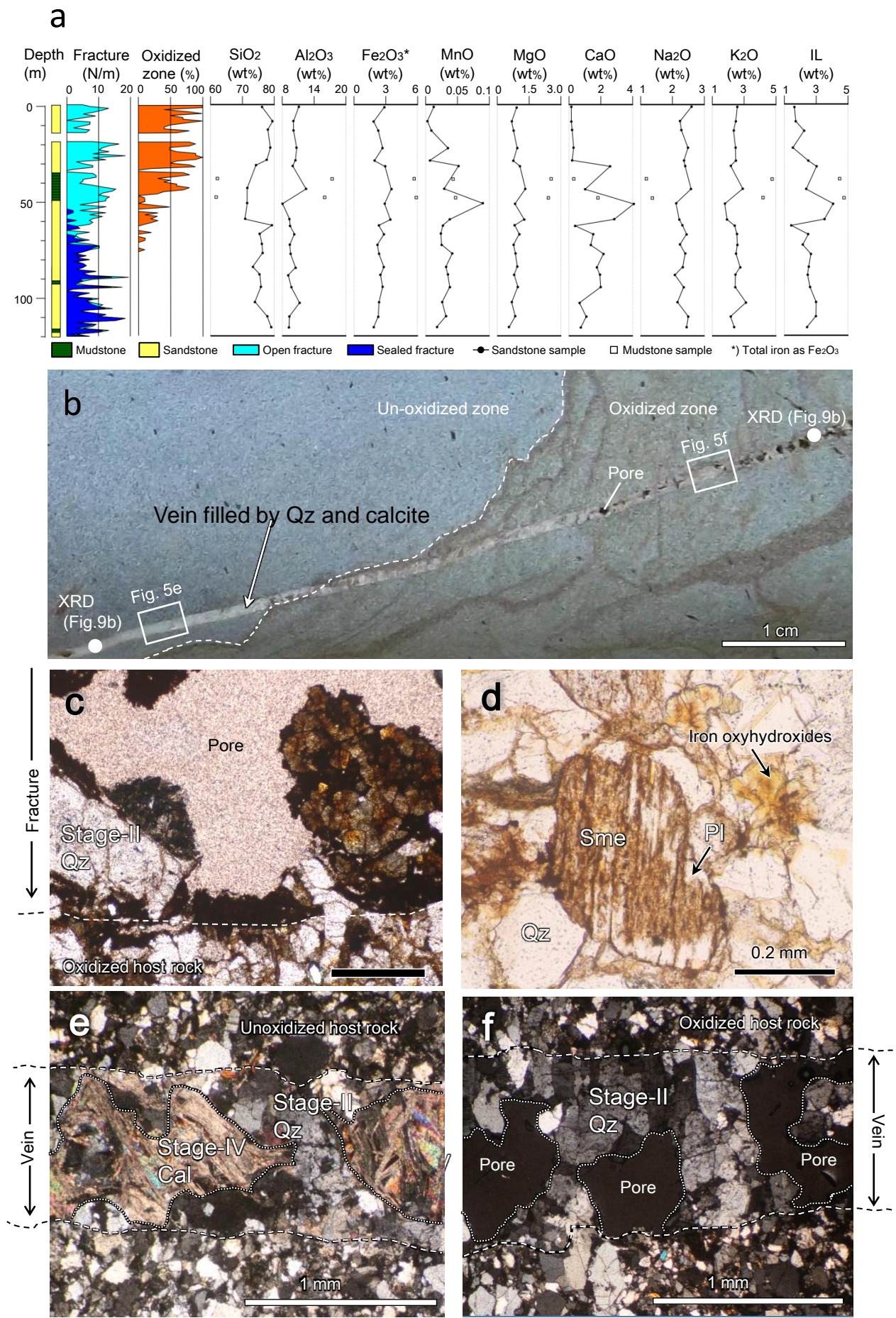


Figure 5



Figure 6

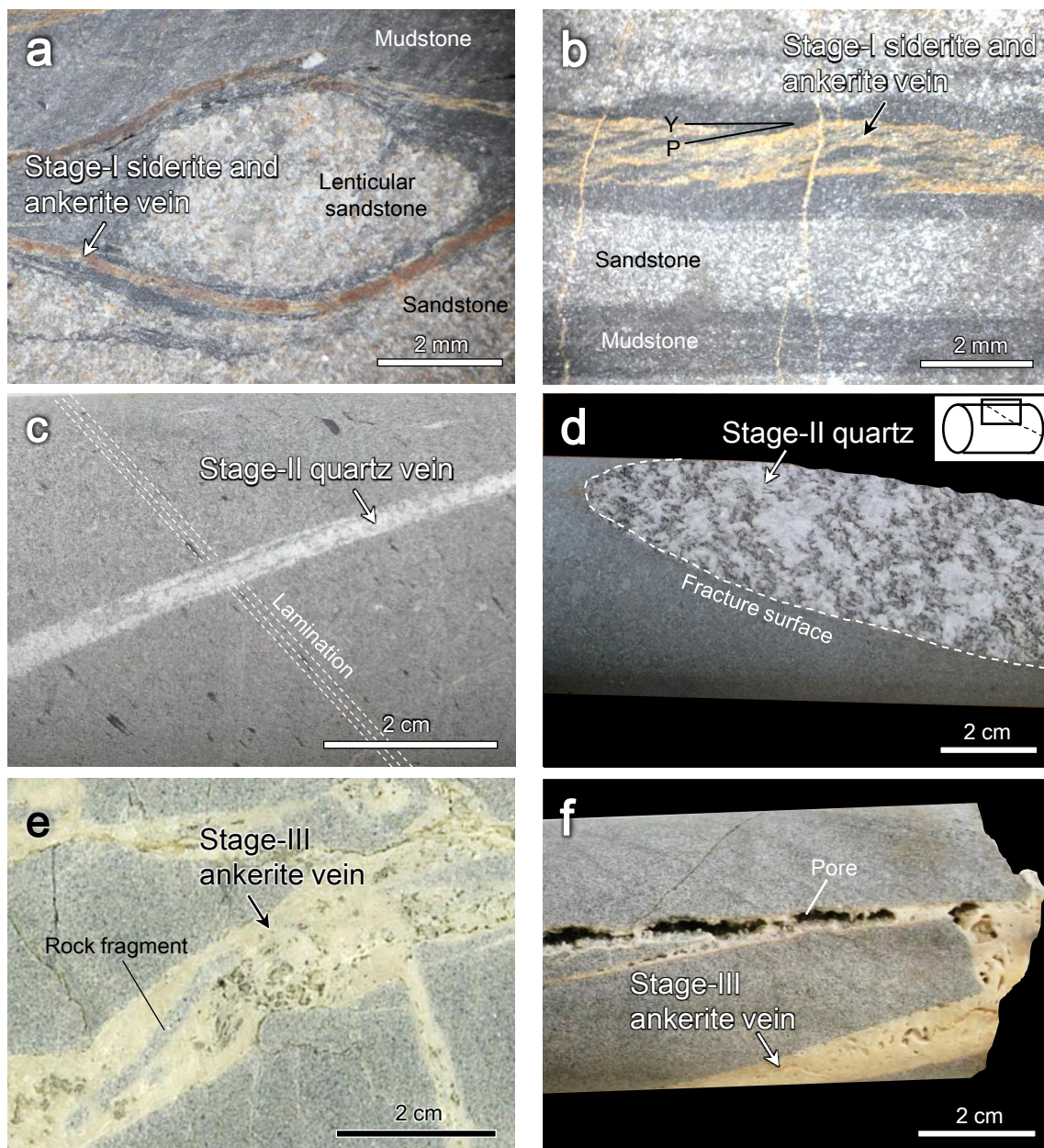


Figure 6



Figure 7

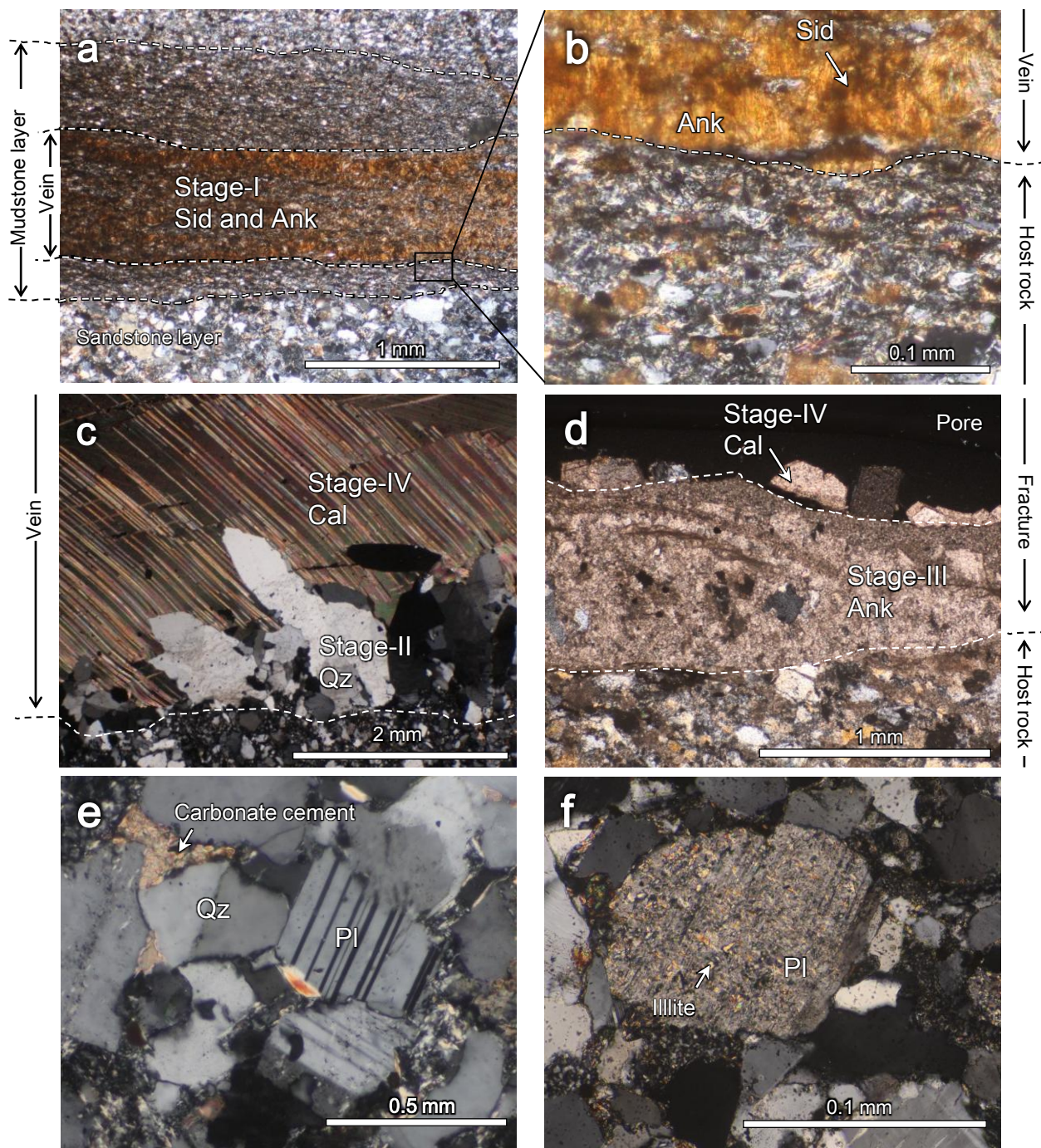


Figure 7

Figure 8

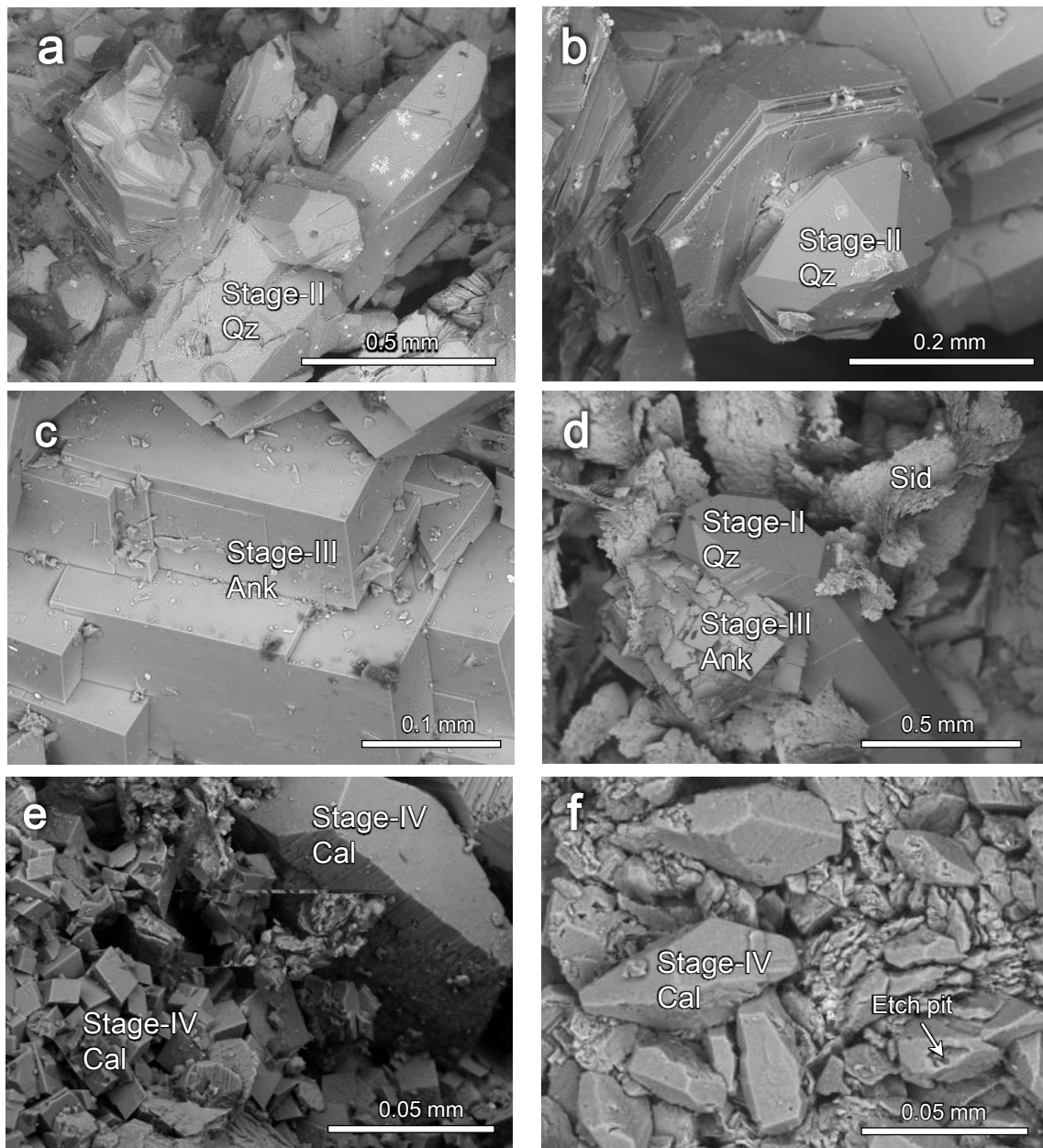


Figure 8

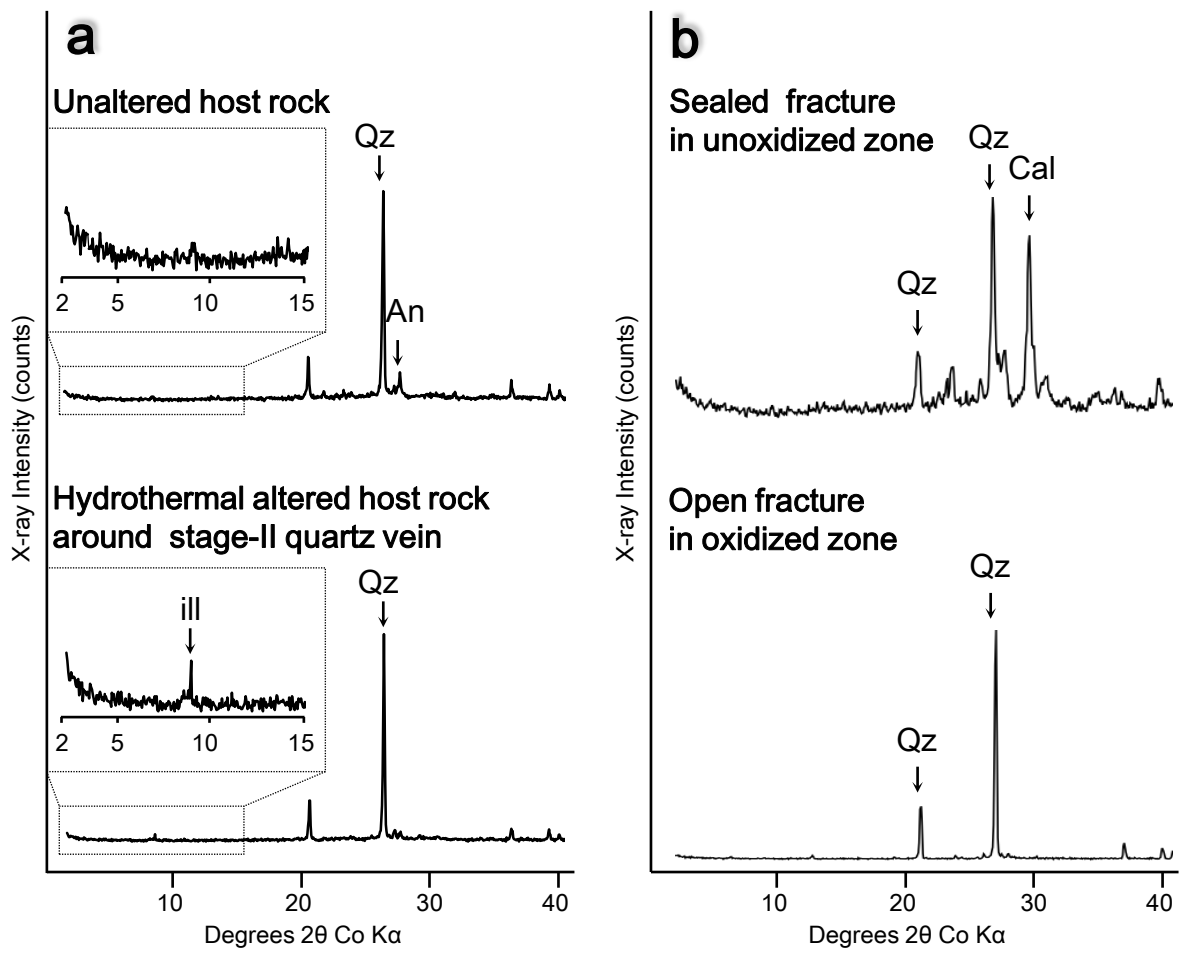


Figure 9



Figure 10

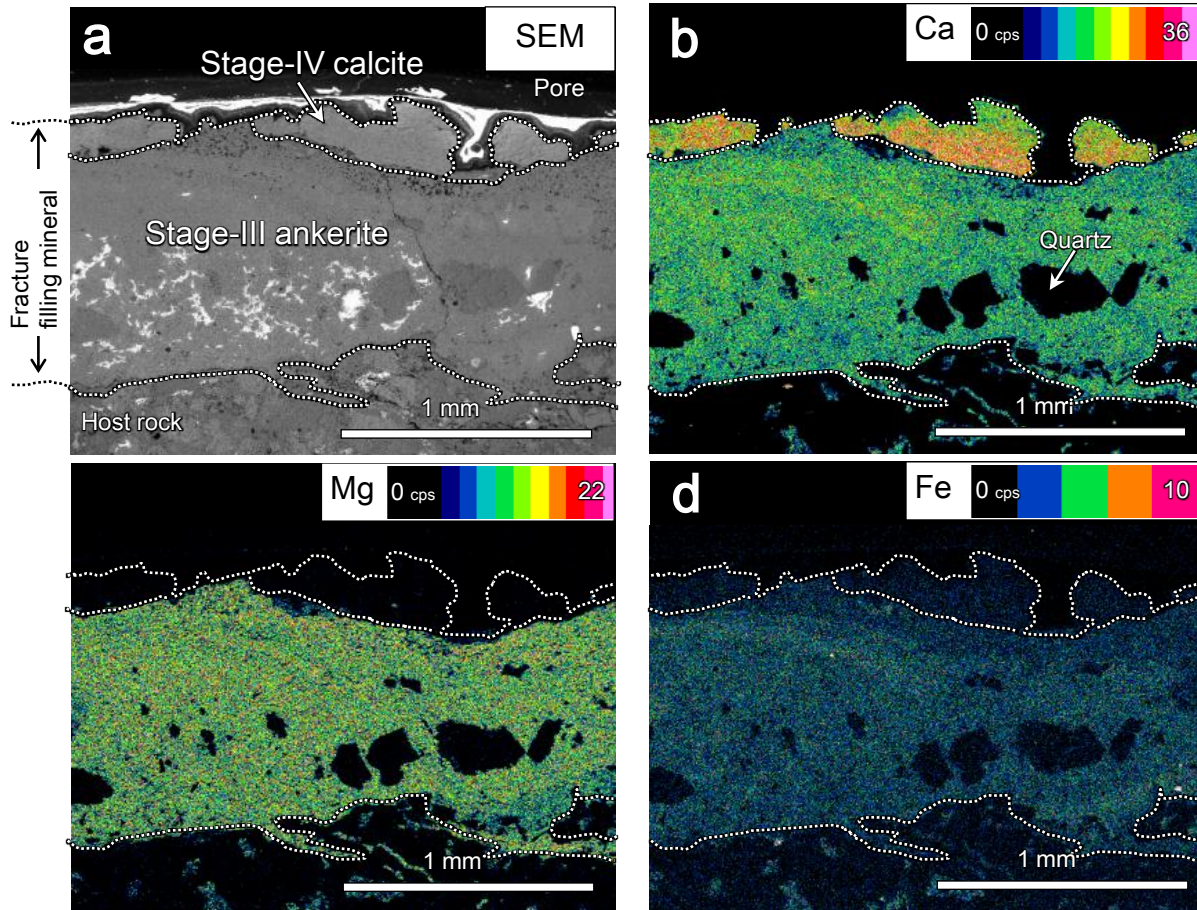


Figure 10



Figure 11

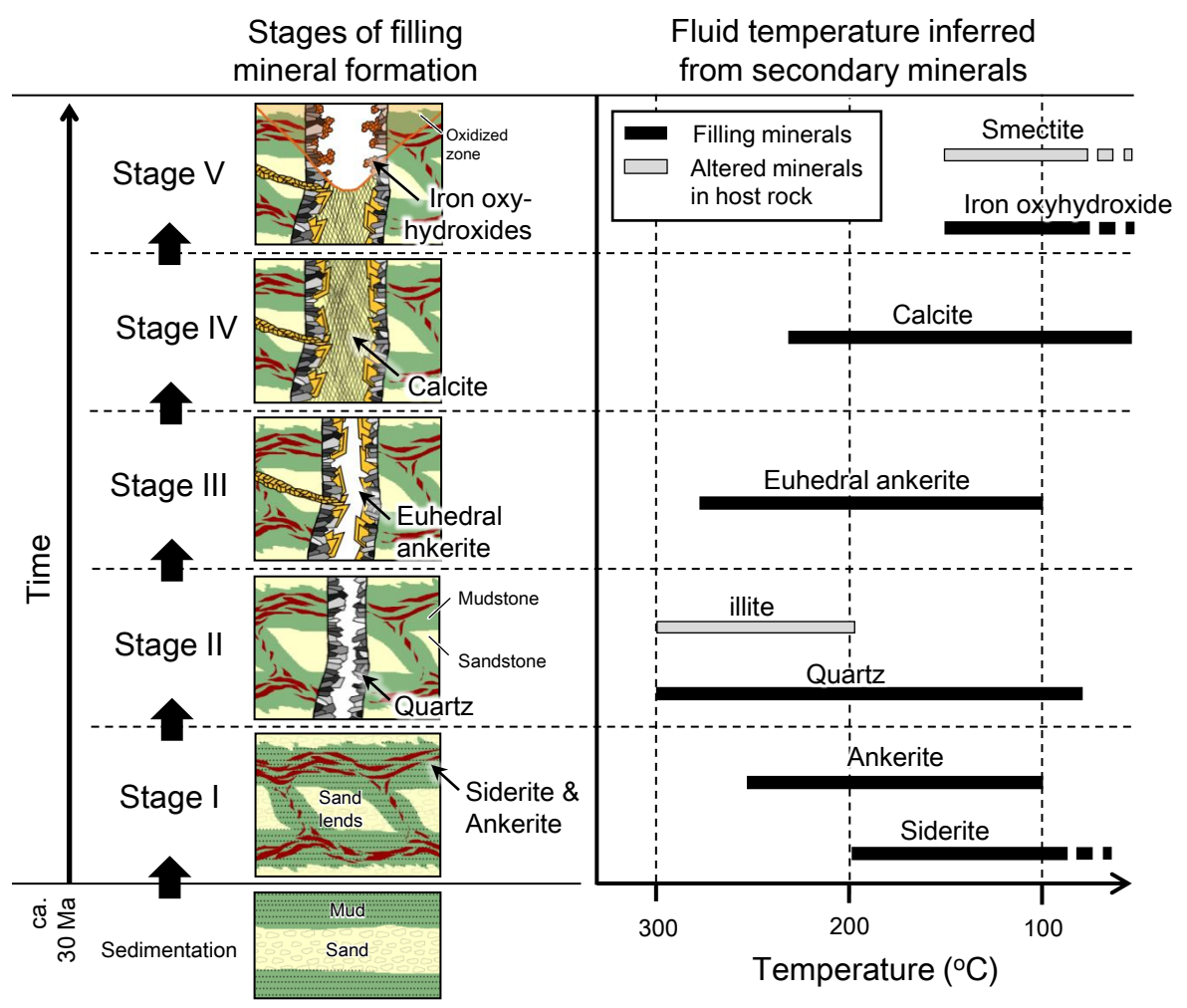
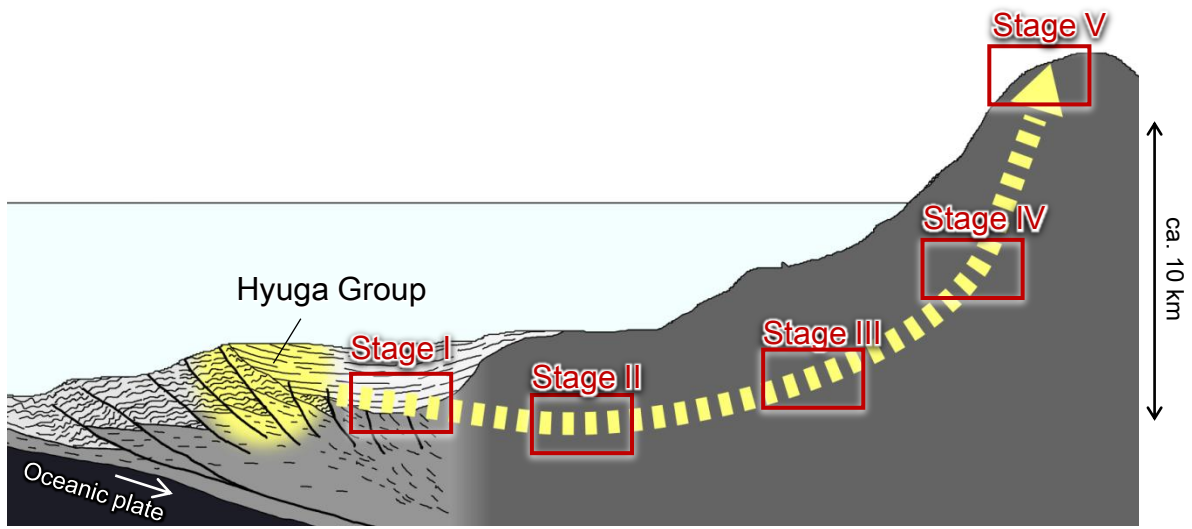


Figure 11



**Table 2**

| Depth<br>(m) | Litho<br>logy | Major Elements XRF (wt%) |                  |                                |                                  |       |      |      |                   |                  |                               | IL<br>(wt%) | Total<br>(wt%) |
|--------------|---------------|--------------------------|------------------|--------------------------------|----------------------------------|-------|------|------|-------------------|------------------|-------------------------------|-------------|----------------|
|              |               | SiO <sub>2</sub>         | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> * | MnO   | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> |             |                |
| 0.9          | Ss            | 76.20                    | 0.44             | 11.12                          | 2.91                             | 0.013 | 0.90 | 0.12 | 2.58              | 2.54             | 0.088                         | 1.61        | 98.51          |
| 8.5          | Ss            | 79.41                    | 0.43             | 10.11                          | 1.90                             | 0.003 | 0.66 | 0.13 | 2.22              | 2.44             | 0.048                         | 1.69        | 99.05          |
| 13.2         | Ss            | 78.10                    | 0.49             | 10.10                          | 2.33                             | 0.009 | 0.75 | 0.18 | 2.26              | 2.31             | 0.054                         | 2.23        | 98.81          |
| 22.3         | Ss            | 78.78                    | 0.55             | 10.67                          | 2.74                             | 0.035 | 0.93 | 0.28 | 2.47              | 2.43             | 0.103                         | 1.51        | 100.48         |
| 28.9         | Ss            | 77.79                    | 0.47             | 10.47                          | 1.97                             | 0.007 | 0.74 | 0.18 | 2.34              | 2.44             | 0.082                         | 2.48        | 98.97          |
| 31.8         | Ss            | 74.37                    | 0.53             | 9.96                           | 2.97                             | 0.052 | 1.05 | 2.53 | 2.38              | 2.12             | 0.114                         | 3.01        | 99.08          |
| 38.5         | Ms            | 62.30                    | 0.81             | 17.43                          | 5.72                             | 0.043 | 2.50 | 0.27 | 1.16              | 4.70             | 0.128                         | 4.45        | 99.51          |
| 43.7         | Ss            | 71.63                    | 0.53             | 12.47                          | 3.57                             | 0.029 | 1.30 | 0.98 | 2.56              | 2.88             | 0.113                         | 2.35        | 98.40          |
| 48.4         | Ms            | 61.92                    | 0.79             | 16.03                          | 5.91                             | 0.047 | 2.36 | 1.76 | 1.34              | 4.13             | 0.149                         | 4.72        | 99.15          |
| 51.4         | Ss            | 71.55                    | 0.31             | 8.03                           | 2.93                             | 0.090 | 0.81 | 4.00 | 2.09              | 1.75             | 0.079                         | 4.04        | 95.68          |
| 59.6         | Ss            | 70.98                    | 0.49             | 9.33                           | 3.48                             | 0.038 | 1.25 | 2.79 | 2.19              | 1.90             | 0.116                         | 3.50        | 96.06          |
| 62.8         | Ss            | 79.40                    | 0.45             | 9.46                           | 2.41                             | 0.027 | 0.79 | 0.36 | 2.29              | 2.37             | 0.088                         | 1.42        | 99.07          |
| 67.3         | Ss            | 75.55                    | 0.41             | 10.27                          | 2.86                             | 0.024 | 1.02 | 1.48 | 2.42              | 2.51             | 0.087                         | 2.48        | 99.10          |
| 72.8         | Ss            | 76.30                    | 0.45             | 9.42                           | 2.25                             | 0.025 | 0.75 | 1.32 | 2.21              | 2.54             | 0.085                         | 2.14        | 97.49          |
| 77.5         | Ss            | 76.48                    | 0.37             | 9.56                           | 2.41                             | 0.042 | 0.84 | 2.11 | 2.38              | 2.45             | 0.103                         | 2.65        | 99.38          |
| 84.5         | Ss            | 73.44                    | 0.46             | 10.47                          | 2.86                             | 0.032 | 0.92 | 1.71 | 2.31              | 2.71             | 0.097                         | 2.51        | 97.51          |
| 88.5         | Ss            | 75.44                    | 0.41             | 9.10                           | 2.55                             | 0.035 | 0.78 | 1.90 | 2.06              | 2.41             | 0.083                         | 2.43        | 97.18          |
| 94.9         | Ss            | 75.93                    | 0.37             | 9.70                           | 2.74                             | 0.038 | 0.95 | 1.95 | 2.33              | 2.40             | 0.086                         | 2.60        | 99.08          |
| 102.9        | Ss            | 74.02                    | 0.42             | 11.24                          | 2.41                             | 0.026 | 0.66 | 0.63 | 2.14              | 3.08             | 0.093                         | 2.98        | 97.69          |
| 110.2        | Ss            | 77.84                    | 0.32             | 9.34                           | 2.34                             | 0.032 | 0.82 | 1.05 | 2.48              | 2.12             | 0.087                         | 2.96        | 99.38          |
| 115.8        | Ss            | 79.18                    | 0.41             | 9.23                           | 1.92                             | 0.018 | 0.54 | 0.71 | 2.42              | 2.34             | 0.092                         | 2.41        | 99.25          |

Ss: Sandstone Ms: Mudstone \*) Total iron as Fe<sub>2</sub>O<sub>3</sub>