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1 **Dawsonite and ankerite formation in the LDX-1 structure, Yinggehai**
2 **basin, South China Sea: An analogy for carbon mineralization in**
3 **subsurface sandstone aquifers**

4
5 Lei Yu^{a, b}, Keqiang Wu^c, Li Liu^{a, *}, Na Liu^a, Xiaoran Ming^d, Eric H. Oelkers^{b, e, *}

6
7 *a. College of Earth Sciences, Jilin University, 130061 Changchun, PR China*

8 *b. Department of Earth Sciences, University College London, Gower Street, WC1E 6BT London, United Kingdom*

9 *c. China National Offshore Oil Corporation (CNOOC) Research Institute, 100028 Beijing, China*

10 *d. The First Monitoring and Application Center, China Earthquake Administration, Tianjin, 300180, China*

11 *e. GET-Université de Toulouse-CNRS-IRD-OMP, 14 Avenue Edouard Belin, 31400 Toulouse, France*

12
13 ***Abstract***

14 The geochemistry and petrology of the LDX-1 structure of the Yinggehai basin, a
15 natural analog of a sedimentary carbon storage site, was investigated to understand the
16 consequences of the charging of CO₂ gas in this system. The rocks in this structure are
17 dominated by subarkose and sublitharenite sandstones. The authigenic minerals formed
18 after CO₂ injection are dawsonite, microcrystalline quartz, kaolinite and ankerite.
19 Dawsonite and ankerite are formed just beneath a CO₂ bearing anticlinal structure due
20 to the reactions between silicate minerals (feldspars and clay minerals) and the fluid
21 phase. Carbon and oxygen isotopic analyses indicate that the main carbon source for
22 dawsonite and ankerite formation was mantle magmatic CO₂. The aqueous activities of
23 sodium and calcium, the partial pressure of CO₂, pH and temperature are the key factors
24 influencing the stability of the dawsonite and ankerite. The presence of the anticlinal
25 structure maintaining a locally high CO₂ partial pressure in the waters beneath this
26 structure is likely responsible for the observed long-term persistence of dawsonite and
27 ankerite in this system.

29 *Keywords: authigenic carbonate minerals, carbon and oxygen isotopes, dawsonite*
30 *stability, carbon capture and storage (CCS), Yinggehai Basin*

31

32 ***1 Introduction***

33 Carbon-dioxide emissions to the atmosphere by anthropogenic industrial
34 activities are a key factor causing global climate change (IPCC, 2005, 2007; Manabe
35 and Stouffer, 1993). The injection of anthropogenic CO₂ into deep geologic
36 formations has been advocated to slow increasing atmospheric CO₂ concentrations
37 and its effect on global climate (Bachu et al., 1994; Bachu, 2003; IPCC, 2005, 2007;
38 Oelkers and Cole, 2008). There are four mechanisms of carbon storage in the
39 subsurface: structural and stratigraphic trapping, residual CO₂ trapping, solubility
40 trapping and mineral trapping (IPCC, 2005; Johnson et al., 2001). Of these, mineral
41 trapping, and in particular in-situ carbon mineralization, is the most stable and safe
42 carbon storage solution (Lackner et al 1995; Johnson et al., 2001; Matter et al., 2016;
43 Oelkers et al., 2008; Power et al. 2013).

44 Sandstone aquifers with impermeable cap-rocks are commonly considered for
45 carbon storage as they have adequate permeability and pore space, and are
46 abundant in the subsurface (Benson and Cole, 2008; IPCC, 2005; Xu et al., 2005). A
47 number of studies have shown that calcite, siderite, magnesite, dolomite, ankerite and
48 dawsonite could form in various sandstones in response to CO₂ injection. (Baker et al.,
49 1995; Fischer et al., 2010; Gao et al., 2009; Gaus et al., 2005; Hellevang et al., 2013;
50 Higgs et al., 2013, 2015; Hitchon, 1996; Klajmon et al., 2017; Liu et al., 2011; Moore
51 et al., 2005; Pauwels et al., 2007; Pearce et al., 2016; Pham et al., 2011; Uysal et al.,
52 2011; Van Pham et al., 2012; Worden, 2006; Xu et al., 2004, 2005, 2007, 2010; Yu et
53 al., 2015; Zhao et al., 2018; Zhou et al., 2014). Of these minerals, dawsonite
54 (NaAl(OH)₂CO₃) is particularly attractive as a carbon storage host as it contains
55 sodium and aluminum, which can be abundant in sedimentary silicates. This mineral,
56 however, is more reactive and less stable than many of the aforementioned divalent

57 metal carbonate minerals (Bénézech et al., 2007; Hellevang et al., 2005, 2011).

58 The LDX-1 structure in the Yinggehai basin of South China Sea provides an
59 insightful analogy for the study of mineral carbonation in sandstone aquifers (Fig. 1).
60 The gas phase in the LDX-1 structure contains as much as 93 volume percent CO₂
61 and this CO₂ has a distinct inorganic carbon isotopic signature (He et al., 2005; Huang
62 et al., 2003). In addition, past studies concluded that the CO₂ gas injection into this
63 structure occurred after that of the hydrocarbon gases (Huang et al., 2004; Sun and
64 Wang, 2000), which is similar to scenarios that might be encountered by injecting into
65 former oil field reservoirs.

66 The purpose of this study is to characterize the mineralogy and paragenesis in two
67 wells drilled into the LDX structure to investigate sandstone diagenesis and carbonate
68 mineral formation in response to the influx of CO₂. Results will be used to gain further
69 insight into the potential for mineral carbonation in sedimentary sandstones as part of
70 subsurface carbon storage efforts.

71

72 **2 Geological setting**

73 The Yinggehai basin, which developed during the Cenozoic, is a natural gas-rich
74 rift basin. It is located between the Indian and South China plate, formed by the
75 combination of lithosphere extension and the deep, strike-slip Red River fault. The
76 direction of this basin is Northwest-Southeast, with a total area of approximately
77 $11 \times 10^4 \text{ km}^2$ (Huang et al., 2009; Wan et al., 2007; Fig. 1a, b). Two northwest-trending,
78 deep-to-basement faults divide the Yinggehai basin into three sub-structural units: The
79 Central Depression, the Ying Dong Slope and the Ying Xi Slope (see Fig 1). The central
80 depression consists of two tectonic units: the Lin Gao uplift and the diapir structure belt
81 (Fig 1b; Zhu et al., 2004). During the Miocene, the Yinggehai basin was filled with
82 argillaceous sediments along the fault and formed a series of diapir structures in the
83 central depression zone (Huang et al., 2009). He et al. (2005) reported that most of the
84 natural gas reservoirs with high CO₂ contents are concentrated in these diapir

85 structures.

86 The basement of the Yinggehai basin is dominated by palaeozoic magmatic rocks
87 (Hao et al., 1998). According to the drilling strata, the Cenozoic sediments include the
88 Eocene Lingtou Formation, the Oligocene Yacheng and Lingshui Formations, the
89 Miocene Sanya, Meishan, and Huangliu Formations, the Pliocene Yinggehai Formation
90 and the Quaternary Ledong Formation. The thickness of the Cenozoic sediments in this
91 basin is up to 16-17 km (Gong et al., 1997; Huang et al., 2004, 2009; Meng et al., 2012;
92 Zhu et al., 2007) (Fig. 2). The Lingtou Formation mainly consists of sandstone and
93 mudstone. The Yacheng and Lingshui Formations are composed of mudstone and silty
94 mudstone interbedded with mudstone. Both the Sanya and Meishan Formations are
95 dominated by calcareous mudstone. The Huangliu, Yinggehai and Ledong Formations
96 are mainly siltstone, sandstone and interbedded mudstone. The Miocene mudstone is
97 the main source rock of natural gas in this basin, while the interbedded mudstone and
98 sandstone of the overlying Huangliu and Yinggehai Formations provide a good
99 reservoir and cap rock system for the basin (Wang and Huang, 2008). According to the
100 logging data, the Yinggehai and Huangliu formations contain the main CO₂ gas
101 reservoirs in the basin.

102 The LDX-1 Structure is a dome structure located in the southeast of the Ledong
103 area in the central depression of the Yinggehai Basin (Fig. 1b). The gas reservoir in the
104 LDX-1 structure is an anticline formed by a mud diapir. The rocks containing the
105 CO₂-rich gas reservoirs consist mainly of the marine sandstones of the Pliocene
106 Yangehai Formation (Fig. 2) and are located at a depth of 392 m to 2300 m (Huang et al.,
107 2004; Li et al., 2005). According to gas measurements, the LDX-1 reservoirs are
108 dominated by hydrocarbon gas and CO₂; the CO₂ content ranges from 41.9% to 78.7%
109 (Huang et al., 2004).

110 There were two major episodes of gas emplacement into the Yinggehai basin, the
111 first from an organic source and dominated by CH₄ and the second from an inorganic
112 sourced and dominated by CO₂. According to the Xie et al., (2014), the arrival of the

113 CH₄ dominated gas was at approximately 3.7 Ma. The CO₂ dominated gas arrived
114 later. Estimates of its arrival time range from 0.3 to 1.9 Ma (Fu et al., 2016; Huang et
115 al., 2005; Wang et al., 2004; Xie et al., 2014). As such this basin provides a close
116 natural analogue to the filling of a former hydrocarbon reservoir with CO₂ as part of
117 subsurface carbon storage efforts.

118

119 ***3 Sampling and research methods***

120 A total 159 sandstone samples were collected from the gas reservoir layers of the
121 LDX-1 structure of the Yinggehai Formation. The samples were collected from the
122 depths of 1841.62 to 1869.02 m (from well LDX-1-1) and of 1958.07 to 1905.13 m
123 (from well LDX-1-4). The compositions of the sandstone samples were determined by
124 counting 300 points in each thin section following the approach of Dickson (1965)
125 using an OLYMPUS BX51 polarizing microscope. To identify the carbonate minerals,
126 all the thin sections were stained with Alizarin Red S and K-ferricyanide solutions
127 following the procedure of Dickson (1965). Authigenic mineral observations and
128 energy spectrum analyses were performed at the Research Center of Paleontology and
129 Stratigraphy of Jilin University, using a JEOL JSM-6700F scanning electron
130 microscope (SEM), equipped with energy dispersive X-ray spectrometer (EDS)
131 analyzer manufactured by Oxford, UK; mineral surfaces were gold coated prior to this
132 analysis.

133 Based on a systematic petrographic study of the sandstone in the gas reservoirs, 10
134 dawsonite-bearing samples were selected for carbon and oxygen isotope analyses using
135 MAT253 isotopic ratio mass spectrometers at the Analytical Laboratory of The China
136 National Nuclear Corporation (CNNC) Beijing Research Institute of Uranium Geology.
137 The analytical method for obtaining stable isotopic compositions is based on past
138 studies such as Liu et al. (2011). Samples were grounded into a powder using an agate
139 mortar and pestle. The ground powers were sieved and the > 74 μm fraction was
140 collected, then dried for 2 h at 105 °C under atmospheric pressure, to remove potential

141 surface volatile phases, before analyzing. For carbon and oxygen isotope analyses, 99%
142 phosphoric acid (produced by Merck KGaA, Darmstadt, Germany) was reacted with
143 crushed whole rock powders at 25 °C or 50 °C (McCrea, 1950). For dawsonite analysis,
144 CO₂ released from samples during the first 4 h reactions at 25 °C was discarded, as this
145 gas likely originated from the decomposition of calcite. After that, the reaction was
146 continued for another 24h and the CO₂ was collected for the analysis of dawsonite
147 isotopic compositions (Becker, 1971; Rosenbaum and Sheppard, 1986; Sharma and
148 Clayton, 1965). For ankerite analysis, the CO₂ released during the first 24 h reaction at
149 25 °C was discarded, as it likely originated from calcite and dawsonite decomposition,
150 then the reaction temperature was raised to 50 °C followed by the collection of the CO₂
151 produced by the decomposition reaction during subsequent 48 h (Uysal et al., 2011).
152 The precision of the analyses is ±0.1‰ for δ¹³C and ±0.2‰ for δ¹⁸O. All reported
153 isotope values in this study are relative to the Belemnite americana from the Peedee
154 Formation (PDB) standard for carbon and Standard Mean Ocean Water (SMOW) for
155 oxygen.

156 All the speciation and solubility calculations were conducted using PHREEQC v.
157 3 (Parkhurst and Appelo, 2013) with its Lawrence Livermore National Laboratory
158 (LLNL) thermodynamic database after adding to it the stability constant for ankerite.
159 The stability of ankerite in this study is based on the formula (Ca(Fe_{0.5}Mg_{0.5})(CO₃)₂)
160 (see below). Its thermodynamic properties were estimated from the
161 stoichiometrically weighted sum of the calcite, siderite and magnesite stability
162 constants (Xu et al., 2004). The thermodynamic properties required for this estimate
163 were calculated using the SUPCRTBL database (Zimmer et al., 2016). The resulting
164 ankerite equilibrium constant and enthalpy of reaction are 0.642 and -69.326 kJ/mol at
165 70 °C and -0.087 and -77.803 kJ/mol 100 °C. Thermodynamic properties in the LLNL
166 database are consistent with those of dawsonite reported by Bénézech et al. (2007).
167 The Truesdell-Jones equation was used to calculate aqueous activity coefficients and
168 the fugacity for CO₂ gas was calculated using the ThermoSolver 1.0 software (Barnes,

169 2006).

170

171 **4 Results**

172 *4.1 Petrographic characteristics*

173 The dawsonite in the LDX-1 structure is hosted in fine-grained subarkose and
174 lithic quartz sandstones. The observed detrital minerals are mainly quartz (16.7% to
175 64.7%), feldspar (up to 12.0%) and rock fragments (up to 23.0%). The modal
176 compositions of the detrital minerals are shown schematically in Fig 3. The feldspar is
177 mainly comprised of plagioclase and also contains small amounts of orthoclase and
178 perthite. The rock fragments mainly consist of metamorphic debris (up to 19%), granite
179 debris (up to 8%), and sedimentary debris (up to 7%).

180

181 *4.2 Authigenic mineralogy and paragenesis*

182 The authigenic minerals observed in the rock samples are dawsonite, quartz,
183 siderite, dolomite, ankerite, mixed-layer clays consisting of illite and smectite, and
184 kaolinite.

185

186 *4.2.1 Dawsonite*

187 Dawsonite is principally found at depths of 1841.27 to 1867.23 m in well
188 LDX-1-1 and 1863 to 2018 m in well LDX-1-4 with its content ranging from 0.2 to 6
189 Vol% as determined by point counting (see above). Dawsonite aggregates nucleate as
190 microcrystalline grains then grow radially outward into the sandstone pores.
191 Dawsonite growth usually terminates at the edge of the detrital minerals (eg. quartz
192 and feldspar). Dawsonite could also be observed growing on dolomite (Fig. 4a, b),
193 potassium feldspar and plagioclase (Fig 4c, d). The EDS results show that the
194 dawsonite mainly consists of carbon, oxygen, sodium and aluminum having weight
195 percents of 7.25 to 22.23, 50.43 to 66.93, 3.58 to 14.69, and 7.27 to 30.26 respectively
196 (see Table 1).

197

198 *4.2.2 Authigenic quartz*

199 Two kinds of authigenic quartz were observed: quartz overgrowths and
200 microcrystalline quartz. The content of authigenic quartz is low, generally less than
201 0.5%. Quartz overgrowths are the among the earliest authigenic silicate minerals
202 observed and are evident due to clay rims between detrital quartz and these
203 overgrowths. The thickness of the quartz overgrowths ranges from 0.01 to 0.06 mm.
204 Furthermore, we observed some radial dawsonite surrounded by quartz overgrowths
205 (see [Fig. 4e](#)), suggesting some of the quartz precipitated concurrently with or after the
206 dawsonite. In addition, SEM images show that the microcrystalline quartz was
207 distributed in sandstone pores sporadically and is associated with kaolinite. This
208 kaolinite is also associated with dawsonite in some places ([Fig. 4f](#)). Such observations
209 further suggest that the microcrystalline quartz formed during same time period as the
210 dawsonite.

211

212 *4.2.3 Siderite*

213 Most siderite was distributed in pores as subhedral intergranular crystals or
214 aggregates along the boundaries of the detrital grains ([Fig. 4g](#)). The content of the
215 siderite ranges from 0.5% to 13.5% in the bulk rock and the crystal sizes range from
216 0.01 mm to 0.03 mm. The color of the siderite is yellow brown to dark brown under
217 single polarized light. The siderite crystals were distributed either in the inner side of
218 quartz overgrowth or near the clay rims surrounding the original quartz grain
219 boundaries, indicating that siderite formation was earlier than or concurrent with the
220 quartz overgrowths.

221

222 *4.2.4 Dolomite*

223 The dolomite content (0.5 to 43 Vol%) varied substantially in the studied cores. As
224 dolomite is not stained by Alizarin Red S and K-ferricyanide solutions, it is readily

225 distinguished from other carbonates. Under the polarizing microscope, some dolomite
226 was observed being replaced by dawsonite aggregates (Fig. 4h). SEM analysis revealed
227 that the ends of some needle-like dawsonite crystals terminate at the faces of dolomite
228 crystals exhibiting a “bridged phenomenon” (Figure 4a, b). Both sets of observations
229 imply that the dolomite formed earlier than the dawsonite, yet the presence of some
230 detrital dolomite cannot be discounted.

231

232 4.2.5 Ankerite

233 Ankerite (0.5 to 36 Vol%) mainly surrounds dolomite crystals as rim-like growths
234 (Fig. 4i) or as euhedral to subhedral intergranular crystals (Fig. 4j, k). Under the Back
235 Scattered Electron (BSE) mode, the ankerite is seen to form of nearly equal ring-like
236 shapes along the dolomite surfaces as it replaced this mineral. Some ankerite is seen to
237 have grown on dawsonite (Fig 4j, k). Such observations suggest that ankerite formation
238 occurred later than both the dolomite and dawsonite. EDS analyses results for ankerite
239 showed that its Ca, Mg, and Fe content ranged from 0.39 to 9.22, 2.4 to 6.52, and 1.47
240 to 7.82 atomic percent respectively (see Table 2), consistent with the formula
241 $\text{Ca}(\text{Fe}_{0.5}\text{Mg}_{0.5})(\text{CO}_3)_2$.

242

243 4.2.6 Clay minerals

244 The XRD results indicate that the clay minerals in the CO₂-containing reservoirs
245 of the Yinggehai Basin mainly consist of mixed-layer illite and smectite, and kaolinite
246 (Huang et al., 2004; Jiang et al., 2015; Tong et al., 2012). The mixed layer illite and
247 smectite commonly surround the detrital minerals as “clay rims”, which could be
248 identified by polarizing microscope. Mixed layer illite and smectite are not found in the
249 sandstone pores, suggesting that it is the earliest formed secondary mineral in the
250 diagenetic sequence. Honeycomb-like authigenic clay is seen to grow on K-feldspar
251 (see Fig. 4l, m). According the EDS results shown in Table 3, most of the smectite and
252 mixed layer illite are Ca depleted. This suggests that the Ca in the smectite and mixed

253 layer of illite and smectite may have been removed over time through water-mineral
254 reactions.

255 Authigenic kaolinite grows as vermicular assemblages in the sandstone pores.
256 Hexagonal kaolinite crystals are found attached to dawsonite crystals (Fig. 4n), at times
257 adjacent to small "etch pits" on the dawsonite surface (Fig. 4o), suggesting that some
258 kaolinite post-dates the dawsonite. However, vermicular kaolinite is commonly
259 interspersed between acicular dawsonite crystals, suggesting that this kaolinite formed
260 slightly earlier than or concurrently with dawsonite (Fig. 4p). In some places ankerite
261 grew on the top of kaolinite aggregates (Fig. 4q). This suggests that the formation of
262 kaolinite might have spanned from the period from when dawsonite grew through that
263 of ankerite formation.

264 Chlorite was not observed in the samples considered in this study. Its presence in
265 the rocks of the LDX system was reported by Fu et al. (2016). Moreover, the presence
266 of chlorite within and below the CO₂ gas reservoirs is inferred as a potential source of
267 the iron leading to ankerite precipitation (see below).

268

269 *4.3 Vertical characteristics of authigenic carbonates in the reservoirs*

270 The dawsonite and ankerite contents across the study area, measured on 159 thin
271 sections, are shown in Fig. 5. Over the depths of this study (from 1841.6 m to 1868.89
272 m), dawsonite (0.7 to 8.3%) and ankerite (1.7 to 26.0%) in the LDX-1-1 well mainly
273 developed near the gas water contact (GWC) (Fig. 5a). Owing to lack of samples, few
274 observations of these minerals were made above the GWC in this well. In well
275 LDX-1-4, the limited measurements of mineral content in the gas reservoirs show the
276 dawsonite and ankerite content ranging from 0.7 to 2.3% and 2.0 to 14.0% above the
277 GWC, whereas the corresponding content results for dawsonite and ankerite under the
278 GWC in this well are 1.0 to 6.3% and 1.0 to 24.0 % (Fig. 5b).

279

280 *4.4 C and O isotope compositions*

281 The stable isotopic compositions of dawsonite and ankerite are shown in [Table 4](#)
282 and [Fig. 6](#). The carbon isotope ($\delta^{13}\text{C}$) values for dawsonite vary from -4.3‰ to -0.6‰
283 with an average value of -2.0‰. The oxygen isotope ($\delta^{18}\text{O}$) values for dawsonite range
284 from +22.4‰ to +24.0‰. The $\delta^{13}\text{C}$ values for ankerite range from -2.6‰ to -0.8‰ with
285 an average value of -1.4‰ and the $\delta^{18}\text{O}$ values range from +22.8‰ to +23.7‰.

286 The measured $\delta^{13}\text{C}$ values of dawsonite and ankerite have been used to estimate
287 the corresponding equilibrium $\delta^{13}\text{C}$ of the CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$) from which they precipitated.
288 The $\delta^{13}\text{C}_{\text{CO}_2}$ for the CO_2 that formed the dawsonite, was estimated assuming dawsonite
289 exhibits an identical CO_2 carbon isotope fractionation as that of calcite, using the
290 equation proposed by [Ohmoto and Rye \(1972\)](#) ([Baker et al., 1995](#)). The calculated $\delta^{13}\text{C}$
291 for the CO_2 in equilibrium with ankerite was estimated assuming its fractionation was
292 identical to the dolomite- CO_2 fractionation equation proposed by [Horita \(2014\)](#). The
293 $\delta^{13}\text{C}$ of the CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$) calculated to be in isotopic equilibrium with dawsonite range
294 from -9.66‰ to -6.69‰ with an average value of -7.90‰. The equilibrated $\delta^{13}\text{C}_{\text{CO}_2}$ for
295 ankerite varies from -7.27‰ to -5.94‰ with a mean value of -6.4‰.

296 The formation temperature for dawsonite and ankerite were calculated from their
297 oxygen isotope compositions. This was done by assuming oxygen fractionation
298 between dawsonite and H_2O is identical to the calcite- H_2O fractionation equation
299 proposed by [O'Neil et al. \(1969\)](#) and that oxygen fractionation between ankerite and
300 H_2O is identical to the dolomite- H_2O fractionation equation of [Horita \(2014\)](#). The ^{18}O
301 value for water used in these calculations was $\delta^{18}\text{O}_{\text{H}_2\text{O}} = +2.7\text{‰}$ ([Deng and Chen, 1994](#)),
302 which was measured in the formation waters of the DFY-1 structure in the
303 Yinggehai-Huangliu Formation of the Yinggehai basin ([Fig. 1](#)). The calculated
304 temperature for dawsonite formation varies from 67.8 °C to 79.6 °C and the calculated
305 temperature of ankerite formation ranges from 89.6 °C to 96.4 °C (see [Table 4](#)). These
306 temperatures are consistent with 1) the earlier formation of dawsonite and 2) the
307 increasing temperature of the study site over time as the basin subsided. Note that the
308 current temperature of the study site is 92 to 103 °C.

309

310 **5 Discussion**

311 *5.1 The origin of the carbon in the dawsonite and ankerite*

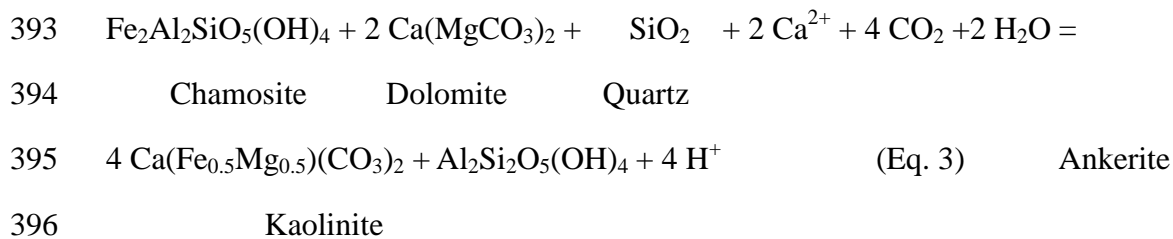
312 The $\delta^{13}\text{C}_{\text{CO}_2}$ of the gas forming dawsonite and ankerite reported above and in
313 Table 4 are similar to the current $\delta^{13}\text{C}$ values in the CO_2 -rich reservoirs of the LDX
314 system; the current $\delta^{13}\text{C}_{\text{CO}_2}$, are reported to range from -8.2‰ to -4.2‰ (He et al.,
315 2005). Moreover, the hydrogen and oxygen isotopic compositions of the formation
316 water in the Yinggehai Basin reservoirs are significantly different from that of
317 meteoric water, which implies the lack of exchange between meteoric water and that
318 present in the LDX system (Deng and Chen, 1994). Such evidence suggests that the
319 CO_2 in the gas reservoir is likely a major carbon source for the both dawsonite and
320 ankerite formation.

321 Carbon dioxide in the LDX gas reservoirs at the present time is likely dominated
322 by magmatic derived CO_2 . Firstly, the $\delta^{13}\text{C}_{\text{CO}_2}$ value in the gas reservoir ranges from
323 -8.2‰ to -4.2‰, which is significantly different from that obtained from kerogen
324 degradation; $\delta^{13}\text{C}_{\text{CO}_2}$ from kerogen degradation ranges from -25‰ to -20‰ (Irwin et
325 al., 1977; Tissot and Welte, 1984) and CO_2 from bacterial fermentation typically has a
326 $\delta^{13}\text{C}_{\text{CO}_2} \sim +15\%$ (Irwin et al., 1977). Secondly, the carbon isotope values of CO_2 in
327 the LDX system exhibits a $\delta^{13}\text{C}_{\text{CO}_2}$ range similar to the -8‰ to -3‰ range observed
328 for CO_2 sourced from mantle-derived magma (Baker et al., 1995; Clayton et al., 1990;
329 Dai, 1996; Ohmoto and Rye, 1972; Rollinson, 2014;). Taking account of the
330 observations summarized above, we suggest that origin of the CO_2 in the LDX-1
331 structures is mantle-derived magma degassing.

332 The timing of dawsonite and ankerite formation can be constrained by the timing
333 of the basaltic magmatism related CO_2 charging of the LDX system. The Yinggehai
334 Formation, where the dawsonite and ankerite developed, was formed between 5.5 Ma
335 and 1.9Ma (Fig. 2). The Honghe fault zone, which controls the formation and
336 distribution direction of Yinggehai basin is still active (Zhu et al., 2009) (Fig. 1). The

365 which may be limited in this system. Note that according to mass conservation, for
366 every 1 cm³ of dawsonite formed from albite by reaction 1, there should be 1.16 cm³ of
367 SiO₂ precipitation (Zhou et al., 2014). However, far less microcrystalline quartz is
368 observed in our system than dawsonite (Fig. 4b), which suggests that some of the SiO₂
369 may have been consumed by other water-mineral reactions.

370 Geochemical calculations results suggest that chlorite dissolution provoked by
371 the charging of the system by CO₂ could provide Fe²⁺ for ankerite formation (Xu et al.,
372 2005, 2007, 2014; Yu et al., 2014). The dissolution of smectite also could provide
373 some of the iron for ankerite growth (Hellevang et al., 2013; Pham et al., 2011;
374 Worden and Morad, 2003; Worden, 2006), as well as some aluminum promoting
375 dawsonite formation. The dissolution of chlorite and smectite coupled to ankerite
376 formation has been observed in the sandstone reservoirs of the Otway basin of
377 Australia,, in the Songliao Basin of China, the Jurassic and late Cretaceous reservoirs
378 of North Sea oil fields, and in the Eocene strata from Wilcox of Texas, (Awwiller,
379 1993; Hendry et al., 2000; Liu et al., 2011; Thyberg et al., 2010; Watson et al., 2004).
380 The chlorite content of the Yinggehai Basin CO₂ bearing reservoirs has been reported
381 to be significantly lower than that in CO₂-free reservoirs (Tong et al., 2012). Similar
382 observations have been reported in wells of the Yinggehei Basin (Huang et al., 2004;
383 Jiang et al., 2015). Such observations suggest that the dissolution of iron bearing clay
384 minerals such as chlorite is the main Fe²⁺ source for ankerite. The Mg²⁺ and some
385 Ca²⁺ in the ankerite crystals could come from dolomite dissolution, as fresh ankerite is
386 observed growing within a dolomite matrix (Fig. 4i). Additional Ca²⁺ can be sourced
387 from the transformation of clays in the system; a number of studies have reported Ca
388 release as smectite transforms to mixed layered clays and illite (e.g. Boles and Frank,
389 1979; McHargue and Price, 1982). A close relation between ankerite and smectite is
390 evident in the studied core samples (see Fig. 7). Taking account of these observations,
391 a representative reaction coupling chlorite dissolution to ankerite precipitation could
392 be expressed as (modified from Kirste et al., 2004; see also Luquot et al., 2012):



397 Note this reaction, balanced on Fe and Mg, requires substantial magmatic CO₂ for
398 ankerite formation, consistent with its carbon isotope composition. This reaction also
399 consumes SiO₂, which may account, at least in part, for the low mass of authigeic
400 quartz in the present day system.

401

402 *5.3 CO₂ partial pressure and carbonate mineral stability*

403 It is likely that both ankerite and dawsonite are formed after the arrival of mantle
404 sourced CO₂, providing a clear analogy for modern carbon capture and storage
405 systems. The observations described in this study indicate that dawsonite is first
406 formed at ~70 °C, followed by ankerite at ~ 90 °C, in response to the arrival of CO₂
407 into the overlying reservoirs. The increase in temperature in the system likely stems
408 from its increased burial depth over time. Ankerite is also reported to be the last
409 forming mineral in the sandstone reservoirs in Songliao (Liu et al., 2011; Yu et al.,
410 2015) and Hailaer basins (Gao et al., 2009). Some kaolinite is seen to precipitate
411 coupled to the dissolution of dawsonite; some dissolution etch pits on dawsonite
412 crystal were evident near the kaolinite (Fig. 4m). Kaolinite precipitation continues as
413 ankerite precipitates, consistent with Eq. (3). The formation of ankerite also appears
414 to be linked to dolomite dissolution.

415 All of these observations are consistent with the phase diagrams shown in Figs. 8
416 to 10. In Fig. 8, the relative stability of dawsonite in the Na₂O-Al₂O₃-SiO₂-CO₂-H₂O
417 system balanced on aluminum and saturated with quartz is shown. Dawsonite and
418 quartz become stable relative to albite at log (*f*_{CO₂}) > 0.15 and 0.9 at 70 and 100 °C,
419 respectively. This diagram thus suggests that albite would be favored to transform to
420 dawsonite as CO₂ fills the reservoirs in accord with reaction 1. As suggested by Fig. 9,

421 some of the precipitated dawsonite and quartz will tend to react to form kaolinite due
422 to an increase in temperature, which tends to shrink the dawsonite stability field. The
423 value of $\log(f_{\text{CO}_2})$ in equilibrium with the assemblage albite = dawsonite + quartz at
424 70 and 100 °C plot as vertical lines on the Fig. 10, which also shows the relative
425 stability field of ankerite + kaolinite relative to that of chlorite, dolomite and quartz
426 consistent with reaction 3. It can be seen that for all $a_{\text{Ca}^{2+}}/a_{\text{H}^+}^2 > \sim 9.7$ at 70 °C and $>$
427 ~ 7.3 at 100 °C, dawsonite would first tend to form before ankerite as the CO₂ partial
428 pressure in the reservoirs increase. The partial pressure of CO₂ in the LDX system
429 would increase as the CO₂ fraction of the gas progressively increased in the reservoirs
430 located just above the studied rock samples (Fig. 5). The persistence of dawsonite and
431 ankerite in this system is assured by the continued presence of the CO₂-rich gas
432 reservoir, which maintains f_{CO_2} at relatively high levels. Note the current temperature
433 of the gas reservoirs are 92.3 and 102.9 °C for well LDX-1-4 and well LDX-1-1
434 respectively, and the corresponding gas pressure in reservoirs, which is dominated by
435 CO₂, are between 18.9 and 43.2 Mpa (China National Offshore Oil Company,
436 personal communication). [Hellevang et al. \(2005\)](#), noted, that dawsonite, would likely
437 rapidly dissolve once it became thermodynamically unstable as the f_{CO_2} decreased in
438 the such systems.

439

440 *5.4 The paragenetic sequence*

441 Based on the observations described above, the proposed paragenetic sequence for
442 the studied dawsonite-bearing sandstones is shown in [Fig. 11](#). Secondary clays (mainly
443 illite and smectite mixed layer clays) began forming before compaction during the early
444 stage of diagenesis and coated detrital minerals as clay rims. Sideite is found to form
445 next; siderite precipitation is readily observed in reducing, non-sulphidic pore waters in
446 the suboxic and methanogenesis zones ([Morad, 1998](#)). Quartz overgrowths are then
447 observed to form, perhaps due to the recrystallization of biogenic SiO₂, but also
448 accompanied with the formation of minor kaolinite in response to feldspar dissolution.

449 Subsequently, dolomite is observed to form, potentially promoted by Ca and Mg
450 release from the dissolution or transformation of the earlier formed clays. After the
451 influx of CO₂ into the reservoir, dawsonite and additional quartz forms from the
452 dissolution of feldspar, and subsequently ankerite and kaolinite forms from the
453 dissolution of dolomite, quartz, chlorite and potentially some clay minerals..

454

455 *5.5 Implications for carbon storage in sandstone reservoirs*

456 The formation and long-term stability of dawsonite and ankerite in the LDX
457 system are likely good analogies for some modern carbon storage systems such as the
458 Shenhua CCS demonstration project in China (Yang et al., 2017). The distribution of
459 dawsonite and ankerite in the LDX reservoirs (Fig. 5) indicates that these minerals
460 can form in the water layers beneath gas water contact (GWC). Some dawsonite and
461 ankerite were also observed above the present day GWC, which may indicate that
462 either 1) the position of the GWC has changed over time or 2) that these phases grew
463 in the gas filled section of the reservoir, potentially on water-wet surfaces. This later,
464 process, however, is likely limited as the dawsonite and ankerite forming reactions 1
465 and 3 consume H₂O. The formation of such carbonate minerals adjacent to the CO₂
466 gas reservoir is also supported by the results of TOUGHREACT calculations reported
467 by Pan et al. (2017) that suggest that when CO₂ is injected into sandstone reservoirs,
468 carbonate minerals would form on both upper and lower layers of the reservoir.
469 Carbonate mineral precipitation in the water layers below the GWC has also been
470 observed in New Zealand sandstone reservoirs (Higgs et al., 2015). As such, we suggest
471 that the CO₂ in the gas reservoir maintains a sufficient CO₂ partial pressure in the
472 formation waters below the GWC to promote the growth and long term stability of
473 dawsonite and ankerite. However, according to the paragenetic sequence determined
474 in this study, kaolinite precipitated from the fluid concurrently with the precipitation
475 of dawsonite and ankerite. Numerous petrographic observations and experimental
476 simulations suggest that kaolinite and dawsonite formation could significantly reduce

477 sandstone permeability (Luquot et al., 2012; Shiraki and Dunn, 2000; Yu et al., 2012).
478 Kaolinite also commonly grows in response to CO₂-feldspar or CO₂-clay mineral
479 interaction (Luquot et al., 2012; Moore et al., 2005; Shiraki and Dunn, 2000; Yu et al.,
480 2012). Shiraki and Dunn (2000) concluded that the precipitation and growth of
481 kaolinite in the pores could block pore throats leading to the reduction of the
482 permeability of reservoir. Similarly, Worden (2006) suggested that the fiber-like crystal
483 morphology of dawsonite would also reduce sandstone permeability. The reduced
484 permeability in the sandstone could slow chemical transport, and including potentially
485 the transport of dissolved CO₂ out of the storage system. Such processes could thereby
486 promote the stability of carbonate minerals in this system. The decrease in
487 permeability could also lead to fluid pressure build up in the gas reservoir as further
488 minerals form in this system.

489

490 **6 Conclusions**

491 This study focused on the mineral reactions provoked by the influx of CO₂ into the
492 subarkose and sublitharenite sandstones of the Yinggehai basin. This system is likely a
493 good analogy for subsurface carbon storage in sandstone hosted hydrocarbon reservoirs
494 as the influxed CO₂ replaces a methane-rich gas phase in an anticlinal structure. This
495 leads to the presence of a CO₂-rich gas phase stable over a ~1-2 million year time frame.
496 The influx of provoked the CO₂ provoked the formation of dawsonite from plagioclase
497 and ankerite and kaolinite likely from chlorite, quartz, and dolomite, at temperatures of
498 68 to 80 °C. and 90 to 96° C, respectively, largely just below the CO₂-gas water
499 interface. The formation of such phases could provide for the mineral storage of some
500 of the CO₂ injected during subsurface carbon storage efforts.

501 The key to maintaining dawsonite and ankerite stability in such systems appears to
502 be preserving a high partial pressure of CO₂. As such, although the formation of these
503 minerals might lead to the storage of CO₂ injected into sandstones as part of
504 engineered geologic storage efforts, such minerals may not provide for the ‘permanent’

505 mineral storage of this gas that one might anticipate from the formation of carbonate
506 minerals such as calcite, which can be stable at far lower CO₂ partial pressure, unless
507 the system tends to become impermeable as due to the formation of various secondary
508 minerals.

509

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516

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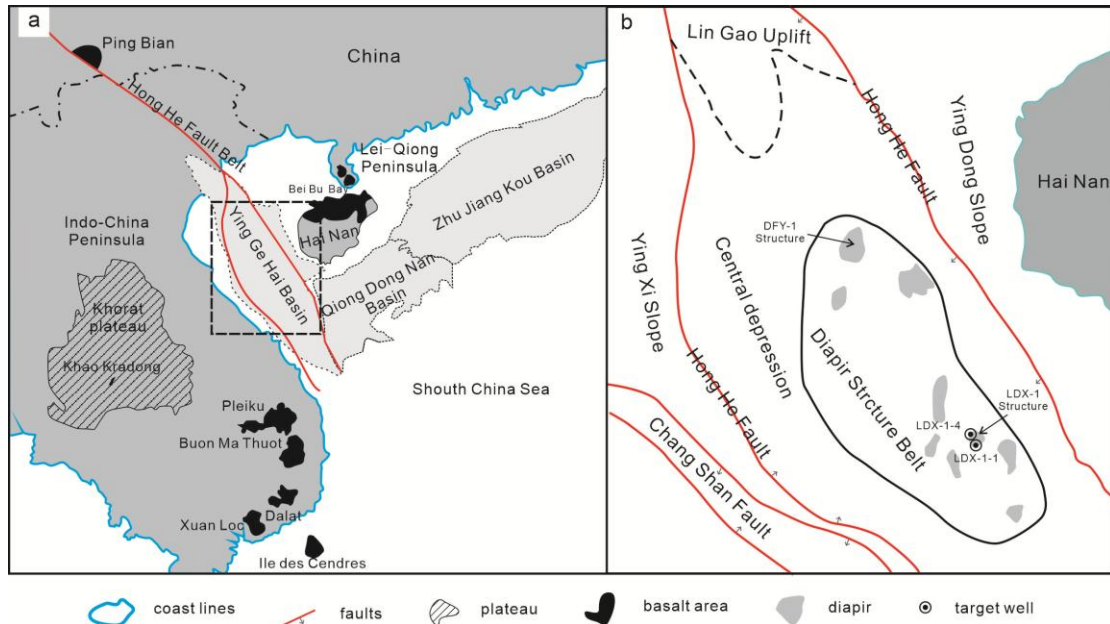
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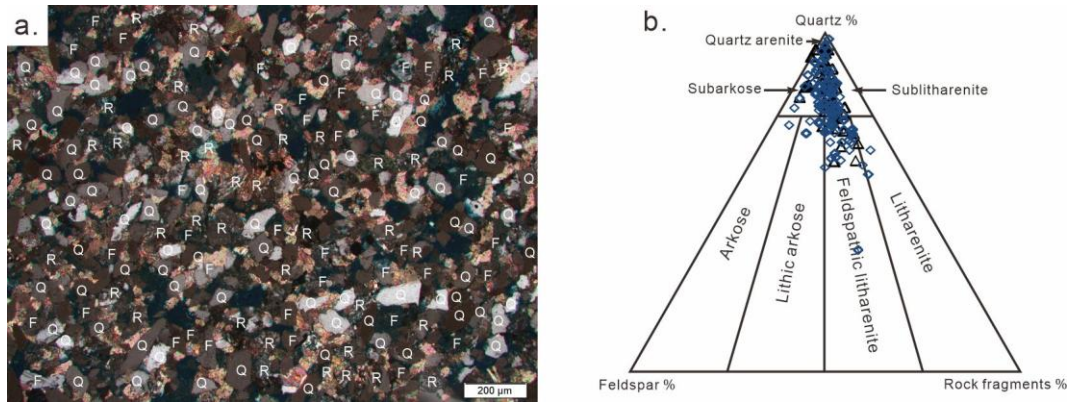
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Figure 1. Location map of LDX-1 structure in Yinggehai Basin, south China Sea area. a) The location of Yinggehai basin and basalt area modified after Shi and Yan (2011), basalt areas are modified from Hoang et al. (1996, 1998), Li et al. (2005), Wang et al. (2001); Zhou et al. (1997) and Zhu et al. (1989), b) Geotectonic units modified after Luo et al., (2003) and Meng et al. (2012).

Period	Formation	Member	Age (Ma)	Maximum Thickness (m)	Lithology	Gas Reservoir
Neogene	Quaternary	Ledong	Q	1250	[Lithology symbols]	
		Pliocene	Yinggehai	N ₂	2200	[Lithology symbols]
	Miocene	Huangliu	N ₃ ¹	780	[Lithology symbols]	
		Meishan	N ₁ ²	1750	[Lithology symbols]	
		Sanya	N ₁ ¹	2950	[Lithology symbols]	
Paleogene	Oligocene	Lingshui	E ₃ ²	Undrilled	[Lithology symbols]	
		Yacheng	E ₃ ¹		[Lithology symbols]	
	Eocene	Lingtou	E ₂		[Lithology symbols]	
		Pre-Paleogene Basement			49.5	[Lithology symbols]

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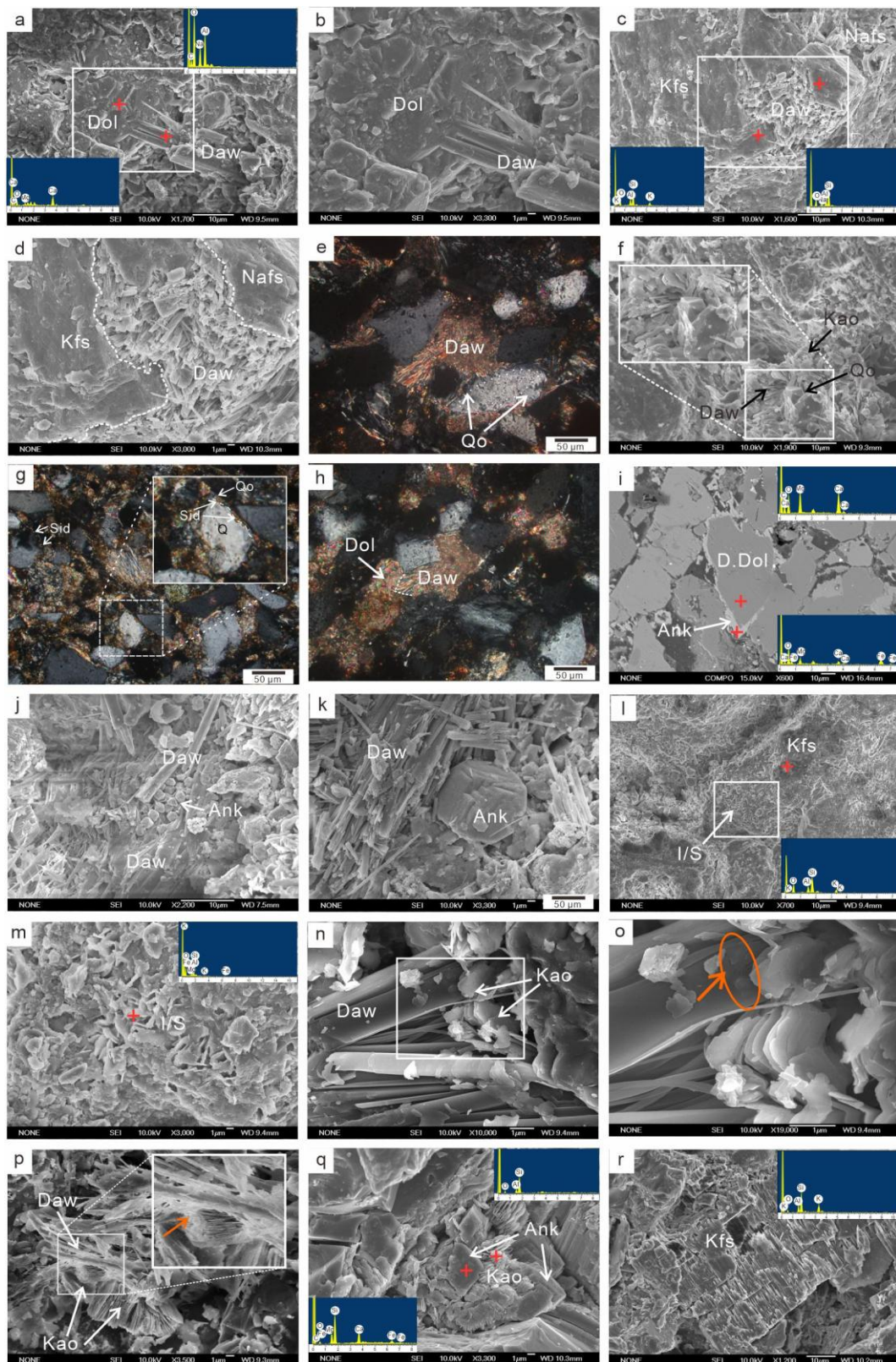
Figure 2. Simplified stratigraphic column of the Yinggehai basin modified after Gong et al. (1997) and Huang et al. (2003).



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844 Figure 3. a) Image of a thin section of a sandstone sample collected from a depth of 1860.72 m in the LDX-1-1 well
 845 showing its detrital minerals: Q=quartz, F=feldspar and R=rock fragment. b) Mineral composition diagram, after
 846 Folk (1968), of the dawsonite-bearing samples from well LDX-1-1 (blue rhombuses) and well LDX-1-4 (black
 847 triangles). All the data were obtained through point-counting - see text.

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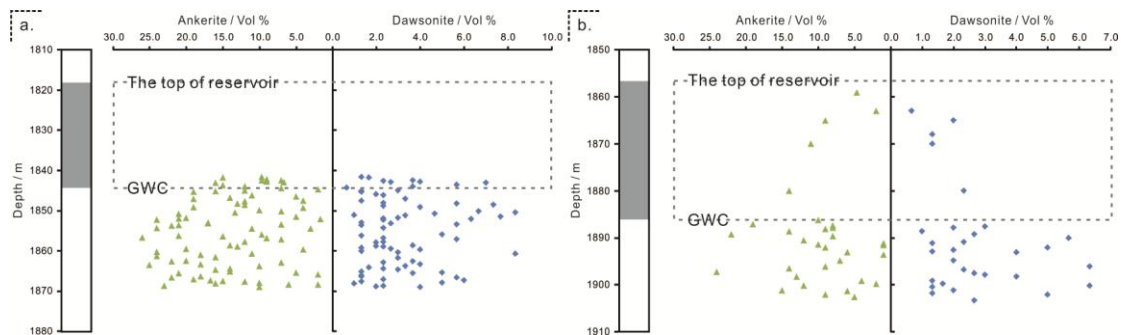


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851 Figure 4. Micrographs of diagenetic minerals. (a, b) Acicular dawsonite growing on top of dolomite (red crosses
 852 are EDS probe spots), SEM; (c, d) Dawsonite replacing feldspar and plagioclase with EDS analysis results (red
 853 crosses are EDS probe spots); (e) Dawsonite replacing quartz overgrowths, thin section micrograph, cross polar; (f)
 854 Microcrystalline quartz grows with kaolinite on the top of drusy dawsonite, SEM;

855 minerals and on the inner side of quartz overgrowths, thin section micrograph, cross polar; (h) Dawsonite replacing
 856 dolomite (dashed line), thin section micrograph, cross polar; (i) Ankerite enclosing and replacing dolomite (red
 857 crosses are EDS probe spots), BSM; (j) rhombic-like ankerite with dawsonite in the pores, SEM; (k) the growth of
 858 rhombic-like ankerite adhering the dawsonite, SEM; (l, m) honeycombed-like illite and smectite mixed layer
 859 coating on detrital K-feldspar (red crosses are EDS probe spots), SEM; (n) kaolinite growing on drusy dawsonite,
 860 SEM; (o) Magnification of white box area in figure (n), some tiny etch pits are observed (red arrow, in the red
 861 circle) on dawsonite potentially caused by the growth of kaolinite, SEM; (p) Acicular dawsonite overlying (red
 862 crosses) kaolinite aggregation; (q) ankerite formed on the top of kaolinite aggregation (red crosses are EDS probe
 863 spots), SEM; (r) dissolution of K-feldspar and EDS results, SEM image. Qo: quartz overgrowth; Daw: dawsonite;
 864 Kao: kaolinite; Sid: siderite; Dol: dolomite; C: Detrital dolomite Ank: ankerite; I/S: illite and smectite mixed layer;
 865 Kfs: K-feldspar; Nafs: Na-feldspar.

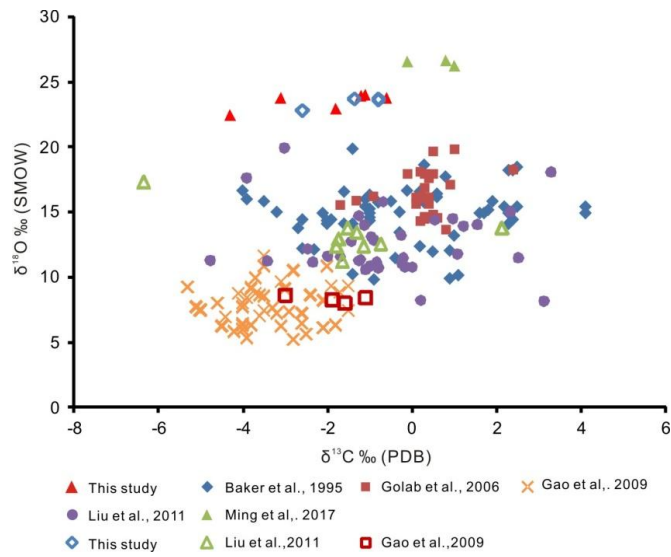
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 875 Figure 5. Plot of volume percent versus depth for dawsonite (blue rhombuses) and ankerite (green triangles) in
 876 well LDX-1-1 (Fig 3a) and well LDX-1-4 (Fig 3b). The filled gray areas and dashed boxes indicate the location of
 877 gas layers, the water layers in the reservoir system are below the gas layers. The gas-water-contact (GWC), as
 878 reported by the China National Offshore Oil Company are located at 1844.1m and 1886.0m depth in wells
 879 LDX-1-1 and LDX-1-4, respectively.

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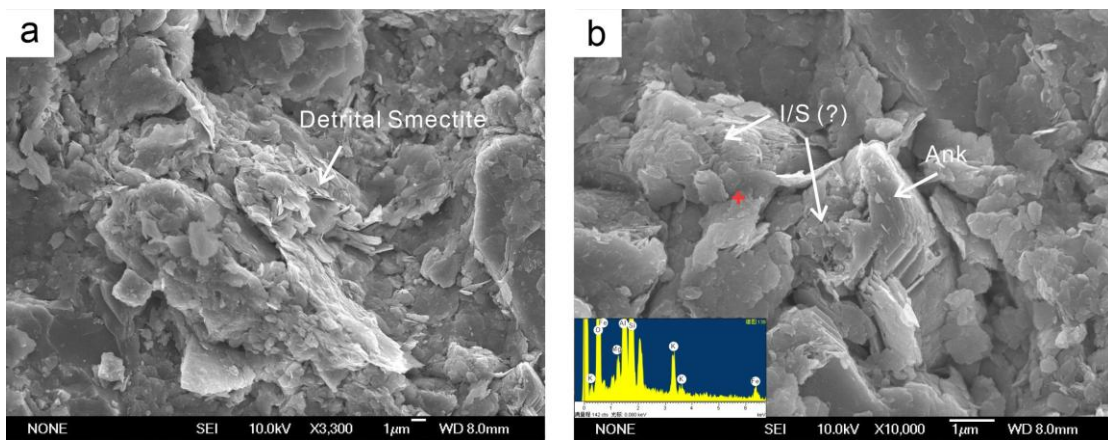


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883 Figure 6. Plot of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ values for dawsonite and ankerite samples. Filled symbols represent the
884 compositions of dawsonite, and open symbols for ankerite. The filled red triangles and open blue rhombus
885 correspond to compositions measured in this study from the LDX-1 structure, Yinggehai basin, China.
886 Compositions of dawsonite from the Bowen-Gunnedah-Sydney basin system in Australia reported by Baker et al.
887 (1995) are shown as filled blue rhombuses, those from the late Permian coal measures of the Upper Hunter Valley
888 in Australia reported by Golab et al. (2006) are shown as filled dark red squares, those of the Cretaceous Hailaer
889 basin in China reported by Gao et al. (2009) are shown as filled yellow crosses, those of the upper Cretaceous
890 Songliao Basin in China reported by Liu et al. (2011) are shown as filled purple circles, and those of the Yaojie
891 coalfield, Minhe basin in China reported by Ming et al. (2017) are shown as filled green triangles. Compositions
892 of ankerite from the Cretaceous Hailaer basin in China reported by Gao et al. (2009) are shown as open red
893 squares, and those of the upper Cretaceous Honggang anticline of the Songliao Basin in China reported by Liu et
894 al. (2011) are shown as open green triangles.

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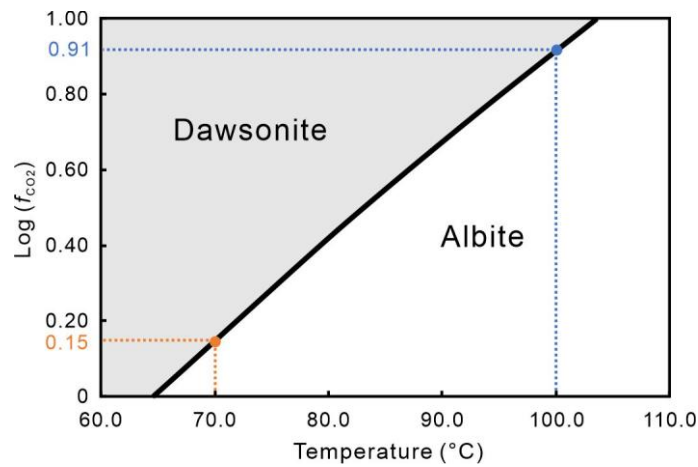


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898 Figure 7. Images of clay minerals observed in this study. (a) detrital smectite in the sandstone and (b) image showing
899 the relationship between smectite and ankerite. Rhombic ankerite crystals grew and adhered to the mixed layer of
900 illite/smectite, suggesting the transformation of smectite could provide some of the materials for ankerite. I/S: mixed

901 layer of illite/smectite; Ank: ankerite.

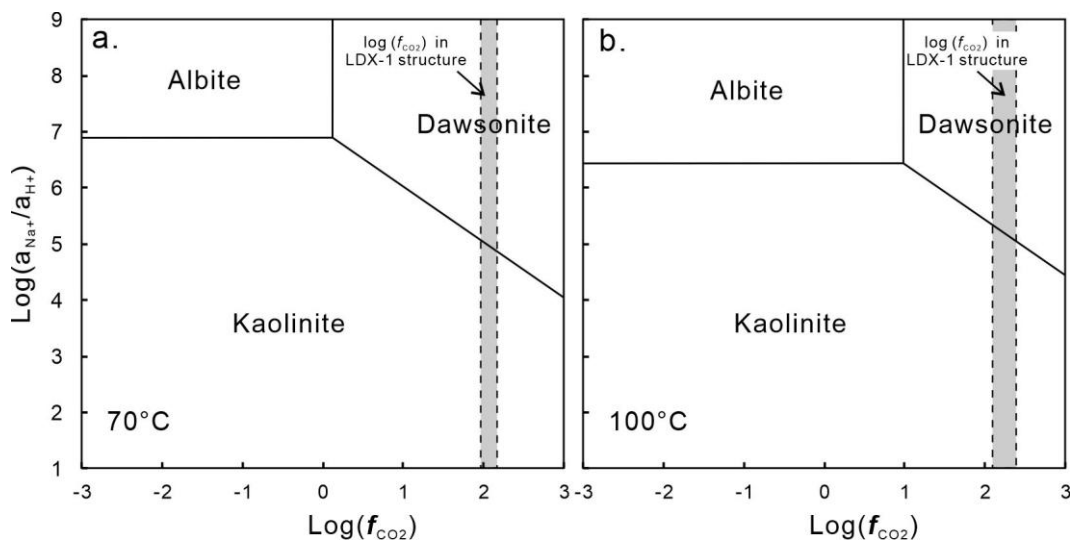
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904 Figure 8 Log fugacity of CO₂ ($\log(f_{\text{CO}_2})$) versus temperature (°C) diagram depicting mineral stability fields in the
905 system Na₂O-Al₂O₃-SiO₂-CO₂-H₂O balanced on Al and at quartz equilibrium. The grey area indicates the stability
906 field of dawsonite, and the white area indicates the stability field for albite. The orange and blue lines highlight the
907 $\log(f_{\text{CO}_2})$ values in equilibrium with dawsonite and albite at 70 and 100 °C, respectively. This figure was
908 generated using PHREEQC together with its llnl database – see text.

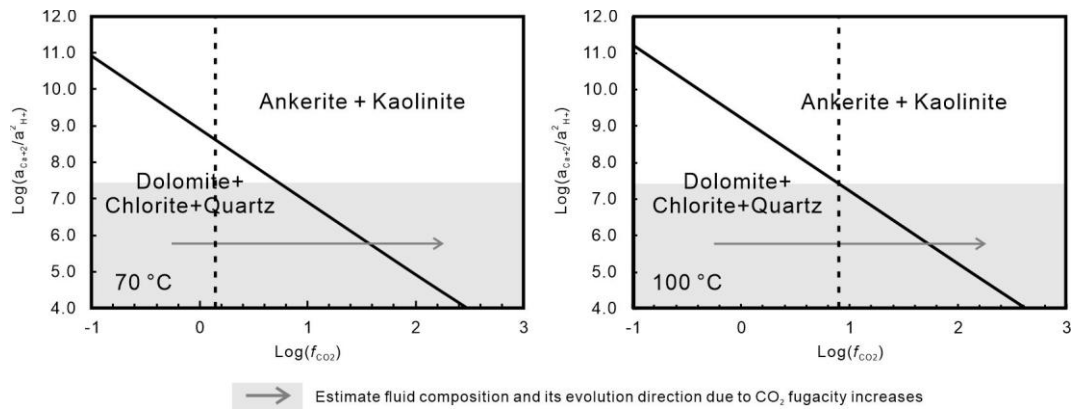
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911 Figure 9. Log fugacity of CO₂ ($\log(f_{\text{CO}_2})$) versus $\log a_{\text{Na}^+}/a_{\text{H}^+}$ diagrams depicting mineral stability fields in the
912 system Na₂O-Al₂O₃-SiO₂-CO₂-H₂O balanced on Al and at quartz equilibrium at 70 °C and 100 °C. The dashed
913 area represents the current $\log(f_{\text{CO}_2})$ range in the reservoirs considered in this study. This figure was generated
914 using PHREEQC together with its llnl database – see text.

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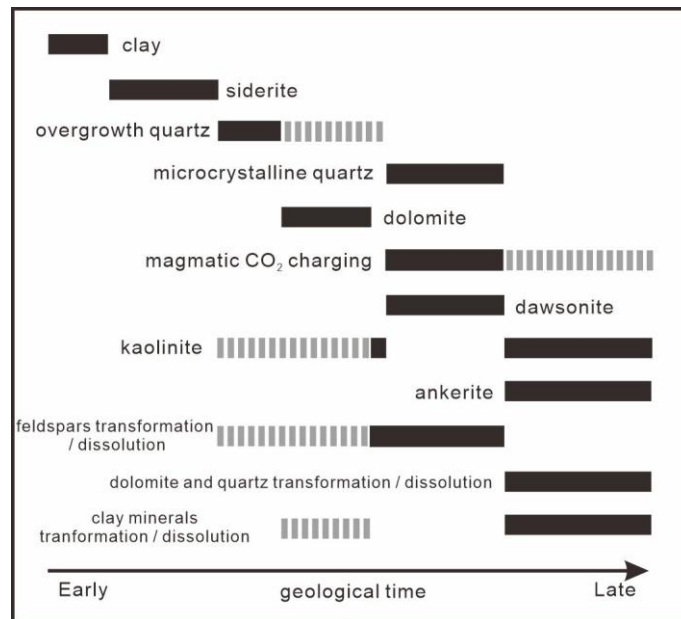
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917 Figure 10. Phase diagram of log CO₂ fugacity (log (f_{CO_2})) versus log $a_{Ca^{2+}}/a_{H^+}^2$. The dashed vertical lines
 918 correspond to equilibrium compositions of reaction 1, whereas the sloped lines correspond to equilibrium
 919 compositions of reaction 3. The grey area is the likely aqueous activity ratio of $a_{Ca^{2+}}/a_{H^+}^2$ in the studied system and
 920 the arrow illustrates the direction of the CO₂ fugacity evolution in the system as the reservoir fills with CO₂. This
 921 figure was generated using PHREEQC together with its llnl database after adding estimated values for the
 922 thermodynamics properties of ankerite— see text.

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Figure 11. Paragenetic sequence for dawsonite-bearing sandstones in this study. The black bars are indicated by petrologic observations, the grey dashed bars are estimated based on the mass balance considerations and reactions (1) and (3).

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Table 1. EDS analysis data for dawsonite.

Well	Weight Percentage, %					Atomic Percentage, %				
	C	Na	Al	O	Si	C	Na	Al	O	Si
LDX-1-1	18.76	4.98	12.99	63.27	n.d.	25.14	3.48	7.75	63.63	n.d.
LDX-1-1	15.88	11.13	14.19	58.8	n.d.	22.01	8.06	8.76	61.18	n.d.
LDX-1-1	11.81	12.44	12.96	55.55	7.23	17.14	9.44	8.38	60.55	4.49
LDX-1-4	14.88	13.8	14.24	57.09	n.d.	20.87	10.11	8.89	60.13	n.d.
LDX-1-4	15.61	12.53	13.7	58.15	n.d.	21.71	9.11	8.48	60.7	n.d.
LDX-1-4	12.62	14.69	17.98	54.72	n.d.	18.19	11.06	11.54	59.21	n.d.
LDX-1-4	12.64	8.37	14.29	57.5	7.2	18.15	6.28	9.14	62	4.43
LDX-1-4	7.83	6.83	8.83	55.28	21.23	11.88	5.41	5.96	62.97	13.78
LDX-1-4	12.58	12.01	19.97	55.44	n.d.	18.13	9.04	12.82	60.01	n.d.
LDX-1-4	9.14	14.68	24.74	51.45	n.d.	13.75	11.54	16.57	58.13	n.d.
LDX-1-1	10.16	13.06	23.91	52.87	n.d.	15.09	10.13	15.81	58.96	n.d.
LDX-1-1	11.59	9.4	23.75	55.26	n.d.	16.9	7.16	15.42	60.52	n.d.
LDX-1-1	18.76	4.98	12.99	63.27	n.d.	25.14	3.48	7.75	63.63	n.d.
LDX-1-1	11.97	10.19	18.04	55.91	3.88	17.36	7.72	11.64	60.86	2.41
LDX-1-1	7.25	12.06	30.26	50.43	n.d.	11.18	9.71	20.76	58.35	n.d.
LDX-1-1	13.42	13.99	16.92	55.67	n.d.	19.16	10.43	10.75	59.66	n.d.
LDX-1-1	13.68	13.29	16.93	56.11	n.d.	19.46	9.88	10.72	59.94	n.d.
LDX-1-1	18.6	7.9	11.21	62.28	n.d.	24.98	5.54	6.7	62.78	n.d.
LDX-1-1	12.75	11.24	20.18	55.83	n.d.	18.34	8.45	12.92	60.29	n.d.
LDX-1-1	10.17	12.49	24.3	53.04	n.d.	15.1	9.69	16.07	59.14	n.d.
LDX-1-4	13.71	7.2	12.99	58.84	7.26	19.43	5.33	8.2	62.63	4.4
LDX-1-4	11.98	13.11	16.51	55.02	3.38	17.39	9.93	10.66	59.92	2.1
LDX-1-4	10.86	13.85	21.98	53.31	n.d.	16	10.65	14.41	58.94	n.d.
LDX-1-4	22.23	3.58	7.27	66.93	n.d.	28.65	2.41	4.17	64.77	n.d.
LDX-1-4	10.18	12.73	24.1	52.99	n.d.	15.12	9.88	15.93	59.07	n.d.
LDX-1-4	12.26	13.58	19.45	54.7	n.d.	17.75	10.27	12.53	59.44	n.d.

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n.d.: not be detected.

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Table 2. EDS analysis data for ankerite

Well	Weight Percent								Atomic Percent							
	C	O	Na	Mg	Al	Si	Ca	Fe	C	O	Na	Mg	Al	Si	Ca	Fe
LDX-1-4	9.66	51.32	n.d.	6.54	n.d.	4.42	6.29	21.77	16.14	64.34	n.d.	5.4	n.d.	3.16	3.15	7.82
LDX-1-4	13.15	52.72	n.d.	8.46	n.d.	n.d.	19.73	5.95	20.52	61.75	n.d.	6.52	n.d.	n.d.	9.22	2
LDX-1-4	10.3	53.98	n.d.	7.09	n.d.	1.77	17.26	9.6	16.53	65.02	n.d.	5.62	n.d.	1.22	8.3	3.31
LDX-1-4	12.96	57.98	n.d.	5.16	2.28	1.72	1.12	18.77	19.89	66.79	n.d.	3.92	1.56	1.13	0.52	6.2
LDX-1-4	16.52	61.57	n.d.	7.64	n.d.	n.d.	0.92	13.35	23.71	66.35	n.d.	5.42	n.d.	n.d.	0.39	4.12
LDX-1-4	12.79	61.42	n.d.	6.25	1.52	2.56	2.73	12.73	19	68.49	n.d.	4.59	1	1.62	1.21	4.07
LDX-1-4	15.63	55.85	n.d.	3.64	1.34	4.16	11.59	7.79	23.37	62.69	n.d.	2.69	0.89	2.66	5.19	2.5
LDX-1-1	13.97	59.87	1.84	5.04	1.69	0.84	12.09	4.66	20.51	66	1.41	3.66	1.1	0.53	5.32	1.47
LDX-1-1	13.39	59.42	n.d.	5.56	n.d.	2.16	12.7	6.78	20.01	66.65	n.d.	4.1	n.d.	1.38	5.69	2.18
LDX-1-1	12.41	60.07	n.d.	3.29	2.27	11.6	3.16	7.2	18.36	66.71	n.d.	2.4	1.49	7.34	1.4	2.29
LDX-1-1	10.25	45.23	n.d.	3.86	2.24	5.18	16.05	17.17	17.73	58.71	n.d.	3.3	1.73	3.83	8.32	6.39

936 **n.d.: not be detected.**

937

Table 3. EDS analysis data for smectite and the mixed layer of illite and smectite

Well	Weight Percentage, %									Atomic Percentage, %								
	C	O	Na	Mg	Al	Si	K	Ca	Fe	C	O	Na	Mg	Al	Si	K	Ca	Fe
LDX-1-1	3.31	57	2.64	0.63	6.64	26.9	1.24	0.37	1.27	5.25	67.91	2.19	0.49	4.69	18.26	0.6	0.18	0.43
LDX-1-1	n.d.	41.41	n.d.	1.22	9.69	35.81	6.72	n.d.	5.14	n.d.	57.05	n.d.	1.11	7.92	28.11	3.79	n.d.	2.03
LDX-1-1	n.d.	37.5	n.d.	1.55	9.06	39.51	4.7	n.d.	7.67	n.d.	53.18	n.d.	1.44	7.62	31.92	2.73	n.d.	3.12
LDX-1-1	n.d.	47.11	1.39	1.93	14.08	26.38	2.12	n.d.	6.99	n.d.	62.32	1.28	1.68	11.04	19.88	1.15	n.d.	2.65
LDX-1-4	n.d.	57.17	0.7	0.99	15.27	22.26	2.53	n.d.	1.08	n.d.	70.24	0.6	0.8	11.13	15.58	1.27	n.d.	0.38
LDX-1-4	n.d.	54.36	n.d.	4.31	8.23	11.71	n.d.	13.46	7.93	n.d.	71.16	n.d.	3.71	6.38	8.73	n.d.	7.03	2.98
LDX-1-4	n.d.	52.97	n.d.	1.18	13.35	26.82	4.82	n.d.	0.87	n.d.	66.92	n.d.	0.98	10	19.3	2.49	n.d.	0.31
LDX-1-4	n.d.	55.21	n.d.	1.52	11.51	27.18	1.39	n.d.	3.18	n.d.	69.01	n.d.	1.25	8.53	19.35	0.71	n.d.	1.14
LDX-1-4	n.d.	45.84	n.d.	1.44	14.38	28.31	3.13	n.d.	6.91	n.d.	61.37	n.d.	1.27	11.42	21.59	1.71	n.d.	2.65
LDX-1-4	n.d.	46.01	n.d.	1.67	12.96	29.18	2.94	n.d.	7.24	n.d.	61.6	n.d.	1.47	10.29	22.25	1.61	n.d.	2.78
LDX-1-4	n.d.	46.45	n.d.	1.52	15.13	26.85	4.9	n.d.	5.16	n.d.	61.77	n.d.	1.33	11.93	20.34	2.67	n.d.	1.96
LDX-1-4	n.d.	52.5	n.d.	1.34	13.43	26.4	2.83	n.d.	3.49	n.d.	66.84	n.d.	1.12	10.14	19.15	1.48	n.d.	1.27
LDX-1-4	n.d.	52.32	1.04	1.26	9.4	29.16	1.99	n.d.	3.28	n.d.	66.71	0.92	1.05	7.11	21.18	1.04	0.79	1.2
LDX-1-4	n.d.	39.97	n.d.	1.14	10.55	39.83	2.53	n.d.	4.37	n.d.	55.06	n.d.	1.04	8.62	31.26	1.43	0.87	1.73
LDX-1-4	n.d.	32.01	n.d.	0.97	12.81	34.05	12.63	n.d.	7.54	n.d.	47.8	n.d.	0.95	11.34	28.97	7.72	n.d.	3.23
LDX-1-4	n.d.	53.67	0.98	0.99	11.99	28.2	2.38	n.d.	1.8	n.d.	67.37	0.86	0.82	8.92	20.16	1.22	n.d.	0.65
LDX-1-1	n.d.	53.91	n.d.	1.68	12.75	25.32	4.2	n.d.	2.13	n.d.	67.96	n.d.	1.4	9.53	18.18	2.17	n.d.	0.77
LDX-1-1	n.d.	61.56	1.25	0.99	9.68	22.71	2.14	n.d.	1.68	n.d.	74.07	1.04	0.79	6.9	15.56	1.05	n.d.	0.58
LDX-1-1	n.d.	63.93	1.67	2.62	8.94	16.76	1.11	n.d.	4.97	n.d.	76.52	1.39	2.06	6.35	11.43	0.54	n.d.	1.7
LDX-1-1	n.d.	35.98	n.d.	1.82	11.82	35.41	8.01	n.d.	6.96	n.d.	51.68	n.d.	1.72	10.07	28.97	4.7	n.d.	2.86

939 n.d.: not be detected.

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Table 4. Carbon and oxygen isotopic compositions for dawsonite and ankerite

Well	Depth	Mineral	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$	Isotopic temp.	$\delta^{13}\text{C}_{\text{CO}_2}$
	m		‰, PDB	‰, PDB	‰, SMOW	°C	‰, PDB
LDX-1-4	1894.8	Dawsonite	-1.2	-6.8	23.9	68.53	-7.39
LDX-1-4	1896.07	Dawsonite	-1.1	-6.7	24.0	67.83	-7.34
LDX-1-4	1897.57	Dawsonite	-0.6	-7.0	23.7	69.94	-6.69
LDX-1-4	1900.2	Dawsonite	-1.8	-7.8	22.9	75.76	-7.44
LDX-1-1	1842.5	Dawsonite	-4.3	-8.3	22.4	79.56	-9.66
LDX-1-1	1863.34	Dawsonite	-3.1	-7.0	23.7	69.94	-9.17
LDX-1-4	1889.07	Ankerite	-2.6	-7.8	22.8	96.44	-7.27
LDX-1-4	1894.8	Ankerite	-0.8	-7.0	23.7	89.56	-5.94
LDX-1-4	1897.57	Ankerite	-0.8	-7.1	23.6	90.31	-5.88
LDX-1-4	1900.2	Ankerite	-1.4	-7.0	23.7	89.56	-6.50

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