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1 **Drilling and sampling a natural CO₂ reservoir: implications**
2 **for fluid flow and CO₂-fluid-rock reactions during CO₂**
3 **migration through the overburden**

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23 **Abstract**

24 This paper presents the initial results of a scientific drilling project to recover core
25 and pressurized fluid samples from a natural CO₂ reservoir, near the town of Green River,
26 Utah. The drilling targeted a stacked sequence of CO₂-charged Jurassic sandstone reservoirs
27 and caprocks, situated adjacent to a CO₂-degassing normal fault. This site has actively
28 leaked CO₂ from deep supercritical CO₂ reservoirs at depth >2km within the basin for over
29 400,000 years. The project objectives were to gather samples to examine reactive fluid flow
30 in the reservoirs, caprocks and faults, during migration of CO₂ through the geological
31 overburden from the deep supercritical CO₂ reservoirs. Downhole fluid sampling and fluid
32 element and isotope geochemistry show that the shallow reservoirs are being actively fed
33 by inflow of CO₂-saturated brines through the faults. Comparisons of shallow and deep fluid
34 geochemistry suggests that: (i) CO₂ and CO₂-charged brines co-migrated from the deep
35 reservoirs, (ii) the CO₂-saturated brines migrating from depth interact with significant
36 volumes of meteoric groundwater in aquifers in the shallower Permian and Jurassic
37 sandstones, diluting the brine composition, and (iii) that a significant fraction of the CO₂
38 migrating from depth is dissolved in these brine-meteoric water mixtures, with >99% of the
39 CO₂ in fluids sampled from the shallow reservoirs being derived during fluid migration, after
40 the fluids left their source reservoir. The ⁸⁷Sr/⁸⁶Sr ratio of the brine flowing through the
41 faults is significantly elevated due to the addition of Sr from silicate mineral dissolution
42 during fluid migration.

43 The association of bleached sandstones in the core with CO₂-rich fluids supports
44 interpretations from elsewhere that CO₂-charged brines with CH₄ or H₂S reductants can
45 dissolve hematite present within the sediment. Analysis of fluid geochemistry and

46 sandstone petrology suggest that the CO₂-rich fluids dissolve carbonate, hematite and
47 gypsum in the reservoirs, as they flow away from the faults.

48 Element and isotope geochemistry of fluid samples from the drillhole and Crystal
49 Geyser constrain mixing models which show that, within the Navajo Sandstone, the
50 reservoir fluids are undergoing complex mixing of: (i) CO₂-saturated brine inflowing from
51 the fault, (ii) CO₂-undersaturated meteoric groundwater flowing through the reservoir and
52 (iii) reacted CO₂-charged brines flow through fracture zones in the overlying Carmel
53 Formation caprock, into the formations above. Such multi-scale mixing processes may
54 significantly improve the efficiency with which groundwaters dissolve the migrating CO₂.

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68 1 Introduction

69 Understanding the geochemical behaviour of carbon dioxide stored in geological reservoirs,
70 over a range of time-scales, is crucial for quantifying the risk of leakage and the geochemical
71 evolution of the stored CO₂ through the life of an individual storage site (see review in
72 Kampman *et al.*, 2013 this issue). CO₂ dissolution in brine will tend to stabilize the CO₂ in
73 storage reservoirs (e.g. Gilfillan *et al.*, 2009) and reactions between CO₂-charged brines and
74 reservoir minerals might either enhance the long-term storage security by precipitation of
75 carbonate minerals or facilitate leakage through mineral dissolution and corrosion of
76 caprocks and fault seals (e.g. Bickle, 2009). A further concern is that migration and intrusion
77 of CO₂ will drive acidification of potable groundwaters which may mobilize potentially toxic
78 trace metals.

79 Buoyant supercritical CO₂ may migrate from a storage reservoir through fractured or
80 corroded caprocks, permeable fault zones or laterally discontinuous seals. Understanding
81 the fluid-fluid and fluid-rock reactions that may retard the migration of CO₂ from deep
82 storage sites to the surface is of critical importance for demonstrating the retentive capacity
83 of the geological overburden, above deep storage reservoirs. Concerns that may arise
84 during the migration of CO₂ through the overburden include escape of CO₂ to the surface
85 and contamination of shallow potable aquifers by: (i) intrusion of CO₂, resulting in
86 dissolution and desorption of potentially toxic metals from minerals by acidic CO₂-charged
87 fluids and (ii) entrainment of deep formation brine with the migrating CO₂, which may
88 contain high concentrations of metals and radionuclides.

89 Fluid-rock reactions involving Fe-oxide minerals are a potential source of
90 contaminants in CO₂-charged groundwaters. Elevated trace metal concentrations from

91 mineral dissolution and pH driven desorption reactions are predicted from modelling
92 studies (e.g. Apps et al., 2010), experiments (e.g. Little and Jackson, 2010) and recent field
93 tests (e.g. Trautz et al., 2012); however shallow CO₂-injection field experiments have not
94 shown hazardous levels of contamination in the short-term (Kharaka et al., 2010; Trautz et
95 al., 2012). The reducing conditions present in deeper geological formations may enable
96 more effective rates of Fe-oxide and Fe-oxyhydroxide dissolution in the presence of
97 elevated CO₂ concentrations (e.g. Frio Brine Pilot Experiment; Kharaka et al., 2006).

98 The efficiency of the geological overburden for dispersing and trapping a migrating
99 CO₂ plume can only be established from engineered CO₂-injection leakage experiments or
100 direct observations from leaking natural CO₂ accumulations, with the latter allowing
101 observations of processes on the timescales required for CO₂ storage. Numerical modelling
102 studies (e.g. Doughty and Myer, 2009; Zhou *et al.*, 2010), while providing valuable
103 information on likely large scale flows and pressure changes, lack the resolution to properly
104 track CO₂ dissolution and fluid-mineral reactions in reservoirs with heterogeneities
105 characteristically on 10 cm scales, given their grid-scales of metres to hundreds of metres.

106 In this paper we discuss the initial results of a core and a downhole fluid sampling
107 campaign during recent scientific drilling of a natural CO₂ system at Green River, Utah. The
108 ~322 m deep vertical hole was drilled in July 2012, penetrating a stacked sequence of CO₂-
109 charged sandstone reservoirs and their intervening caprocks. These shallow reservoirs are
110 filled through a normal fault system through which CO₂ and CO₂-charged fluids migrate from
111 deep supercritical CO₂ reservoirs at depth within the basin. We present the initial results of
112 surface and downhole fluid sampling during drilling of the CO₂ reservoirs and some
113 preliminary observations from the recovered core. Analytical methods to recover pH and
114 CO₂ content of pressurized fluid samples onsite are presented. Element and isotope

115 geochemistry of the fluid samples recovered from the drill hole are used to examine fluid
116 flow, fluid-fluid mixing and fluid-rock reactions in the faulted CO₂-reservoirs. The results are
117 supported by: (i) published analyses of brine compositions from the deep supercritical CO₂
118 reservoirs sampled during oil well exploration drilling and (ii) long-term sampling and
119 monitoring of fluid geochemistry from Crystal Geyser sourced from the underlying CO₂
120 reservoirs. Interpretation of the fluid-rock reactions occurring within the CO₂ reservoirs
121 inferred from the fluid geochemistry is supported by preliminary petrographic and
122 mineralogical observations from the core.

123 **1.1 Leaking natural CO₂ reservoirs of the South Western USA**

124 The greater Colorado Plateau and Southern Rocky Mountains region, USA, contains a
125 number of natural CO₂ reservoirs (Allis *et al.*, 2001; reviewed in Bickle *et al.*, 2013). This
126 includes the stacked sequence of CO₂-reservoirs in Jurassic, Permian and Carboniferous
127 sediments of the northern Paradox Basin, near the town of Green River, Utah (Fig. 1-3).
128 Many of these natural reservoirs have contained CO₂ securely for thousands to millions of
129 years. This has been used to argue for the stability of CO₂ in geological reservoirs and that
130 the long-term integrity of caprocks can be preserved in the presence of CO₂ and CO₂-
131 charged fluids. Whilst it is expected that a well-sited CO₂ storage facility will not leak, some
132 natural CO₂ reservoirs (such as the Green River site) have conductive features where CO₂
133 and CO₂-charged fluids are able to escape from deep reservoirs of supercritical CO₂ to
134 surface. The accumulations at Springerville-St Johns Dome, Arizona and Green River, Utah
135 currently leak CO₂ through faults and possess fault-associated, surface travertine deposits
136 attesting to CO₂ leakage in the recent and geological past (Fig 3; Allis *et al.*, 2005, Burnside
137 *et al.*, 2013; Gilfillan *et al.*, 2011; Kampman *et al.*, 2012; Keating *et al.*, 2010, 2012, 2013).
138 Radiometric dating of these surface travertine deposits attest to leakage from the St Johns

139 Dome accumulation for >350ka (Embid and Crossey, 2009) and from the Green River
140 accumulation for >400ka (Burnside *et al.*, 2013; Kampman *et al.*, 2012). The long-lived
141 nature of CO₂ accumulations penetrated by large conductive faults raises a number of
142 important questions about the rates and mechanism of leakage from deep geological
143 reservoirs to the surface. What are the intrinsic permeabilities of faults at depth to
144 supercritical/gaseous CO₂ and/or CO₂-charged brines? What impact does fluid-rock
145 reactions with supercritical CO₂ and CO₂-charged fluids have on fault permeability? Does
146 surface CO₂ leakage at these sites reflect migration of a discrete CO₂-phase or degassing of
147 CO₂-charged fluids in the shallow subsurface? Are these natural reservoirs being
148 continuously recharged with CO₂ or are leakage rates sufficiently small so as not to dissipate
149 the accumulations over geological time-scales? Some of these questions may be addressed
150 by drilling and sampling of fluids and rock core from the reservoirs, faults and geological
151 overburden.

152 **2 Green River Natural CO₂ Accumulation and Hydrology**

153 CO₂-charged fluids leak to surface along the Green River anticline where they form a series
154 of CO₂ springs and geysers, including the spectacular Crystal Geyser (Fig. 3; Assayag *et al.*,
155 2009; Baer and Rigby, 1978; Burnside *et al.*, 2013; Dockrill and Shipton, 2010; Evans *et al.*,
156 2004; Gouveia and Friedmann, 2006; Gouveia *et al.*, 2005; Han *et al.*, 2013; Heath, 2004,
157 2009; Kampman *et al.*, 2009, 2012; Pasala *et al.*, 2013 Shipton *et al.*, 2005; Shipton *et al.*,
158 2004; Vrolijk *et al.*, 2005). The natural springs discharge from the footwalls of the Little
159 Grand Wash and Salt Wash normal faults but abandoned oil exploration and water wells
160 leak CO₂ over a wider region (Fig. 1-4). Oil exploration drilling has encountered
161 accumulations of: (i) CO₂ gas and CO₂-charged brine in the Navajo Sandstone at depths of

162 ~200-350 m, (ii) CO₂ gas and CO₂-charged brine in the Jurassic Wingate Sandstone at depths
163 of ~400-500 m, (iii) accumulations of supercritical CO₂ and CO₂-charged brine in the Permian
164 White Rim Sandstone at depths of ~800-900 m, and (iv) supercritical CO₂ and CO₂-charged
165 brine in Carboniferous (Pennsylvanian and Mississippian) aged carbonate and evaporite
166 deposits at depths >900m (Fig. 2; Jay Beach, Delta Petroleum pers. comm. 2007; Drilling
167 Reports e.g. Navajo Sandstone - Greentown State 36-11, API 4301931462; Wingate -
168 Greentown Federal 26-43D, API 4301931547; White Rim - Green Town Federal 35-12, API
169 4301931507).

170 The surface exposures, CO₂ springs along the fault zones, stacked sequence of
171 reservoirs, the relatively shallow depth (160-350m) of the upper CO₂-bearing reservoir, the
172 Navajo Sandstone and the prior knowledge of the site made it an excellent drilling target to
173 document processes within a leaking CO₂-charged system.

174 2.1.1 Structural Geology

175 The Little Grand Wash and Salt Wash normal faults are 35-40 km in lateral extent
176 and contain a clay gouge core, surrounded by a fault damage zone of high angle open
177 fractures orientated parallel to the fault (Dockrill and Shipton, 2010; Shipton *et al.*, 2004,
178 2005; Vrolijk *et al.*, 2005). Formation top data from oil exploration drill-holes constrains the
179 penetration depth of the faults to at least the Carboniferous strata, and they probably
180 penetrate deeper. Dockrill and Shipton (2010) conclude that the faults are laterally sealing
181 towards the fault center, with throws of 250-300 m, but become laterally transmissive
182 towards the fault tips, where reservoir-reservoir rock is juxtaposed (Fig 4; Dockrill and
183 Shipton, 2010). Buoyant supercritical and gaseous CO₂ is thought to accumulate at the crest
184 of the Green River anticline, adjacent to the two faults, beneath the south dipping fault
185 seals. Open fractures in the fault damage zone allow CO₂ and CO₂-charged brines to escape

186 upwards under artesian head, from the deep supercritical CO₂ reservoirs (Fig. 3-5; e.g.
187 Pasala *et al.*, 2013). CO₂-leakage points away from the faults (Fig. 3; Tumble Weed Geyser
188 and Chaffin Ranch Geyser) occur where exploration or water well drill-holes penetrate fluids
189 in the Navajo Sandstone flowing horizontally away from the fault tips under a regional
190 hydraulic head (Hood and Patterson, 1984; Kampman *et al.*, 2009). Details of the local
191 hydrology are discussed in Kampman *et al.*, (2009) and the regional hydrology is discussed in
192 Hood and Patterson (1984).

193 2.1.2 Ancient Travertine Deposits

194 Ancient travertine deposits overlie damage zones in the footwall blocks of both the
195 Little Grand Wash and Salt Wash faults (Fig. 3; Burnside *et al.*, 2013; Kampman *et al.*, 2012).
196 The travertine mounds are localized to the intersection of the faults with the apex of the
197 Green River anticline and the mounds are distributed along a considerable portion of the
198 faults' lengths to the east and west (Fig. 3). U-Th dating of the deposits attests to leakage of
199 CO₂ from the site for at least the last 400ka (Burnside *et al.*, 2013). Kampman *et al.*, (2012)
200 argue that there were successive pulses of CO₂-leakage with a periodicity controlled by
201 climate driven changes in formation fluid over-pressure and the hydraulic behaviour of the
202 faults. Pulses of CO₂ and CO₂-charged brine injection, recorded by changes in the
203 geochemistry of surface travertines, are argued to have been accompanied by increased
204 rates of CO₂ degassing from the faults. These pulses occurred at the transition from local
205 glacial to interglacial conditions following climate warming and crustal unloading during
206 drainage of pluvial lakes and the retreat of mountain glaciers in the region (Kampman *et al.*,
207 2012).

208 2.1.3 Crystal Geyser, Tenmile Geyser and the Green River Airport Well

209 The modern day Crystal Geyser erupts from an abandoned exploration drill-hole
210 Ruby #1 State Well drilled in 1935, which reached a total depth of ~800m in the upper
211 portions of the Permian White Rim Sandstone (Baer and Rigby, 1978). The drill-hole was
212 uncased and is now rubble filled below a depth of ~15 m, having been dynamited in the
213 1990s (Han *et al.*, 2013; Shipton *et al.*, 2004). It is likely that the drillhole is only weakly or
214 non-transmissive at depths greater than the Navajo Sandstone. The saline fluid expelled
215 from Crystal Geyser is thought to predominantly originate from the Navajo Sandstone, and
216 emanation temperatures are consistent with a fluid largely derived from this depth (Baer
217 and Rigby, 1978; Heath *et al.*, 2009; Kampman *et al.*, 2009). The waters expelled from
218 Crystal Geyser and the CO₂-springs have previously been shown to contain variable mixtures
219 of meteoric waters, derived from areas of groundwater recharge in the San Rafael Swell
220 (Hood and Patterson, 1984), and evaporite derived brines from the deep Carboniferous
221 formations input along with the CO₂ (Kampman *et al.*, 2009; Wilkinson *et al.*, 2009).

222 Two other important CO₂-springs in the area, discussed in this study, are Tenmile
223 Geyser and the Green River Airport Well. Tenmile Geyser escapes from an abandoned
224 petroleum exploration well, situated within hangwall block of the Salt Wash Graben fault.
225 The spring is notable for the large fraction of deeply derived brine in the expelled fluid
226 (Kampman *et al.*, 2009), elevated concentrations of N₂, Ar, He and CH₄ in the exsolved gas
227 (this study) and an anomalous CO₂/³He ratio (Wilkinson *et al.*, 2009). The Green River
228 Airport well escapes from exploration drill-hole Grand Fault 14-24. This drill-hole was sited
229 within the footwall block of the Little Grand Fault, on the westerly limb of the Green River
230 anticline and originally penetrated to the base of the Mississippian Leadville Limestone at
231 3.2km. This CO₂-spring emits warm (~27°C) fluid sourced from the Navajo Sandstone, and

232 lies on a fluid flow path running along the length of the Little Grand Fault, up-stream of
233 Crystal Geyser (Fig. 3). It is the most proximal spring to zones of groundwater recharge in
234 the San Rafael Swell, and contains CO₂ inputs from depth without the addition of significant
235 brine from deeper formations (Kampman *et al.*, 2009).

236 **3 Field Sampling and Analytical Methodology**

237 **3.1 Scientific Drilling**

238 Drilling of hole CO2W55 was carried out from 2nd-28th July, 2012, using a CS4002 Truck
239 Mounted Core Drill by DOSECC Inc (Fig. 5). The drilling and fluid sampling methods are
240 presented in detail in Kampman *et al.*, 2013a. The drill site is located on the footwall block
241 of the Little Grand Wash Fault (Fig. 2, 5; 38.93792 N, -110.13892 W, 1238 m Elev.), ~90m
242 north of the main fault trace of the Little Grand Fault and ~285 m to the west of Crystal
243 Geyser (Fig 5). The fault damage zone in the vicinity of the drill site currently emits dry CO₂
244 gas (Allis *et al.*, 2005; Han *pers comms*, 2013) and has hosted CO₂ and CO₂-charged fluid
245 discharge in the geological past, being overlain by ancient travertine deposits (Dockrill and
246 Shipton, 2010; Doelling, 1994; Shipton *et al.*, 2004).

247 3.1.1 Core Stratigraphy and CO₂-Charged Zones

248 The vertical hole was drilled to a depth of 322.5 m using DOSECC's hybrid coring
249 system with >99% core recovery (Fig. 6). Fluid samples were collected during drilling from
250 fluid returns to surface and using a wireline downhole fluid sampling tool to recover fluid
251 samples at formation pressures. The drill hole transected three Jurassic formations; the
252 Entrada Sandstone, Carmel Formation and Navajo Sandstone (Fig. 6-7).

253 From surface, the drill-hole transected ~35 meters of marine and lacustrine red
254 siltstone facies of the 'Earthy' Entrada Sandstone member which grade into the 115 m-thick

255 aeolian dune deposits of the lower Entrada Sandstone, with intercalated marginal marine
256 and sabkha influences throughout (see Crabaugh and Kocurek, 1993). The basal units
257 comprise fine-to medium-grained quartz-arenite to subarkosic sandstone (76–89 wt%
258 quartz, 8.5–16.5 wt% K-feldspar, 2.2–6.5 wt% plagioclase, and trace muscovite, tourmaline,
259 apatite and zircon), variably cemented with quartz, calcite and dolomite (Beitler et al., 2004;
260 Wigley *et al.*, 2012). Free CO₂ gas and CO₂-charged fluids were first encountered in the basal
261 35-150 m of the Entrada Sandstone, which is not overlain by a regional caprock, indicating
262 that thin siltstone layers (such as those within the Entrada) can act as effective seals to the
263 upward migration of CO₂ and CO₂-charged fluids. Zones of CO₂-bearing fluids were identified
264 based on the presence of CO₂-degassing in intervals of the core, and CO₂-charged fluid
265 returns to surface.

266 Below the Entrada lies the Carmel Formation (top at 149 mbs), a 50 m-thick complex
267 sequence of three laterally gradational lithofacies including: (i) interbedded, unfossiliferous
268 red and grey shale and bedded gypsum, (ii) red and grey mudstone/siltstone, and (iii) fine-
269 grained sandstone. These are interpreted as marine sediments deposited in quiet, subtidal
270 conditions under the influence of periodic hypersaline water and form a regional seal
271 (Blakey *et al.*, 1997; Peterson and Turner-Peterson, 1989). Within the Carmel Formation the
272 drill core intersected a ~17m thick fracture zone comprising a ~6m thick core containing
273 meter scale blocks of siltstone and shale breccia hosted in remobilized gypsum beds. These
274 are bound by a zone of intense fracturing, comprising low (1-20°) and high angle (70-89°)
275 gypsum-filled open fractures over a ~2m thick interval in the hangwall and ~9m thick
276 interval in the footwall. The footwall fractures are characterized by high-angle 70-80°
277 striated surfaces with mm to cm normal offsets. The footwall fracture zone was found to
278 bear CO₂-charged fluid.

279 The Carmel Formation is underlain by the ~122m thick Navajo Sandstone which
280 regionally and locally is a homogenous unit comprising thick sets of high-angle cross-
281 bedded, well-sorted, fine- to medium-grained aeolian sandstone with internal stratification
282 (see Verlander, 1995 and references therein). The entire cored interval of the Navajo
283 Sandstone was found to contain CO₂-charged fluid. The Navajo Sandstone in the northern
284 Paradox Basin is a quartz-arenite to subarkosic fine-to medium-grained sandstone,
285 dominated by quartz (72–86 wt.%) and K-feldspar (6–11 wt.%) with minor amounts of
286 plagioclase (1–3 wt%) and trace heavy mineral fractions of tourmaline, apatite and rutile (<1
287 wt.%) (Beitler *et al.*, 2005; Cooley *et al.*, 1969; Harshbarger *et al.*, 1957; Parry *et al.*, 2004).
288 Primary quartz and feldspar grains are rimmed with hematite and goethite (Beitler *et al.*,
289 2005), the sediment is cemented by dolomite (and occasional calcite) and weathered
290 feldspar grains are altered to illite, smectite and kaolinite (Zhu *et al.*, 2006).

291 The Entrada and Navajo Sandstone sampled in the core and in surface outcrops
292 contain zones of open high angle fractures adjacent to the fault, with assemblages of
293 gypsum and pyrite mineralization on the fracture walls (Fig. 6-7). The sandstone units of the
294 middle and lower Entrada Sandstone and the entire sequence of the Navajo Sandstone have
295 been bleached pale white-yellow by dissolution of hematite grain coatings, which normally
296 give these sandstone units a distinctive red colour (Fig. 7). The host rock surrounding high
297 angle fractures are also bleached. The lower portions of siltstone and claystone seals within
298 the Entrada Sandstone and at the base of the Carmel Formation caprock have been
299 bleached by dissolution of hematite grain coatings where they are in contact with the CO₂-
300 rich fluids.

301 No continuous free gas flow (other than that degassed from the fluid within the well-
302 bore) was observed at the well-head whilst drilling in the Navajo Sandstone, even when the
303 hole was unweighted with drilling mud, suggesting that the drill-hole did not penetrate a
304 free CO₂-gas cap, or at least not a substantial one. Pockets of free CO₂ gas were, however,
305 encountered in the shallower Entrada Sandstone at depths of ~50 mbs and ~140 mbs. The
306 CO₂ gas pockets were identified during tripping out of the rods from the drill-hole, where
307 the gas/fluid ratio in fluid returns to surface would rapidly increase when the base of the
308 rods encountered a zone in the formation containing CO₂-gas.

309 Across the anticline, the Jurassic Sandstone reservoirs and deeper Carboniferous and
310 Permian strata in the basin are over-pressured, which drives fluid flow from depth through
311 the faults (Fig 8). Shut-in pressures were recorded periodically during drilling. Zero shut-in
312 pressure was observed during drilling through the Entrada Sandstone, Carmel Formation
313 and through much of the upper Navajo Sandstone, suggesting pressure communication
314 between the formations transected by the drill-hole and Crystal Geyser (which as a flowing
315 well acts as a pressure release). Within the basal Navajo Sandstone a maximum shut-in
316 pressure of 13.8 bar was measured at surface at a drill-hole depth of 221 mbs, equivalent to
317 a downhole pressure of 35.5 bar and formation overpressure of 12.8 bar. This shut-in
318 pressure may overestimate the formation pressure due to accumulation of CO₂ gas within
319 the borehole during measurement which elevates the measured pressure at the wellhead.
320 Regional measurements of hydraulic head in wells penetrating the Navajo Sandstone (Hood
321 and Patterson, 1984) imply a local water head of 46m, equivalent to a formation pressure of
322 26.2 bar and formation overpressure of 3.4 bar.

323 3.2 Fluid Sampling from Drill-hole CO₂W55

324 The reactivity of geological fluids primarily depends on their dissolved CO₂ content
325 and pH. The solubility of CO₂ in formation fluids is highly dependent on pressure and
326 temperature, with fluids saturated in CO₂ at formation conditions rapidly degassing CO₂ at
327 the surface. These degassing processes make sampling of high-pressure fluids from CO₂
328 reservoirs challenging. Accurate measurements of in-situ dissolved CO₂ concentration and
329 pH are crucial for monitoring the progress of CO₂ dissolution and for the prediction of
330 mineral stability and fluid-mineral reactions.

331 Wireline downhole fluid sampling is the most practical means of repeat sampling of
332 pressurized fluids during borehole drilling. Commercially available wireline fluid samplers
333 include the Leutert Bottom Hole Positive Displacement Sampler (PDS sampler), which has
334 previously been used to recover pressurized fluid samples from deep boreholes and
335 geothermal fields (Fig. 9A; Kietäväinen *et al.*, 2013; Regenspurg *et al.*, 2010). The PDS
336 sampler can be used to recover formation fluid samples (~0.6 L) at reservoir pressure from
337 which dissolved gases can be collected (e.g. Regenspurg *et al.*, 2010) and on which in-situ pH
338 and dissolved CO₂ concentrations can be measured on pressurized samples at surface (Fig.
339 9B-D).

340 Both open-hole and downhole fluid samples were collected from drill-hole CO₂W55
341 during drilling. Surface fluid samples were collected from fluid returns to surface and the
342 driller's depth at the time of collection was used to estimate their source depth. Fluid
343 samples were collected from the Entrada Sandstone and Carmel Formation when the drill-
344 hole was at a depth of 98 m and 188 m, respectively. Downhole fluid samples were collected
345 from the Navajo Sandstone at formation pressures using the PDS sampler during the course

346 of drilling. Four fluid samples (~0.6 L) were collected at depths of 206 m, 224 m, 276 m and
347 322 m. In order to collect un-degassed and uncontaminated fluids, the PDS sampler was
348 lowered to the base of the hole and: (i) the hole was allowed to flow for 15-45 minutes to
349 flush out the drilling mud using the natural overpressure of the formation, (ii) the hole was
350 shut in to allow pressure recovery for 1-2 hours and (iii) the sampler was then left down
351 hole for 5-6 hours to collect a fluid sample. Full details of the drilling and fluid sampling
352 methods are presented in Kampman *et al.*, 2013a.

353 3.3 Onsite measurement of dissolved CO₂ and pH

354 The recovered fluid samples in the downhole sampler were transferred into pre-cleaned
355 high-pressure piston separator sample cylinders at a field laboratory, using a hydraulic
356 transfer pump. Details of pH and dissolved CO₂ concentration measurements on the
357 pressurized fluid samples are presented in Kampman *et al.*, 2013a. Fluid pH and dissolved
358 CO₂ concentrations were measured in the field laboratory using high pressure apparatus
359 (Fig. 9C-D), generally within a few hours of sample collection. An aquilot of the fluid sample
360 was pumped from the piston sample cylinders at pressure through a high-pressure pH rig
361 (Fig 9C; Corr Instruments). The pH probe was calibrated prior to each analysis using pH 3,
362 4.01, 6 and 7 reference buffer solutions. The pH cell was flushed with formation fluid until a
363 stable pH was attained and the fluid pH recorded.

364 A second aquilot of sample was pumped at pressure into a 30mL micro piston
365 separator cylinder filled with 15mL of 3M KOH solution (Fig 9D), to capture the dissolved
366 CO₂ in solution by conversion to CO₃²⁻ and precipitation as K₂CO₃ from which total CO₂
367 concentration could be determined by gran titration. A sample of the exsolved CO₂ gas for
368 analysis of carbon and noble gas isotope ratios was then collected from the piston sample

369 cylinder by degassing the fluid into evacuated lengths of copper tubing, sealed by cold
370 welding. The remaining fluid was then pumped through 0.2 μm nylon filters and stored in
371 pre-cleaned high-density polyethylene bottles, prewashed with filtrate; one sample acidified
372 to pH 2–3 with 6M HCl and one un-acidified sample for chemical analyses. An aliquot of
373 each sample was prepared and alkalinity was determined immediately by gran titration in
374 the field.

375 **3.4 Sampling of CO₂ Springs**

376 Individual samples were collected from the nine CO₂-springs along the Green River anticline
377 during field seasons in 2006 (Kampman *et al.*, 2009), 2007 and 2010. Fluid Eh, pH and
378 alkalinity were measured in the field using a platinum ORP electrode, field pH meter and by
379 gran titration, respectively. Fluid samples were collected and prepared as above. Samples
380 for gas composition analysis (CO₂, N₂, Ar, O₂ and CH₄) were collected into tubes of annealed
381 copper, flushed with sample gas, and sealed by swage clamps.

382 **3.5 Monitoring and Sampling Crystal Geyser**

383 Prior to drilling of hole CO₂W55, in 2007, a time-series fluid and gas sample set was
384 collected from the build-up to, and during, a short duration (~1.5 hours) large magnitude
385 Type B eruption of Crystal Geyser. A day prior to drilling of hole CO₂W55 a Level Logger was
386 installed at a depth of ~5 m in the conduit of Crystal Geyser, to monitor changes in
387 temperature and water level of the geyser during the drilling.

388 Within a single eruption cycle (SEC; Fig. 10) Crystal Geyser exhibits a bimodal eruption
389 pattern of large eruption events that last between 1-1.5 hours (Type B; Han *et al.*, 2013) and
390 5-7 hours (Type D; Han *et al.*, 2013) and which occur every 7-10 hours or 20-30 hours,
391 respectively (see also; Gouveia and Friedmann, 2006; Gouveia *et al.*, 2005). Type B and D

392 eruptions are separated by periods of small frequent low magnitude ‘bubbling events’ that
393 occur approximately every 15 minutes, termed Type A and C eruptions following the
394 nomenclature of Han *et al.*, (2013) (Fig. 11). Both small and large eruptions are
395 characterised by a drop in pressure and temperature at the mouth of the geyser and the
396 magnitude of this drop is related to the magnitude of the eruption (Han *et al.*, 2013). CO₂-
397 degassing within the geyser conduit is thought to initiate at a depth of ~120m (Assyag *et al.*,
398 2009). The bimodal pattern of eruptions appears to have evolved through time with
399 eruption durations increasing towards the present (Fig. 11). Only a single Type B eruption
400 was observed during drilling and Type D eruptions were of significantly longer duration (~24
401 hours) and lower frequency (every ~70 hours) than data previously reported for Crystal
402 Geyser.

403 3.6 Analytical Geochemistry

404 The element and isotopic composition of fluids sampled from the drillhole are presented in
405 table 1 and 2, from the CO₂ springs in table 3 and Crystal Geyser in table 5. Major (Na⁺, K⁺,
406 Ca²⁺, Mg²⁺) and minor elements (Al³⁺, B³⁺, Ba²⁺, Fe²⁺, Li⁺, Mn²⁺, Rb⁺, SiO₂, Sr²⁺) were
407 measured on acidified samples by Varian Vista-PRO simultaneous inductively coupled
408 plasma-atomic emission spectrometry (ICP-AES) at the University of Cambridge following
409 the method given in de Villiers *et al.*, (2002) using a mixed standard with cation proportions
410 specifically designed to match the waters to minimise matrix effects. All samples were
411 analysed in two separate runs with reproducibility within ±2%. Analyses were performed
412 against international water standards T-167, T-143, P35, LGC6019 and ION-20 which
413 reproduce to better than ±6% (2σ) for all elements analysed and often < ±1.0% (2σ; Na⁺, K⁺,
414 Ca²⁺, Mg²⁺, Fe²⁺, Li⁺, Mn²⁺, SiO₂, Sr²⁺). Fluid anion (Br⁻, F⁻, Cl⁻ and SO₄²⁻) composition was

415 measured on unacidified samples using a Dionex ICS-3000 Ion Chromatography system at
416 the University of Cambridge. Analyses were performed against international water
417 standards T-167, T-143, P35 and LGC6019 which reproduce to better than $\pm 2\%$ (2σ) for all
418 elements analysed and often $< \pm 0.2\%$ (2σ ; Br^- , Cl^- and SO_4^{2-}).

419 Analysis of major and minor gases (CO_2 , O_2 , N_2 , Ar, CH_4 , H_2S) sampled from the CO_2 -
420 springs was carried out at the British Geological Survey, Wallingford by gas chromatography,
421 using a porous polymer column and a flame ionisation detector (Darling and Goody, 2006;
422 Table 4). The detection limit of this method is better than 1 part per million by volume
423 (ppmv).

424 3.6.1 Fluid Stable Isotopes

425 The $\delta^{18}\text{O}$ and δD of unacidified fluid samples was determined by cavity ringdown
426 spectroscopy using a Picarro L2130-i Analyzer with autosampler injection, in the Godwin
427 Laboratory, University of Cambridge. Each sample was injected nine times into the
428 vaporizer, with the first three results being rejected to avoid memory effects from the
429 previous samples. Values for the final six injections were averaged with in-run precision
430 better than $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.5\text{‰}$ for δD (2σ). Sets of six analyses were performed
431 with bracketing internal standards to calibrate the results to V-SMOW and to account for
432 drift. Internal standards were calibrated against V-SMOW, GISP, and SLAP. All results are
433 reported in parts per thousand (‰) relative to V-SMOW. External error was estimated by
434 repeated analysis of internal standards giving $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1\text{‰}$ for δD (2σ).

435 Sulphur and oxygen isotopes of aqueous sulphate were analysed in the Godwin
436 Laboratory at the University of Cambridge. The $\delta^{34}\text{S}_{\text{SO}_4}$ was determined through combustion
437 in excess oxygen in a Flash EA furnace, coupled by continuous flow to a Delta V Mass
438 spectrometer. The $\delta^{18}\text{O}_{\text{SO}_4}$ was determined through pyrolysis in a TC/EA coupled by

439 continuous flow to a Delta V Mass Spectrometer. Both samples for sulphur and oxygen
440 isotopes were run with NBS 127 standards bracketing sets of samples (NBS 127
441 $\delta^{34}\text{S}_{\text{SO}_4}=20.3\text{‰}$, NBS127 $\delta^{18}\text{O}_{\text{SO}_4}=8.6\text{‰}$). Samples were corrected to NBS127 to account for
442 drift in the mass spectrometer over the course of a run. Data is presented as an average of
443 several replicate measurements with the 2σ standard deviation based on these replicate
444 analyses.

445 3.6.2 Fluid and mineral Sr-isotopes

446 Rock samples for detailed analysis were selected from: (i) representative sections of the
447 Navajo Sandstone in the CO2W55 core (sample depths: 227.8 and 259.7m), (ii) gypsum beds
448 from the Carmel Formation in the CO2W55 core and, (iii) outcrop samples of gypsum and
449 calcite veins associated with bleached portions of the exhumed Entrada Sandstone from Salt
450 Wash Graben, studied by Wigley *et al.*, 2012, 2013a 2013b (Table 6). Powdered samples
451 underwent sequential leaching to obtain solutions for Sr-isotopic analysis of gypsum, and
452 the silicate and carbonate fractions of the sandstones. This was supplemented with a single
453 representative sample of Navajo Sandstone, obtained from a CO₂-free drill-hole Blaze #1-C
454 (USGS core repository, Denver, USA. API: 4301930215) located ~25km to the north east of
455 the Green River anticline (Fig. 1). Samples were subjected to a multi-step sequential
456 leaching procedure using: (i) deionized water, (ii) 10% cold acetic acid (to extract the
457 carbonate fraction) and, (iii) 1M cold HCl (to remove any remaining carbonate). A final
458 solution was produced from the silicate residue using HF digestion.

459 $^{87}\text{Sr}/^{86}\text{Sr}$ of acidified fluid samples and leachates were determined at the University
460 of Cambridge. Strontium was separated by standard cation exchange methods using Dowex
461 50W x8, 200-400 mesh resin with the strontium isotopic ratios determined on the Sector 54
462 VG mass-spectrometer at Cambridge using triple collector dynamic algorithm and

463 normalised to $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.1194 using an exponential fractionation correction (Bickle *et al.*,
464 2003). The internal standard NBS 987 gave 0.710263 \pm 0.000009 (1σ) on 158 separate
465 measurements made during the course of these analyses. Strontium blanks were always
466 less than 250pg and negligible for the Sr concentration of these samples.

467 3.6.3 Quantitative Mineralogy

468 A representative suite of samples of the Navajo Sandstone were selected from the
469 CO2W55 core for quantitative mineralogical analysis by XRD at Aachen University (table 7).
470 Rock samples are crushed manually in a mortar. Special care is taken to avoid strain
471 damage. Crushed material is milled with a McCrone Micronising mill (15 minutes) to assure
472 uniform crystallite sizes. Milling is done in ethanol to avoid dissolution of water-soluble
473 components and strain damage to the samples. An internal standard (Corundum, 20 wt.%) is
474 added before milling. All reported mineral compositions relate to the crystalline content of
475 the analysed samples.

476 Mineral quantification is performed on diffraction patterns from random powder
477 prepares. Sample holders are prepared by means of a side filling method, which minimises
478 preferential orientation. The measurements are done on a Huber MC9300 diffractometer
479 using $\text{CoK}\alpha$ -radiation produced at 40 kV and 40 mA. The sample is illuminated through a fixed
480 divergence slit (1.8 mm, 1.45°), a graphite monochromator and 58 mm, 0.3 mm spacing
481 soller slits. The diffracted beam is measured with a scintillation detector. Counting time is 20
482 seconds for each step of $0.02^\circ 2\theta$. Diffractograms are recorded from 2° to $92^\circ 2\theta$.
483 Quantitative phase analysis is performed by Rietveld refinement. BGMN software is used,
484 with customised clay mineral structure models (Ufer *et al.*, 2008).

485 **4 Results and Discussion**

486 The following sections discuss the results of geochemical measurements on open-hole and
487 downhole fluid samples collected from the CO₂W55 drill-hole in 2012. The results are
488 compared to geochemical measurements on fluid samples from the wider CO₂-springs and
489 eruptions of Crystal Geyser. Interpretation of the data is supported by published formation
490 fluid chemistries from CO₂-charged reservoirs in the deeper Permian White Rim Sandstone
491 and Pennsylvanian Paradox Formation obtained during oil exploration drilling on the Green
492 River anticline (Supplementary Table 1; Breit and Skinner, 2002). Element and isotope
493 geochemical profiles and mixing diagrams are used to constrain the sources of fluids in the
494 CO₂ reservoirs and fault, fluid flow, fluid-fluid mixing and fluid-rock reaction in the CO₂-
495 charged sandstones. The results are compared to preliminary petrographic and
496 mineralogical observations from core-samples to constrain the CO₂-promoted fluid-rock
497 reactions.

498 **4.1 CO₂ concentrations, alkalinity and pH in downhole fluid samples**

499 In-situ CO₂ concentrations and fluid pH within the Navajo Sandstone were measured on
500 pressurized downhole fluid samples collected during drilling (Table 1). CO₂ concentrations
501 measured from high pressure samples increase systematically from 511 mmol/L to 927
502 mmol/L towards the base of the Navajo Sandstone (Fig. 12A-B; Table 1). Fluid pH decreases
503 from 5.3 to 5.1 and alkalinity increases from 51 mmol/L to 64 mmol/L from the top of the
504 formation to the base (Fig. 12A). The measured total dissolved CO₂ concentrations and
505 concentrations estimated from the measured in-situ pH and alkalinity using PHREEQC
506 (Parkhurst and Appelo, 1999) are in good agreement (Fig. 12B). Gradients of the theoretical
507 concentration of CO₂ at saturation in the Navajo Sandstone were calculated using the

508 equations of Duan *et al.*, (2006) and the measured fluid salinity profile, a temperature
509 profile estimated from a local geothermal gradient of 21.2 °C/km (Heath *et al.*, 2009), a
510 surface temperature of 12 °C and a hydrostatic pressure gradient (Fig 12B). The measured
511 CO₂ concentrations at the base of the formation are close to theoretical CO₂ saturation at
512 hydrostatic pressures, and decrease up-wards becoming increasingly undersaturated at
513 shallower depths.

514 **4.2 Gas geochemistry and groundwater redox state**

515 The CO₂-charged groundwaters within the Navajo Sandstone are mildly reducing (Table 3).
516 The Eh of the fluid emanating from the CO₂-springs, measured using a platinum ORP
517 electrode, ranges from ~0mV to ~-50mV. Such Eh measurements are susceptible to
518 incorporation of O₂ in the turbulent spring waters, and these measurements most likely
519 represent an upper bound.

520 The composition of the gas exsolved from the CO₂-springs (Table 4) is dominated by
521 CO₂ (80.5 to 97.1%), with minor quantities of N₂ (2.27 to 18.1%) and Ar (0.54 to 1.91%), and
522 trace CH₄ (73 to 247 vpm). The redox state of the spring waters was calculated using
523 PHREEQC and the measured CO₂/CH₄ ratio of the exsolved gas, (assuming the fluids are CO₂
524 saturated at depth and given near quantitatively exsolution of the gas taking into account
525 that ~10% of the CO₂ remains in the fluid when they degas) and this implies a fluid Eh in the
526 range of ~-100 to -150mV, which represents a lower bound.

527 **4.3 Element and isotope geochemistry: Overview**

528 The fluid samples from the Entrada Sandstone and Carmel Formation were collected
529 at surface. The fluid samples from the Navajo Sandstone include both the four samples
530 collected downhole at formation pressure and thirteen samples collected at surface.

531 Cementation of the drillhole during the course of drilling isolated the Entrada Sandstone
532 and Carmel Formation after they had been sampled, preventing significant contamination of
533 fluids sampled from the Navajo Sandstone with fluids from these shallower reservoirs.
534 Within the Navajo Sandstone, scatter is observed in the open-hole fluid samples collected at
535 surface compared to the downhole samples (Figs. 14-15, 17, 18), probably due to mixing of
536 fluids from different source depths within the well-bore and possible contamination during
537 collection at surface. This is especially apparent for deeper samples from the Navajo, where
538 these fluids are likely mixed with fluids from shallower portions of the formation, as they
539 ascend to surface. Due to this apparent fluid mixing within the wellbore the surface sampled
540 fluids from the Navajo Sandstone are presented but are not used in our interpretation.

541 The fluid samples collected from the Entrada Sandstone, Carmel formation fracture
542 zone and the detailed profile through the Navajo Sandstone reveal systematic trends in fluid
543 element and isotope geochemistry with depth (Fig. 12-18; Table 1-2). The acidic fluids of the
544 Entrada, Carmel and Navajo formations contain high concentrations of Na, K, Cl, SO_4^{2-} and
545 HCO_3^- , and concentrations of these elements generally increase with depth within the drill-
546 hole (Fig. 13-14). These CO_2 -charged Ca-Mg-Na-K-Cl- SO_4^{2-} - HCO_3^- waters share a genetic
547 relationship, which is evident from mixing plots of fluid element and isotope geochemistry
548 (see discussions below). Within the Navajo Sandstone, concentrations of most major (Na, K,
549 HCO_3^- , Cl and SO_4^{2-}) and some minor elements (B, Br, Li, Rb) increase systematically from the
550 top to the base of the formation (Fig 13-14). The observed increase in fluid salinity towards
551 the base of the Navajo formation is accompanied by progressively heavier S-, O- and D-
552 isotopic compositions and increasingly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 15-17).

553 The gradients in fluid chemistry (B, Br, Li, Rb, Na, K, Cl) and dissolved CO_2
554 concentrations are shown below to reflect conservative mixing between two components

555 inferred to be: (i) deeply sourced CO₂-saturated brines flowing vertically into the formations
556 from the Little Grand Wash fault and (ii) CO₂-undersaturated fluid dominated by meteoric
557 groundwater flowing horizontally into the fault zone. The dense CO₂-saturated brines
558 introduced along the faults are presumed to flow along the base of the formations, and mix
559 with meteoric fluid. A second suite of elements (Al, Si, Sr, Ca, Mg, Fe and Mn) and the Sr-
560 isotopic compositions of the fluids sampled from the borehole exhibit non-conservative
561 behaviour in the brine endmembers and mixtures. In the sections below, element and
562 isotope mixing diagrams and Sr-isotopic analysis of minerals are combined with
563 mineralogical and petrographic observations and used to show that these components of
564 the fluids are buffered by fluid-rock reactions involving gypsum, carbonate (dolomite and
565 calcite) and hematite.

566 **4.4 Fluid-fluid interactions: brine-meteoric water mixing**

567 Fluid sampled from the drill-hole, Crystal Geyser and the regional CO₂-springs are
568 enriched in halogens (e.g. Cl, Br), sulphate, and alkali and alkaline metals (e.g. Na, K, B, Li,
569 Rb) typical of brines derived from evaporite formations (Fig. 13-14; e.g. Warren, 2010). The
570 Paradox Basin contains thick deposits of evaporites in the Middle Pennsylvanian Paradox
571 Formation and brine-rich aquifers in the Pennsylvanian Hermosa Formation and
572 Mississippian Leadville Limestone (Fig 2; Hanshaw and Hill, 1969; Hite, 1968; Wengerd and
573 Strickland, 1954). Intrusion of brine from these formations into overlying meteoric aquifers
574 occurs in several places across the Paradox Basin (e.g. Spangler *et al.*, 1996 Naftz *et al.*,
575 1997). All the fluids sampled from the drillhole, Crystal Geyser and the wider CO₂ springs
576 plot along arrays in Br/Cl, Li/Cl, B/Cl and Rb/Cl space, with element/Cl ratios consistent with
577 brines derived from the Paradox Formation (Fig 19; brine chemistries from Rosenbauer *et*
578 *al.*, 1991 and the USGS formation water database; Breit and Skinner, 2002). Within the

579 Navajo Sandstone, increasing fluid salinity is accompanied by increasingly heavy $\delta^{18}\text{O}$ and
580 δD isotope ratios (Fig. 15), reflecting mixing of isotopically heavy brines from the Paradox
581 formation with isotopically light meteoric groundwater (c.f. Kampman *et al.*, 2009;
582 Wilkinson *et al.*, 2009). In $\delta^{18}\text{O}$ and δD space, all fluid samples plot on a two-component
583 mixing array between meteorically derived groundwater, lying on the North American
584 Meteoric water line, and brines from the Carboniferous formations (Fig. 20; Paradox
585 Formation brine stable isotopic composition from Spangler *et al.*, 1996; $\delta^{18}\text{O} = 2.2\text{‰}$ and δD
586 $= -42\text{‰}$).

587 Fluid salinity and $\delta^{18}\text{O}$ and δD ratios increase in the order Entrada < Carmel < Navajo
588 drill-hole < Crystal Geyser fluid < regional CO_2 springs (Fig. 14-16). The concentrations of Br
589 and Cl (and possibly B, Li and Rb concentrations and $\delta^{18}\text{O}$ and δD ratios) appear to act as
590 conservative tracers in these sandstone reservoirs, being little affected by fluid-rock
591 reaction. Some scatter in Br concentrations in the most saline of the springs may reflect
592 variability in the composition of the brine inputs. The brine-meteoric dilution line is
593 preserved in formation fluid samples collected from CO_2 -reservoirs in the White Rim
594 Sandstone and Carboniferous strata during oil exploration drilling on the anticline,
595 suggesting mixing of meteoric groundwaters at depth within the basin (Fig. 21-22,
596 Rosenbauer *et al.*, 1991; Breit and Skinner, 2002).

597 The fraction of Carboniferous brine in the CO_2 springs, calculated from the
598 conservative tracers (Cl and Br), exhibits a minimum at Airport Well, where CO_2 enters the
599 Navajo Sandstone without significant inputs of Carboniferous brine, and a maximum of
600 5.14% in the most saline of the regional CO_2 springs. Carboniferous brine inputs increase
601 along fluid flow paths within the Navajo Sandstone parallel to the faults, sampled by the
602 CO_2 -springs (Fig. 23). Within the CO2W55 drillhole the brine fraction increases

603 systematically with depth; the Entrada Sandstone fluid contains 0.55% Carboniferous brine;
604 the Carmel fracture zone fluid contains 0.69% Carboniferous brine and within the Navajo
605 Sandstone the Carboniferous brine fraction increases with depth from 0.71% at the
606 formation top to 1.93% at the base, where fluid enriched in Carboniferous brine flowing in
607 from the fault is sampled. Crystal Geyser contains a maximum of 2.99% Carboniferous brine
608 in the most saline fluid sampled. It is located close to the main fault trace (Fig. 3; ~45m
609 versus 90m for the drill-hole) and it is therefore likely that Crystal Geyser samples more
610 Carboniferous brine enriched fluid within the Navajo Sandstone, before it is diluted with
611 meteoric groundwater during flow away from the fault (where it is then subsequently
612 sampled from the drill-hole).

613 **4.5 Fluid-Rock Reaction**

614 4.5.1 Fluid-rock reactions in Jurassic sandstones: regional and local sandstone bleaching

615 Dissolution of hematite grain coatings is a common feature within the Jurassic red-
616 bed sandstones of the Paradox Basin and wider geographic region, where it produces
617 spectacular wide-spread zones of sandstone bleaching, which records passage of the
618 bleaching fluid. The bleaching has variously been attributed to reaction with buoyant
619 hydrocarbons and methane rich brines (Beitler *et al.*, 2003, 2005; Chan *et al.*, 2000; Garden
620 *et al.*, 2001; Parry *et al.*, 2004, 2009) and with dense CO₂-charged brines containing
621 methane or sulphide reductants (Loope *et al.*, 2010, 2011; Potter-McIntyre *et al.*, 2013;
622 Wigley *et al.*, 2012, 2013a, 2013b). Such acid-reductive hematite dissolution is possible with
623 a wide range of naturally occurring sources of acidity (e.g. CO₂, organic acids, H₂S) and
624 reductants (e.g. CH₄, HS⁻, H₂S) and different combinations most likely act as the bleaching
625 agent in different places. At Green River bleaching of exhumed portions of the red-bed
626 Entrada Sandstone has previously been attributed to the passage of CO₂-charged brines,

627 with minor quantities of dissolved CH₄ (Wigley *et al.*, 2012). The presence of these CO₂-rich
628 brines has been inferred from analysis of CO₂-CH₄ bearing fluid inclusions within secondary
629 mineral phases and from the isotopic composition of secondary carbonate cements
630 associated with the bleaching (Wigley *et al.*, 2012; Wigley *et al.*, 2013b).

631

632 4.5.2 Fluid-rock reactions in the CO2W55 drill-hole

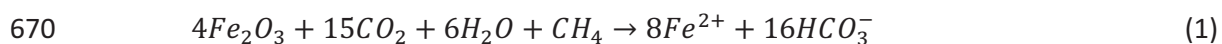
633 The concentrations of Ca, Mg, Sr, Fe, Mn, Si, Al and SO₄, and ⁸⁷Sr/⁸⁶Sr, δ³²S_{SO42} and
634 δ¹⁸O_{SO42} ratios in fluids sampled from the Entrada, Carmel and Navajo formations are
635 decoupled from the simple Carboniferous brine-meteoric groundwater mixing trends (Fig.
636 16-18, 33). The concentrations of these elements are most likely altered by fluid-rock
637 reactions with the primary sources being: dolomite cements within the Navajo Sandstone,
638 dolomite and calcite cements within the Entrada Sandstone, gypsum beds and veins in the
639 Carmel and Entrada formations and hematite and clay grain coatings within the sandstones.
640 Results of sequential leaching for Sr-isotopic composition of the dolomite and silicate
641 fractions of the Navajo Sandstone from the CO2W55 core, and of gypsum beds and veins
642 from the Carmel Formation and Entrada Sandstone are presented in figure 24. Samples of
643 gypsum veins in the Entrada Sandstone from the CO2W55 core were supplemented with
644 samples of gypsum and calcite veins sampled from fracture zones in outcrops of bleached
645 portions of the Entrada Sandstone at Salt Wash Graben (Table 6; Fig. 8, 24). Their Sr-isotopic
646 composition are compared to samples of hematite concretions and calcite veins from
647 bleached portions of the Entrada Sandstone where the bleaching is thought to occur
648 without significant inputs of CO₂ (Fig. 24; Chan *et al.*, 2000).

649 Fluids sampled from the base of the Navajo Sandstone are undersaturated in
650 carbonate (Fig. 25A), hematite (Fig. 25B), feldspar (Fig. 25C-D), clay (Fig. 25C-D), sulphate

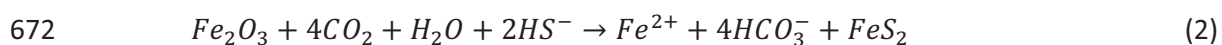
651 (Fig. 25E) and silica (Fig. 25F) minerals. The saturation state of most minerals increases from
652 the base of the formation to the top, with dolomite, hematite, albite, kaolinite, K-feldspar
653 and quartz reaching saturation, or over-saturation at the top of the formation. Similarly
654 elevated mineral saturation states are observed in fluids sampled from the Entrada
655 Sandstone and Carmel Formation (Fig. 25).

656 Within the Navajo Sandstone fluid sample profile the Ca, Mg, Sr, Fe, Mn, Si and Al
657 concentrations are relatively constant through the formation increasing near the top of the
658 reservoir, close to the contact with the Carmel formation (Fig. 18). The downhole fluid
659 samples from the Navajo Sandstone exhibit changes in Ca, Mg and Sr concentration and
660 Mg/Ca and Sr/Ca ratios that are consistent with the dissolution of dolomite (Fig. 26).
661 Quantitative mineralogy of representative samples from the Navajo Sandstone show that
662 the CO₂-charge reservoir unit is depleted in hematite, calcite and feldspar and enriched in
663 dolomite and clay, compared to a compilation of representative unbleached Navajo
664 Sandstone samples from the wider Paradox Basin (Fig. 27). The dissolution of hematite grain
665 coatings, assemblages of gypsum and pyrite in open fractures and presence of dissolved CH₄
666 in the reservoir fluids suggests the bleaching reactions may occur through a series of linked
667 reactions involving CO₂ as well as a range of reduced species following reaction
668 stoichiometries such as:

669



671



673

674 The fluids contain high concentrations of dissolved sulphate; reduced sulphur species may
675 be present in a meta-stable state, arising from inorganic reduction involving other reduced
676 species or from the activity of sulphur reducing bacteria, commonly present in groundwater
677 systems (e.g. Chapelle *et al.*, 1992). The distribution of dolomite in the core is highly
678 heterogeneous with some areas containing extensive zones of pore-occluding Fe-rich
679 dolomite cements, whilst other areas are free of cement and contain abundant secondary
680 porosity (Fig. 27, 28). The dolomite cements are Fe-rich, complexly zoned and overgrow
681 corroded Fe-poor cores, interpreted to be original early diagenetic dolomite cement (Fig 28A-
682 B). The zoned cements contain evidence of variable repeated dissolution and reprecipitation
683 events, with the amount of dissolution-reprecipitation increasing towards the base of the
684 core (Fig. 28C).

685 The Entrada Sandstone fluid is enriched in Ca, Mg, Sr, Fe and SO₄ relative to fluid
686 from the Carmel Formation and Navajo Sandstone, without a corresponding change in
687 conservative ion tracer (Fig. 13, 17, 18). Elevated concentrations of Ca, Mg, Sr and SO₄ and
688 lower ⁸⁷Sr/⁸⁶Sr ratios in the Entrada Sandstone most likely reflect additions of Sr to the fluid
689 from the dissolution of dolomite and/or calcite and gypsum. High concentrations of Fe in
690 the Entrada Sandstone fluid are in excess of those expected for dissolution of carbonate
691 minerals (Fig. 26) and most likely reflect dissolution of hematite grain coatings present in
692 the Entrada Sandstone. Depressed ⁸⁷Sr/⁸⁶Sr ratios in the Carmel Formation (Fig. 17) may
693 reflect inputs of low ⁸⁷Sr/⁸⁶Sr from the dissolution of gypsum beds in-contact with the fluid
694 hosting fracture zone.

695 **4.6 Fluid sources and fluid-fluid mixing during eruptions of Crystal Geyser**

696 Time-series fluid samples collected from Crystal Geyser exhibit a systematic trend in fluid
697 element and isotope geochemistry through the course of an individual eruption (Fig. 29-30).

698 Changes in fluid geochemistry and temperature coincide with the onset of an eruption and
699 these changes reflect sampling of fluids from different source depths. During the build-up to
700 an eruption the geyser predominantly samples Na-K-Cl-SO₄-HCO₃ enriched fluid from the
701 Navajo Sandstone (Fig 29); as an eruption initiates Ca-Mg-Sr-Fe-Mn enriched fluid is
702 increasingly sampled and this is thought to originate from the Entrada sandstone (Fig 30).
703 These fluid end-members mix within the geyser conduit. This mixing process is evident from
704 element and isotope mixing diagrams, where fluids sampled from the geyser plot along
705 binary mixing arrays between the most saline fluid sampled by the geyser and the Entrada
706 fluid end-member (Fig 31, 32). Increased concentrations of Ca, Mg, Sr, Fe and Mn are
707 accompanied by shifts in the ⁸⁷Sr/⁸⁶Sr ratio of the fluid as the geyser samples less radiogenic,
708 carbonate enriched waters from the Entrada Sandstone. The compositional trends are
709 accompanied by changes in fluid temperature from ~18.5 °C in the build-up to an eruption,
710 declining to ~16.8 °C during the eruption as inflow of fluid from the shallower cooler
711 Entrada Sandstone reservoir increases (Fig. 12). The proportion of Entrada Sandstone Fluid
712 in the erupted fluids varies from a minimum of ~1-7% during the build-up to an eruption, to
713 a maximum of ~31% during a large Type B eruption.

714 **4.7 Complex fluid-fluid mixing within the reservoirs and fault**

715 In Br versus Cl space the fluids sampled from the drill-hole, springs and geyser plot
716 along a single linear binary mixing line reflecting variable dilution of the Carboniferous brine
717 inputs by meteoric groundwaters (Fig 31A & C). In plots of Sr (or Ca, Mg, Fe and Mn) versus
718 Cl (or Br) the fluids plot on a mixing plane due to inputs to the fluid from mineral dissolution
719 (Fig 31B, 31D-F 32). Below, we discuss mixing phenomena that happen at different spatial
720 scales and result from the mixing of fluids which are themselves already mixtures of
721 Carboniferous brine and meteoric groundwaters; the spatial sampling of fluids within the

722 Navajo Sandstone allows sampling of fluids at different stages of mixing, such that each pair
723 of samples that spatially brackets another sample are 'end-members' to the intermediate
724 mixture. The term end-member is used here to define any pair of fluid samples that bracket
725 an intermediate mixture, and does not necessarily imply that the end-member is a pure
726 fluid (i.e. end-members are also mixtures)

727 The fluids sampled from the drill hole and Crystal Geyser plot on two distinct binary
728 mixing arrays, with one common end-member representing saline CO₂-charged brine from
729 the fault (Fig. 31D-F; Fault Brine). This common end-member (Fault Brine) is estimated as
730 the most saline fluid sampled by Crystal Geyser, which also demarks the intersection of
731 binary mixing lines in Sr-Cl space. Samples taken during the eruption of Crystal Geyser plot
732 along a linear array between a Carboniferous brine-rich end-member (Fault Brine) and an
733 end-member fluid that may be derived from the Entrada Sandstone (Entrada Sandstone
734 Fluid). This end-member is distinctively enriched in Sr, Ca, Mg and Fe, most likely derived
735 from carbonate and hematite dissolution (Fig. 31D-F). Downhole fluid samples from the
736 Navajo Sandstone plot along an array between a Carboniferous brine-rich end-member
737 (Fault Brine; with a slightly less radiogenic Sr-isotopic composition than the saline fluid
738 sampled from Crystal Geyser) and an end-member fluid similar in composition to the
739 fracture zone in the Carmel Formation (Fig. 31D-F; Carmel Fm. Fluid). The fluid sample
740 profile through the Navajo Sandstone contains between ~54% 'Fault Brine' at the base of
741 the formation, decreasing to ~1% at the formation top. These trends and proportions are
742 similarly observed in plots of ⁸⁷Sr/⁸⁶Sr versus 1/Sr and 1/Cl (Fig. 31). The three 'end-member'
743 fluids 'Fault Brine', 'Entrada Sandstone Fluid' and 'Carmel Fm. Fluid' are themselves
744 mixtures of Carboniferous brine and meteoric groundwater. They also bracket the
745 intermediate mixtures of fluids sampled within the Navajo Sandstone and from Crystal

746 Geyser. It is likely that fluids within the Entrada Sandstone and Carmel fracture zone will
747 have a range of compositions, but as only two samples were collected, they are treated as
748 representative of the fluids present in these formations, which likely have a range in
749 compositions.

750 The validity of these mixing models can be tested by using the mixing arrays defined
751 by fluid sampled from Crystal Geyser and the downhole fluids sampled from the Navajo
752 Sandstone to estimate the solute chemistry of the end-member fluids. The solute chemistry
753 of the end-member fluids can be estimated from the mixture compositions and their
754 element/Cl ratios, and the measured Cl concentrations of the inferred end-members. The
755 results are presented in table 8 and show that the mixing models generally predict the
756 solute chemistry of the end-members within ± 10 -15% for most elements, with Fe being a
757 notable exception, and better than $< \pm 5\%$ for many. The model predicts the composition of
758 the Entrada end-member reasonably well, which relies on the array defined by fluids
759 sampled from Crystal Geyser; this mixing happens quickly within the conduit of Crystal
760 Geyser, and is thus less susceptible to modification by fluid-rock reaction. The model is less
761 able to predict certain elements (notably Ca, Mg, Sr, Fe Mn, and HCO_3) in the Fault Brine and
762 Carmel Formation end-member compositions, estimated from the mixing array defined by
763 the downhole Navajo fluid samples, possibly because fluid mixing and fluid flow rates here
764 are slow, relative to the rates of potential fluid rock reactions involving carbonate and Fe-
765 oxide minerals.

766 Within the Navajo Sandstone Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase
767 systematically with depth, becoming increasingly radiogenic towards the base of the
768 formation and as salinity increases, to a maximum $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71213 (Fig 17; 31E-F).
769 In fluids sampled by Crystal Geyser, Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase as

770 salinity, and brine fraction of the sampled fluid increases, to a maximum $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of
771 0.712726, in the most saline fluid sampled (Fig 31E-F). Carboniferous age brines from the
772 Paradox Basin typically have non-radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, close to Pennsylvanian or
773 Mississippian seawater (e.g. Fig 24-25; 0.70845 to 0.70864; Spangler *et al.*, 1996 Naftz *et al.*,
774 1997). The radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the CO_2 -charged brines flowing into the Navajo
775 Sandstone from the fault reflects addition of radiogenic Sr from silicate mineral dissolution
776 reactions during migration of the CO_2 -charged brines from depth.

777 Sr concentration and Sr-isotope gradients in the Navajo Sandstone reflect a
778 combination of fluid-rock reaction and fluid-fluid mixing trends between Sr-rich radiogenic
779 CO_2 -saturated brines flowing in from the faults, low $^{87}\text{Sr}/^{86}\text{Sr}$ meteoric enriched fluids
780 flowing laterally into the fault zone and low $^{87}\text{Sr}/^{86}\text{Sr}$ fluids descending from the fracture
781 zone in the Carmel Formation. These mixing plots suggest that within the Navajo Sandstone:
782 (i) the most saline fluids sampled from the drillhole is derived from dilution of a
783 Carboniferous brine rich fluid comparable to fluid sampled by Crystal Geysir, and presumed
784 to be input along the base of the formation from the fault, (ii) that this brine-rich fluid mixes
785 with CO_2 -charged, but brine-poor, fluid flowing parallel to the fault, similar to that sampled
786 earlier on the flow path by Airport Well, (iii) this mixture then flows through fractures into
787 the overlying Carmel Formation caprock.

788 This interpretation is supported by data on the isotopic composition of SO_4^{2-} in these
789 fluids, which reflect sequential dilution of fluid enriched in isotopically heavy sulphate with
790 an isotopically light sulphate-rich fluid flowing horizontally into the fault zone, which then
791 flows upwards through fractures in the Carmel Formation caprock (Fig. 33). A conceptual
792 model illustrating the overall patterns of fluid flow and fluid-fluid mixing within the fault
793 and region surrounding the drill-hole is presented in figure 34.

794 **4.8 Estimating dissolved CO₂ concentration in end-member fluids**

795 Cross plots of the fraction of end-member fluids in downhole fluid samples from the Navajo
796 Sandstone versus their measured DIC form linear arrays from which the total DIC of end-
797 member fluids can be estimated (presented in Fig. 35). The inflowing Carboniferous brine
798 from the fault and Carmel Formation fluid end-members have estimated DIC concentrations
799 of 1.37 mol/L and 0.56 mol/L respectively, of which 1.30 mol/L and 0.50 mol/L are dissolved
800 CO₂, the remainder being HCO₃⁻. The estimated CO₂ concentration of fluid flowing into the
801 Navajo Sandstone from the fault is higher than the average theoretical CO₂ saturation
802 (~1.08 mol/L) at formation temperature and fluid pressure for fluid within the Navajo
803 Sandstone, at the site of Crystal Geyser. This suggests that the brine end-member may be
804 degassing as it decompresses within the fault zone. The estimate of the theoretical CO₂
805 solubility was calculated using the equations of Duan et al. (2006), using the fluid
806 composition of the fault brine end-member, a geothermal gradient of 21.2°C/km and a
807 hydrostatic pressure gradient. The theoretical CO₂ saturation for fluid from within the
808 Carmel fracture zone is 0.68 mol/L, and the estimated CO₂ concentration corrected for
809 alkalinity is 0.50 mol/L, suggesting the fluid sampled from the fracture zone maybe CO₂-
810 undersaturated.

811 **4.9 Estimating CO₂ dissolution during CO₂ and CO₂-charged brine migration from the** 812 **deep supercritical reservoirs**

813 The shallow Jurassic Entrada (0.55% Carboniferous brine) and Navajo Sandstones (1.93%
814 Carboniferous brine) and the deeper Permian White Rim Sandstone reservoirs (10.73%
815 Carboniferous brine) are fed by flow of CO₂-saturated brines from deep supercritical CO₂-
816 charged Carboniferous reservoirs (Fig. 2, 21). The dissolved CO₂ concentrations in brines of
817 the deeper Permian White Rim Sandstone and Carboniferous formations can be estimated

818 from the CO₂-solubility equations of Duan *et al.*, 2006 and the known salinity, pressure and
819 temperature gradients through the basin (Fig 21); the theoretical saturated CO₂
820 concentrations in the White Rim Sandstone and Carboniferous formations are ~1.3 mol/L
821 and ~0.4-0.8 mol/L, respectively. The migrating Carboniferous brines undergo substantial
822 dilution with meteoric groundwaters in the shallow reservoirs and fault; this would lead to a
823 concomitant dilution of the dissolved CO₂ concentration of the brines. The amount of
824 dissolved CO₂ in the Permian and Jurassic sandstone reservoirs, that originates as a
825 dissolved phase in the CO₂-charged Carboniferous brines, can be estimated from the CO₂/Cl
826 of the Carboniferous brine (0.42:4.2 moles/L) and the measured or estimated CO₂/Cl ratios
827 of the sandstone formation fluids (White Rim: 1.32:0.45 moles/L and Navajo: 0.93:0.08
828 moles/L). The Carboniferous brine-meteoric groundwater dilution factors imply that >~99%
829 of the CO₂ in fluids sampled from the Navajo Sandstone is derived after the fluids have
830 migrated from the Carboniferous reservoirs, with ~75% of the dissolved load being acquired
831 during migration from the White Rim Sandstone to the Navajo Sandstone. This implies that:
832 (i) both free phase CO₂ and brine co-migrate from the deep Carboniferous reservoirs, (ii)
833 that brine-meteoric water mixing in the vicinity of the fault zone is an effective means of
834 dissolving this migrating CO₂ and, (iii) that such fluid-fluid interactions can efficiently retard
835 the migration of free phase CO₂ to the surface. A significant fraction of the CO₂-migrating
836 from the deeper Carboniferous reservoir is then likely transported away from the faults by
837 regional groundwater flow (e.g. Bickle and Kampman, 2013).

838 **5 Conclusions**

839 For the first time core and pressurized downhole fluid samples have been obtained
840 from a natural CO₂ reservoir and caprock. The CO2W55 drill-hole transected a series of CO₂-

841 charged reservoirs within the Jurassic Entrada and Navajo Sandstones, and a CO₂-charged
842 fracture zone in the Carmel Formation caprock. Fluid geochemistry and analysis of in-situ pH
843 and CO₂ concentrations, using pressurized fluid sampling whilst drilling, shows that the
844 reservoirs are being fed by active inflow of CO₂-saturated brines from the faults, originally
845 derived from reservoirs of supercritical CO₂ in Carboniferous strata at depths of >2km. The
846 evidence for CO₂-saturated fluids at the base of the Navajo requires that a mixture of
847 Carboniferous brine and free-phase CO₂ must be introduced from the fault zone. The
848 absence of a free CO₂ gas cap within the Navajo Sandstone requires that this gas is
849 effectively dissolved and dissipated in the Navajo Sandstone formation fluids. Pockets of
850 free CO₂-gas were encountered in the shallow Entrada Sandstone, suggesting that the CO₂-
851 saturated fluids degas within the fault and shallow reservoirs above the base of the Navajo
852 Sandstone, and that this free CO₂ gas is the source of the surface CO₂ flux. Comparison of
853 the sampled fluid geochemistry to analyses of brine compositions from the deep White Rim
854 Sandstone and Carboniferous CO₂ reservoirs suggests that: (i) CO₂ and CO₂-charged brines
855 co-migrated from the deep reservoirs, (ii) the CO₂-saturated brines migrating from depth
856 interact with significant volumes of meteoric groundwater in aquifers in the shallower
857 Permian and Jurassic sandstones, diluting the brine composition, and (iii) that a significant
858 fraction of the CO₂ migrating from depth is dissolved in these migrating brine-meteoric
859 water mixtures, with >99% of the CO₂ in fluids sampled from the Navajo Sandstone being
860 derived during fluid migration, after the fluids left their source reservoir. The ⁸⁷Sr/⁸⁶Sr ratio
861 of the inflowing brine is significantly elevated for ratios expected for Sr in Carboniferous
862 brines, requiring significant fluid-rock reaction and addition of radiogenic Sr from silicate
863 mineral dissolution, during fluid migration.

864 Element and isotope geochemistry of fluid samples from the drillhole and Crystal
865 Geyser constrain mixing models which show that within the Navajo Sandstone the reservoir
866 fluids are undergoing complex mixing of: (i) CO₂-saturated Carboniferous brine inflowing
867 from the fault, (ii) CO₂-undersaturated meteoric groundwater flowing through the reservoir
868 and (iii) reacted CO₂-charged brines flow through fracture zones into the formations above.
869 Element and isotope geochemistry of time-series fluid samples from Crystal Geyser reveals
870 that the geyser is fed by fluids from both the Entrada and Navajo Sandstones. Onset of a
871 large-scale eruption coincides with a change in this fluid source. Whether the change in fluid
872 source is a response or a trigger for the onset of the eruptions is not known.

873 CO₂-charged fluids flowing through the Navajo Sandstone both dissolve and
874 precipitate dolomite at different spatial and temporal scales. CO₂-charged fluids flowing
875 through the Entrada Sandstone dissolve dolomite, calcite, gypsum and hematite. The
876 hematite content of the Navajo and Entrada Sandstones is significantly reduced where they
877 are in contact with the CO₂-charged fluids, bleaching it from red to pale white. This suggests
878 that the CO₂-charged brines have dissolved the hematite grain coatings originally present in
879 the sediment, supporting interpretations from elsewhere that CO₂-charged brines with CH₄
880 or H₂S reductants can cause sandstone bleaching.

881 The results of this study highlight the important potential retentive capacity of the
882 geological overburden above deep CO₂ reservoirs, for retarding CO₂ migration to the
883 surface. This capacity is site specific and future CO₂ storage programs should include a study
884 of the formations overlying the target reservoir including the hydrodynamics, permeability
885 and fluid geochemistry of overlying aquifers, in order to understand the likely migration
886 pathways of leaking CO₂-charged fluids and the trapping potential of the geological
887 overburden.

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1133 **Figure 1** Geological features of the Paradox Basin and surrounding region. (a) Structural
 1134 provinces of the Paradox Basin and bordering uplifts (redrawn after Condon, 1997). (b) Main
 1135 structural features of the Northern Paradox Basin, in the vicinity of the study area. The
 1136 outlined area in grey is the maximum extent of the Pennsylvanian evaporite formations
 1137 which demarks the extent of the Paradox Basin. Yellow stars denote the locations of CO₂-
 1138 charged springs or regions of dry CO₂ exhalations.

1139

1140 **Figure 2** Generalized stratigraphic section for the Green River area. Thickness data compiled
 1141 from Trimble and Doelling (1978) and Hintze (1993). Hydrological data from Hanshaw and
 1142 Hill (1969) and Hood and Patterson (1984).

1143

1144 **Figure 3** Geological map of the Green River anticline showing locations of the Little Grand
 1145 Wash and Salt Wash Graben normal fault systems, CO₂-springs and location of drill-hole
 1146 CO2W55 (base map redrawn after Doelling, 2001 & Kampman *et al.*, 2009). The distribution
 1147 of ancient travertine mounds along the faults is highlighted, reflecting sites of paleo-CO₂
 1148 leakage (drawn from maps in Dockrill and Shipton, 2010). Structure contours are the height
 1149 of the top surface of the Navajo Sandstone above sea level, the main shallow CO₂ bearing
 1150 reservoir. Groundwater flow trajectories in the Navajo Sandstone are also shown (after
 1151 Hood and Patterson, 1984 and maps in Kampman *et al.*, 2009). Meteoric fluid flows from
 1152 recharge zones in the San Rafael Swell to the north-west to zones of discharge in the Green
 1153 River. The CO₂ and CO₂-charged brines flowing up the faults, mix with meteoric fluids in the

1154 Navajo Sandstone and flow parallel to the faults where they are sealing, and to the south-
1155 east where they are transmissive, being driven by the regional gradient in groundwater
1156 head.

1157

1158 **Figure 4** Geological cross section parallel to the plane of the Little Grand Wash Fault and
1159 perpendicular to the axis of the Green River anticline constructed with stratigraphic data
1160 from oil exploration drill holes (after Solum pers comms. 2012). Drillhole locations shown
1161 are for the CO2W55 drillhole, Crystal Geysers, Airport Well and the Green Town Federal 36-
1162 11 drill hole which transected CO₂-charged reservoirs in the Permian and Carboniferous
1163 stratigraphy. The cross section shows the distribution of the main CO₂ reservoir horizons in
1164 the Permian and Jurassic stratigraphy; the White Rim Sandstone, Wingate Sandstone,
1165 Navajo Sandstone and Entrada Sandstone. The juxtaposition of reservoir rocks in the
1166 footwall and hangwall blocks is shown. The position of a hypothetical gas-water contact is
1167 shown for each reservoir formation, controlled by the position of the reservoir spill point.
1168 The location of fluid samples collected from the CO₂W55 drillhole are shown (red stars,
1169 orange and yellow triangles).

1170

1171 **Figure 5** Cross section of the region surrounding drill hole CO₂W55 showing the location of
1172 the Little Grand Wash fault system, including the northerly fault transected by the drill hole
1173 (limited exposure precluded mapping this at surface), and the CO₂-driven cold water geyser
1174 at Crystal Geysers. The transect taken by the drill-hole is projected on the left-side of the
1175 figure. The general structure of the fault is also shown using information from field mapping
1176 and in Shipton *et al.*, (2004) and Dockrill and Shipton, (2010).

1177

1178 **Figure 6** Sedimentary log of the core recovered from drill-hole CO₂W55 showing the main
1179 geological features of the three units, the Entrada Sandstone, Carmel Formation and Navajo
1180 Sandstone, transected by the drill-hole. Zones of CO₂-degassing core and hydrocarbon
1181 bearing zones are also shown.

1182

1183 **Figure 7** A) Sandstone bleaching in exhumed portions of the Entrada Sandstone, Salt Wash
1184 Graben. B) High angle fracture zones adjacent to the fault with zones of intense bleaching
1185 and gypsum and pyrite mineralization on the fracture walls. C) Bleached halo around open
1186 mineralized fracture D) Bleached halo around high angle fracture in the Entrada Sandstone,
1187 CO₂W55 core. E-F) Gypsum and pyrite filled fracture in the bleached Entrada Sandstone G)
1188 Bleached Siltstone-sandstone contacts from CO₂-hosting sections of the Entrada Sandstone.
1189 H) Sections of gypsum beds and gypsum filled fracture zone in the Carmel formation I)
1190 Bleached claystone at the interface between the Carmel caprock and CO₂-charged Navajo
1191 Sandstone J) Bleached Navajo Sandstone.

1192

1193 **Figure 8** A) Formation pressures estimated for the Jurassic through to the upper
1194 Carboniferous stratigraphy of the Green River anticline. Formation pressures are estimated
1195 from mud weight gradients used in oil exploration drill holes. Also shown is the theoretical
1196 hydrostatic pressure gradient. B) The difference between the hydrostatic pressure gradient
1197 and formation pressures estimated from mud weight data are used to estimate the
1198 formation overpressure. This represents an upper bound and actually formation over
1199 pressure may be less than the estimate. Reservoirs become increasingly overpressured with
1200 depth due primarily to the artesian nature of this portion the Paradox Basin.

1201

1202 **Figure 9** A) Schematic diagram of the Leutert Positive Displacement Bottomhole Sampler
1203 redrawn from www.leutert.com. B-C) Photograph and schematic diagram of the high-
1204 pressure pH rig constructed to measure fluid pH on samples recovered using the PDS
1205 sampler. D) Schematic diagram of the micro-piston cylinder system used to capture
1206 dissolved CO₂ by mixing sample with an excess of KOH solution.

1207

1208 **Figure 10** Crystal Geyser level logger data (water temperature and water level) during
1209 drilling of scientific drill-hole CO2W55. The level logger was installed at a depth of ~5m
1210 below the mouth of the geyser. Typically, a single eruption cycle (SEC) of Crystal Geyser is
1211 composed of two major eruption events (Type B and D eruptions) of varying duration and
1212 frequency, each preceded by small frequent bubbling events (Type A and C eruptions), and
1213 each followed by a recharge period (R¹ and R²; nomenclature following Han *et al.*, 2013).
1214 Type B and D eruptions comprise short duration large magnitude and long duration low
1215 magnitude eruptions, respectively. During the drilling of hole CO2W55 the typical pattern of
1216 eruptions, eruption durations and frequent was significantly perturbed. Only a single Type B
1217 eruption was observed of much reduced magnitude and duration. An increased duration
1218 and reduced frequency of Type D eruptions was observed (see Fig 10). Also shown are
1219 drillers depths and formation intervals for hole CO2W55 at various times during the course
1220 of drilling. Periods of cementing, redrilling cement, fluid sampling, flowing the hole and
1221 waiting are also shown.

1222

1223 **Figure 11** A) A compilation of eruption duration and frequency data for Crystal Geyser from
1224 various studies from 1978 to 2010, redrawn after Han *et al.*, 2013. B) Eruption data for
1225 Crystal Geyser during drilling of hole CO₂W55.

1226

1227 **Figure 12** A) In-situ pH measured on pressurized samples and alkalinity determined by gran
1228 titration in the field. B) Dissolved CO₂ concentrations measured directly on titrated samples
1229 and recalculated from measured pH and alkalinity. Also shown is the theoretical CO₂
1230 solubility curved calculated for a hydrostatic pressure gradient, local geothermal gradient
1231 and measured salinity profile using the equations of Duan *et al.*, 2006.

1232

1233 **Figure 13** Anion concentrations (and boron) in fluid samples collected from Jurassic CO₂-
1234 charged reservoirs, during drill-hole CO2W55. Downhole fluid samples collected from the
1235 Navajo sandstone using the Leuterts wireline sampler (red squares) are number 1-4 in order
1236 of sample depth. Samples from the Entrada Sandstone (yellow triangle), Carmel Formation
1237 (orange triangle) and Navajo Sandstone (pink squares) were collected at surface when the
1238 hole was flowing.

1238

1239 **Figure 14** Major and minor cation concentrations (Na, K, Li, Rb) in fluid samples collected
1240 from the Jurassic CO₂-charged reservoirs, from drill-hole CO2W55.

1241

1242 **Figure 15** δ¹⁸O and δD isotope ratios of fluids sampled from the CO2W55 drill-hole.

1243

1244 **Figure 16** δ³⁴S_{SO4} and δ¹⁸O_{SO4} of sulphate in fluids sampled from the CO2W55 drill-hole.

1245

1246 **Figure 17** Sr concentrations and Sr-isotope ratios in fluid samples collected from the Jurassic
1247 CO₂-charged reservoirs, during drill-hole CO2W55.

1248

1249 **Figure 18** Groundwater chemistry of CO₂-charged fluids from drill-hole CO₂W55 showing
1250 profiles for elements buffered by fluid-rock reaction; Ca, Mg, Sr, Fe, Mn, Al and Si.

1251

1252 **Figure 19** Element cross plots of fluid chemistry from the CO₂W55 drill-hole, Crystal Geyser
1253 and other CO₂-springs from the Green River anticline. The ratio of halogen, alkali and
1254 alkaline metals are consistent with fluid mixing between dilute meteoric fluid and brine
1255 derived from the Paradox Formation, which is enriched in B, Br, Cl, Li, K, Na, Rb and SO₄²⁻.
1256 Paradox Valley brine compositions taken from Rosenbauer *et al.*, (1991).

1257

1258 **Figure 20** δ¹⁸O and δD isotope ratios for fluid of Navajo Sandstone fluids from the CO₂W55
1259 drill-hole and CO₂-springs from the Green River anticline from this study and from Heath *et*
1260 *al.*, (2009). The CO₂-charged fluids deviate from the North American Meteoric Water Line, as
1261 defined by local surface waters from Mayo *et al.*, (1992), due to mixing with isotopically
1262 heavy saline brines from the Paradox Formation (δ¹⁸O: 2.19‰ and δD -42‰; Spangler *et*
1263 *al.*, 1996).

1264

1265 **Figure 21** A-B) Basin scale salinity profiles for formation fluid samples from the brine-rich
1266 Carboniferous aquifers and White Rim Sandstone, recovered during oil exploration drilling
1267 on the Green River anticline. Elevated salinity in the White Rim and Jurassic sandstone
1268 aquifers reflects intrusion of the CO₂-charged brines from depth. C) HCO₃ concentrations in
1269 formation fluid samples. Alkalinity in Carboniferous, White Rim and Jurassic sandstone
1270 aquifers are elevated due to fluid-rock reactions between the CO₂-charge fluids and
1271 carbonate and silicate reservoir minerals. D) Basin-scale CO₂ solubility curve

1272

1273 **Figure 22** Element cross plot showing dilution of Carboniferous brines by mixing with
1274 meteoric fluids in the shallower CO₂-reservoirs of the White Rim Sandstone and Jurassic
1275 Sandstones. Brine compositions from Rosenbauer *et al.*, (1991) and Breit and Skinner,
1276 (2002).

1277

1278 **Figure 23** Brine inputs along flow paths within the Navajo Sandstone, parallel to the Little
1279 Grand Wash and Salt Wash faults, calculated from Cl and Br concentrations in the spring
1280 waters and end-member fluids.

1281

1282 **Figure 24** ⁸⁷Sr/⁸⁶Sr for fluids and minerals relevant to this study. From bottom to top this
1283 includes the Sr-isotopic composition of; i) brine from the Paradox Formation, Greater Aneth
1284 oil field (Spangler *et al.*, 1996); (ii) typical groundwaters from the Navajo Sandstone where
1285 CO₂ is absent (Naftz *et al.*, 1997); (iii) the Green River CO₂ springs, which sample fluid
1286 primarily from the Navajo Sandstone (Kampman *et al.*, 2009); (iv) Crystal Geyser (this study);
1287 (v-vii) CO₂W55 Navajo, Carmel and Entrada Sandstone fluids (this study); (viii-xi) CO₂-
1288 deposited aragonite veins from the Little Grand Wash and Salt Wash faults (Kampman *et al.*,
1289 2012); (x) Calcite and gypsum veins from bleached Entrada Sandstone, Salt Wash Graben;
1290 (xi) Carmel Fm. gypsum beds from the CO₂W55 core; (xii) Navajo Sandstone Fe-dolomite
1291 cements from the CO₂W55 core; (xiii) Silicate fractions of the Navajo and Entrada
1292 Sandstones from regional compilation of samples and the CO₂W55 core (this study and
1293 Truini and Longworth, 2003) (xiv) carbonate fractions of typical diagenetic calcite and
1294 dolomite cements from the Navajo and Entrada Sandstones (this study and Goldstein *et al.*,

1295 2008) and; (xv) calcite veins and hematite concretions associated with regional hydrocarbon
1296 bleaching of the Jurassic Sandstones (Chan *et al.*, 2000).

1297

1298 **Figure 25** Saturation index for (A) carbonate, (B) Fe-bearing, (C-D) silicate, (E) sulphate and
1299 (F) silica minerals in fluids sampled from the CO2W55 drillhole calculated using PHREEQC.

1300

1301 **Figure 26** Cross plots of carbonate and metal-oxide derived solutes for fluids from the
1302 CO₂W55 drill-hole. Also shown are Mg/Ca and Sr/Ca ratios for the carbonate fraction of
1303 leachates from samples of the Navajo Sandstone from the CO2W55 core.

1304

1305 **Figure 27** Quantitative mineralogy from; (i) XRD analysis of representative samples from the
1306 Navajo Sandstone from the CO2W55 core and; (ii) a compilation of quantitative mineralogy
1307 of representative unbleached samples of the Navajo Sandstone (from data in Chan *et al.*,
1308 2000; Beitler *et al.*, 2005).

1309

1310 **Figure 28** Back scatter electron (BSE) images of carbonate cements within samples of the
1311 Navajo Sandstone from the CO2W55 drillhole, and from a nearby drill core where CO₂ is
1312 absent. Increasing brightness in the backscatter images relates primarily to increasing Fe-
1313 concentration in the mineral. (A) Typical Fe-poor diagenetic dolomite cements in samples
1314 from the Big Hole #2 core (see Figure 1 for location). (B) Zonally zoned dolomite cements
1315 from the upper CO2W55 core showing Fe-poor cores of original diagenetic cement
1316 overgrown by Fe-rich rims. (C) Complexly zoned Fe-rich dolomites with evidence for
1317 extensive dissolution-precipitation, from the lower intervals of the Navajo Sandstone,
1318 in contact with the low pH brine inputs.

1319

1320 **Figure 29** Time-series fluid chemistry from the build-up to and eruption of a Type B eruption
1321 of Crystal Geyser. Samples were collected in 2007, prior to drill of hole CO2W55.
1322 Temperature, Na, K, Cl and SO₄²⁻ concentrations and O-isotope of the expelled fluid evolve
1323 as the geyser initially samples brine enriched fluid from the Navajo Sandstone then
1324 progressively incorporates meteoric enriched fluid from the shallower cooler Entrada
1325 Sandstone reservoir.

1326

1327 **Figure 30** Time-series fluid chemistry from the build-up to and eruption of a large short
1328 duration Type B eruption of Crystal Geyser. Samples were collected in 2007, prior to drill of
1329 hole CO2W55. Fluid chemistry evolves as the geyser samples different CO₂-reservoirs;
1330 initially sampling brine enriched fluid from the Navajo Sandstone followed by influx of Ca,
1331 Mg, Sr, Fe, Mn enriched fluid from the Entrada Sandstone, as a major eruption initiates.

1332

1333

1334 **Figure 31** Mixing diagrams for Br, Cl and Sr concentrations and Sr-isotopes ratios for fluids
1335 from drill-hole CO₂W55 and time-series fluid samples from Crystal Geyser. Navajo
1336 Sandstone drill-hole fluid samples plot along mixing lines between CO₂-saturated brine
1337 flowing in from the fault and dilute CO₂-undersaturated fluids descending from the fracture
1338 zone in the Carmel Formation. Time-series samples from an eruption of Crystal Geyser plot
1339 along a mixing line between the most saline fluids sampled from the geyser and fluid from
1340 the Entrada Sandstone that is enriched in Sr (and Ca, Mg, Fe and Mn) from the dissolution of
1341 carbonate and Fe-oxides in the host reservoir. In 1/Sr versus Sr-isotope space, Navajo

1342 Sandstone surface fluid samples collected from the drill-hole show depletions in Sr
1343 concentrations without a corresponding change in the Sr-isotope ratio. This reflects loss of
1344 Sr from solution by the precipitation of carbonate minerals.

1345

1346 **Figure 32** Mixing diagrams for Na, Ca, Mg and Mn versus Cl in fluids from the CO2W55
1347 drillhole. (A) The fluids contain high concentrations of Na and changes in Na-Cl
1348 concentrations are dominated by fluid-fluid mixing trends. The Na concentration in the
1349 inflowing brine is elevated relative to concentrations expected for pure brine dilution, which
1350 may reflect enrichment of Na due to fluid-mineral reactions involving feldspar. (B-D) Ca, Mg
1351 and Mn concentrations in fluids sampled from the Navajo Sandstone are variably enriched
1352 and depleted in Ca relative to concentrations expected for pure fluid-fluid mixing,
1353 suggesting fluid-rock reactions involving carbonate and Fe-oxide minerals buffer the solute
1354 concentration.

1355

1356 **Figure 33** The S- and O-isotopic composition of sulphate versus sulphate concentrations in
1357 fluid samples from the drill-hole and Crystal Geyser. Mixing lines calculated for mixing of the
1358 Carmel Formation end-member and the most saline fluid sampled by Crystal Geyser are
1359 shown.

1360

1361 **Figure 34** Conceptual model of fluid flow, fluid mixing and fluid-rock reaction in the vicinity
1362 of drill-hole CO2W55. CO₂ and CO₂-saturated brine migrate through the fault from
1363 supercritical reservoirs of CO₂ in Carbonate formations at depth, mixing with meteoric
1364 groundwaters in fault and in sandstone aquifers in the White Rim and Wingate Sandstones.
1365 This dilutes the brine composition and the migrating CO₂ is progressively dissolved. Highly
1366 diluted CO₂-saturated brine eventually enters the base of the Navajo Sandstone, where it
1367 flows along the base of the formation mixing with CO₂-enriched groundwaters horizontally
1368 along the fault. CO₂-charged brines also enter the Entrada Sandstone where the flow laterally
1369 dissolving carbonate and hematite. These solute enriched solutions descend through the
1370 Carmel Formation, where they dissolve gypsum, before flowing into the upper portions of
1371 the Navajo Sandstone.

1372

1373 **Figure 35** The change in dissolved inorganic carbon concentrations (DIC) in downhole fluid
1374 samples from the Navajo Sandstone versus (i) Cl concentration and (ii) of brine derived from
1375 the fault, from the Navajo Sandstone. In these CO₂-charged acidic waters DIC is
1376 predominantly CO₂(aq) with some HCO₃⁻.

1377

1378 **Table 1.** Geochemistry of fluids sampled from the CO2W55 drill-hole. *sample
1379 contaminated with drilling mud.

1380

1381 **Table 2.** Isotope geochemistry of fluids sampled from the CO2W55 drill-hole

1382

1383 **Table 3.** Element and isotope geochemistry of fluids sampled from the CO₂-springs sampled
1384 in 2007.

1385

1386 **Table 4.** Composition of gas exsolved from the CO₂-springs sampled in 2007.

1387

1388 **Table 5.** Composition of gas exsolved from the CO₂-springs sampled in 2007.

1389

1390 **Table 6.** Element and isotope geochemistry of time-series samples from Crystal Geyser
1391 sampled in 2007.

1392

1393 **Table 6.** Sr-isotope geochemistry of leachates from rock samples used in this study.

1394

1395 **Table 7.** XRD data of Navajo Sandstone samples from the CO2W55 drill-hole.

1396

1397 **Table 8.** Estimated and measured composition of end-member fluids.

1398

1399 **Supplementary Table 1.** Geochemistry of fluids sampled from oil exploration drill-holes on
1400 the Green River anticline (references in text).

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1404

Figure 1

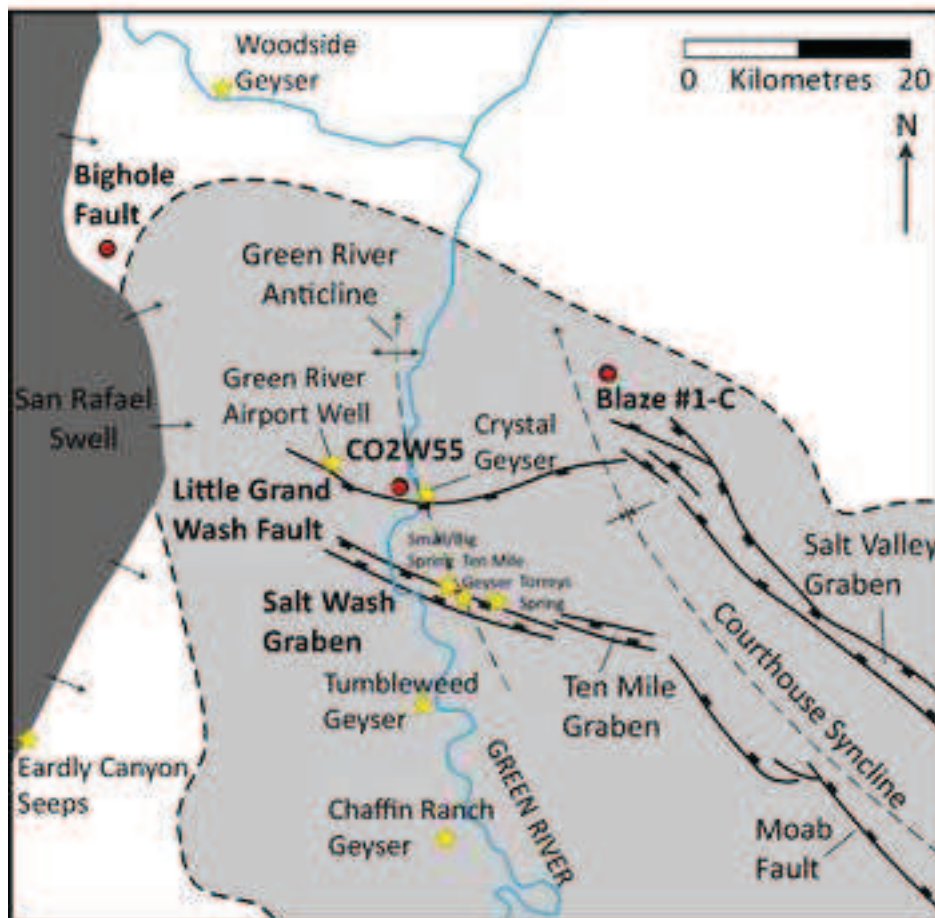
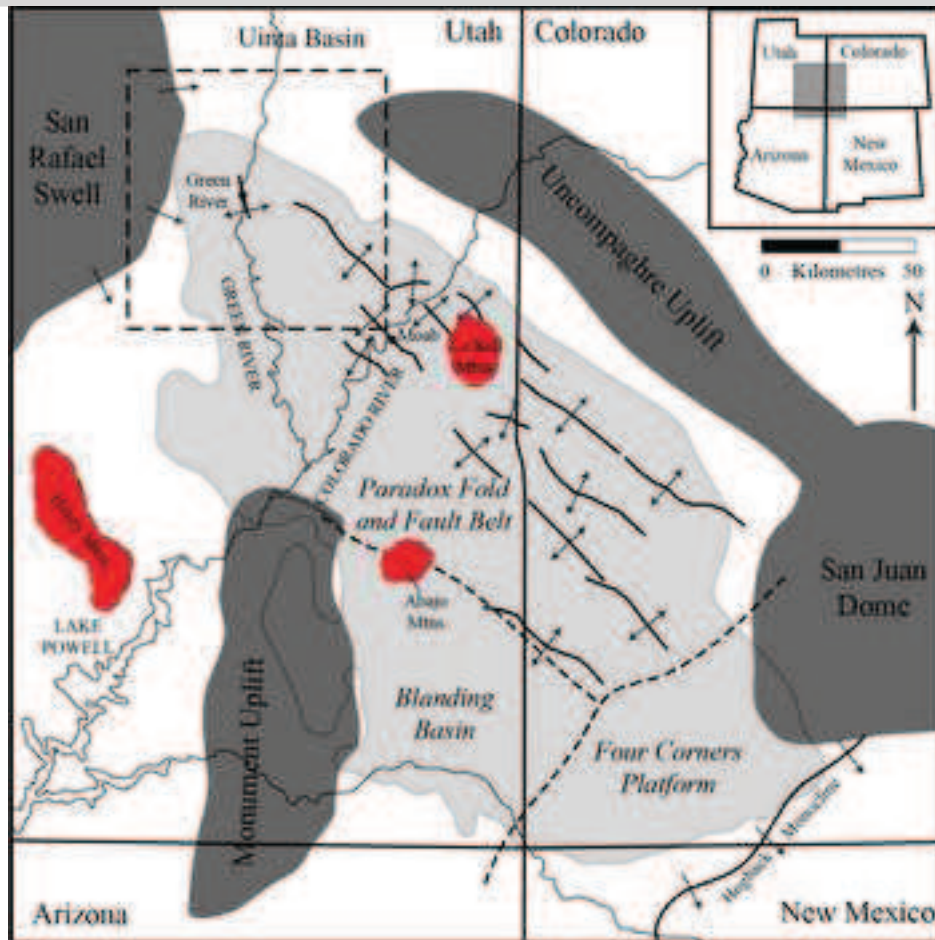


Figure 2

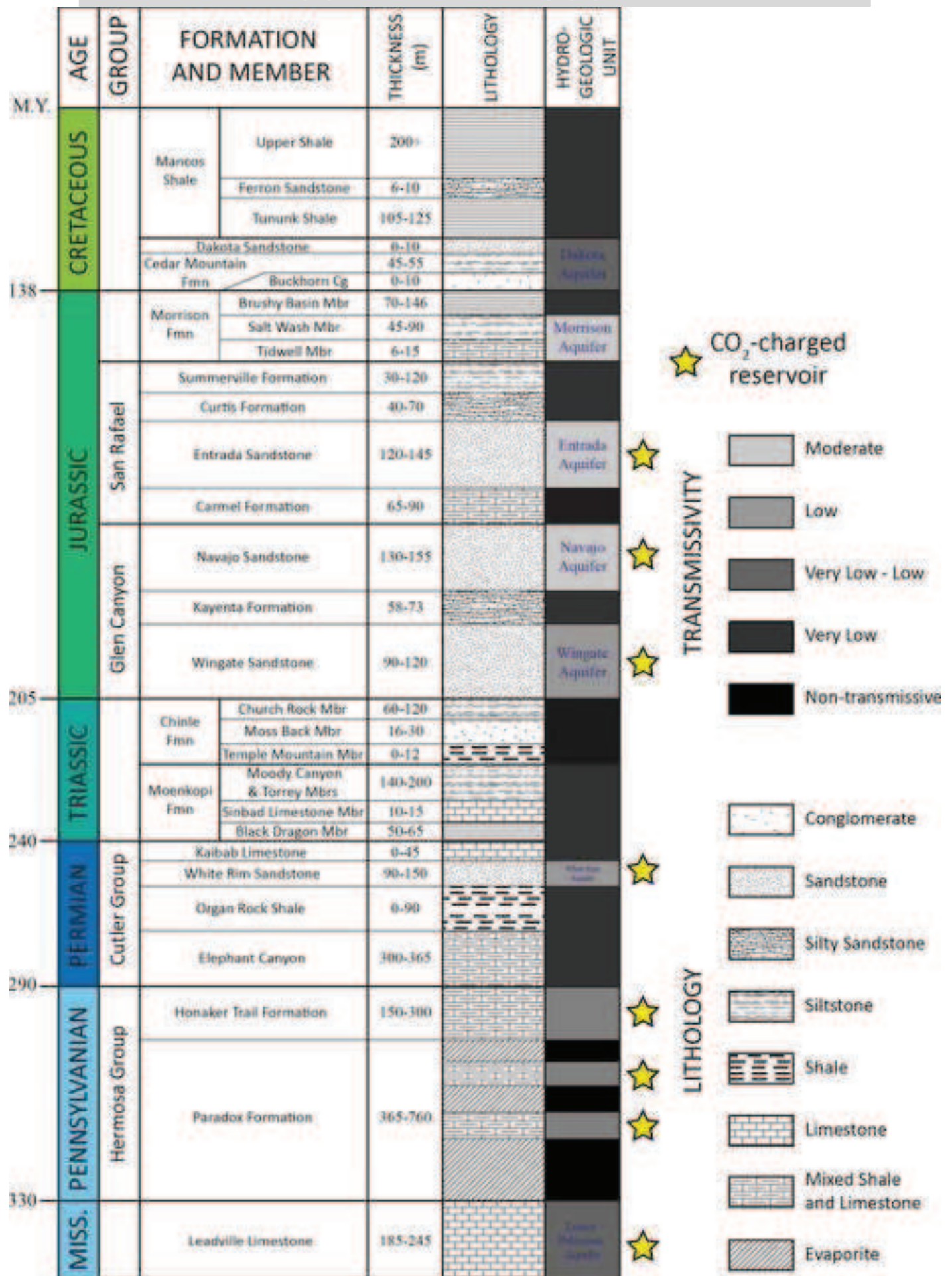
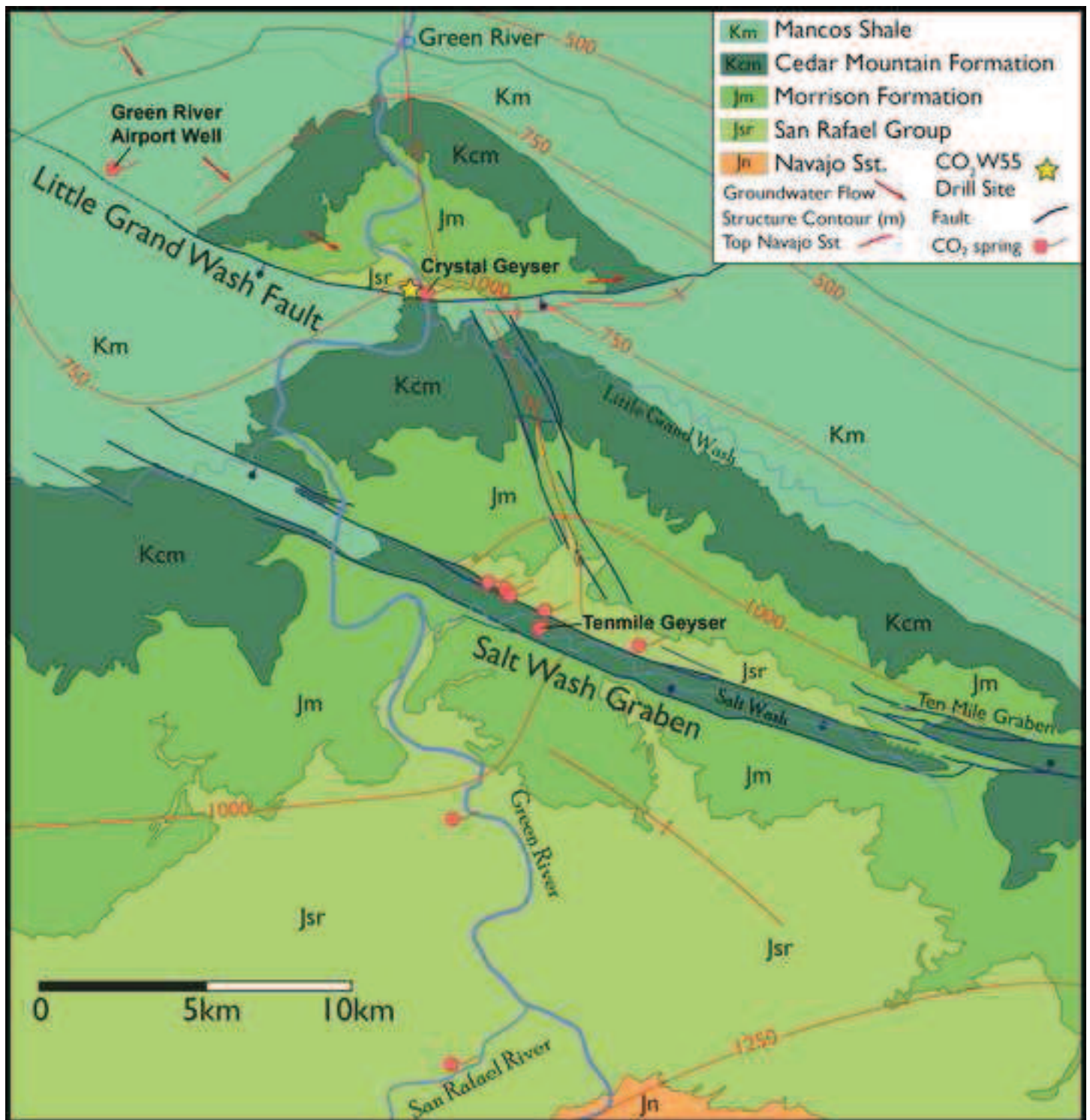


Figure 3



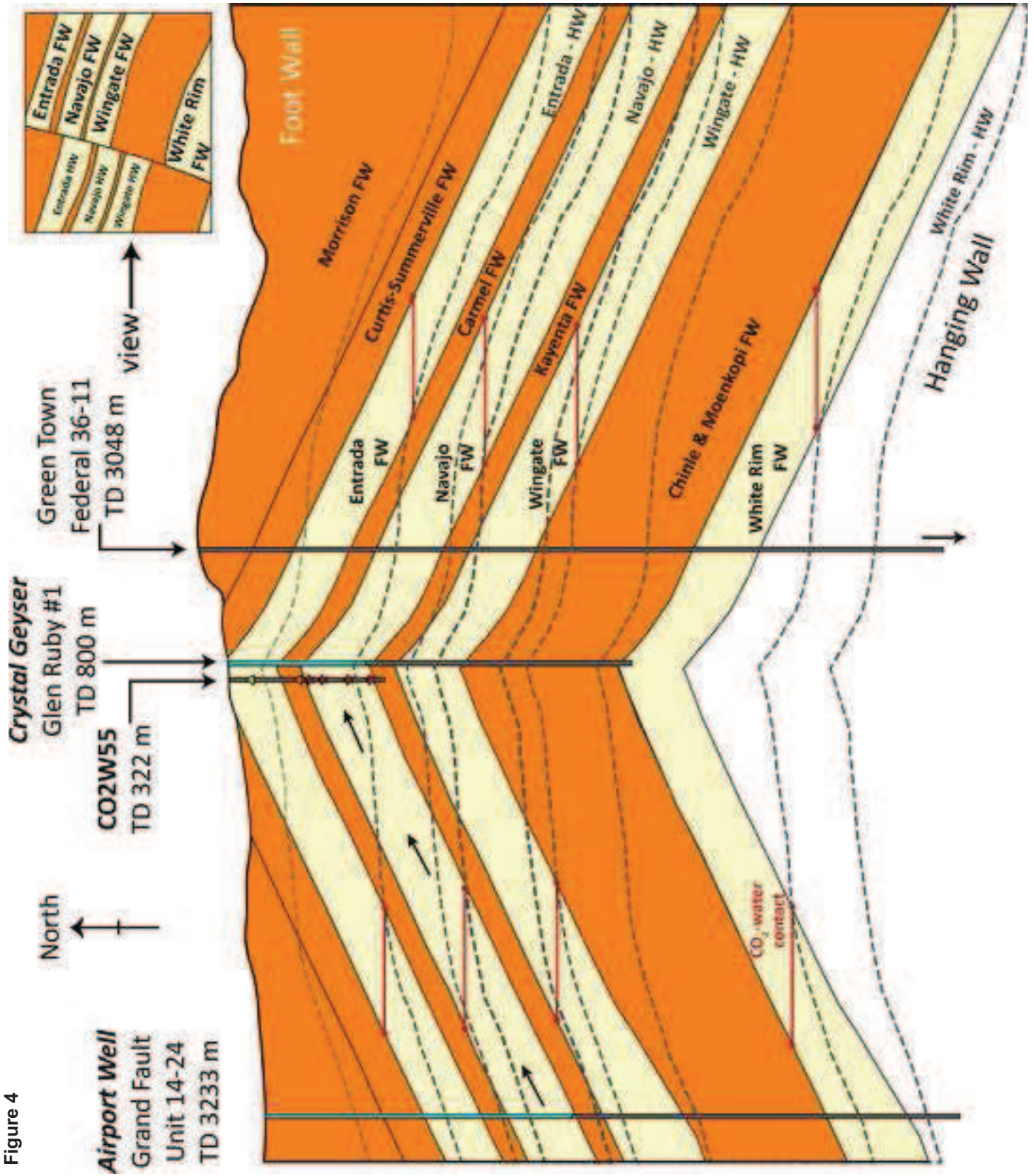


Figure 4

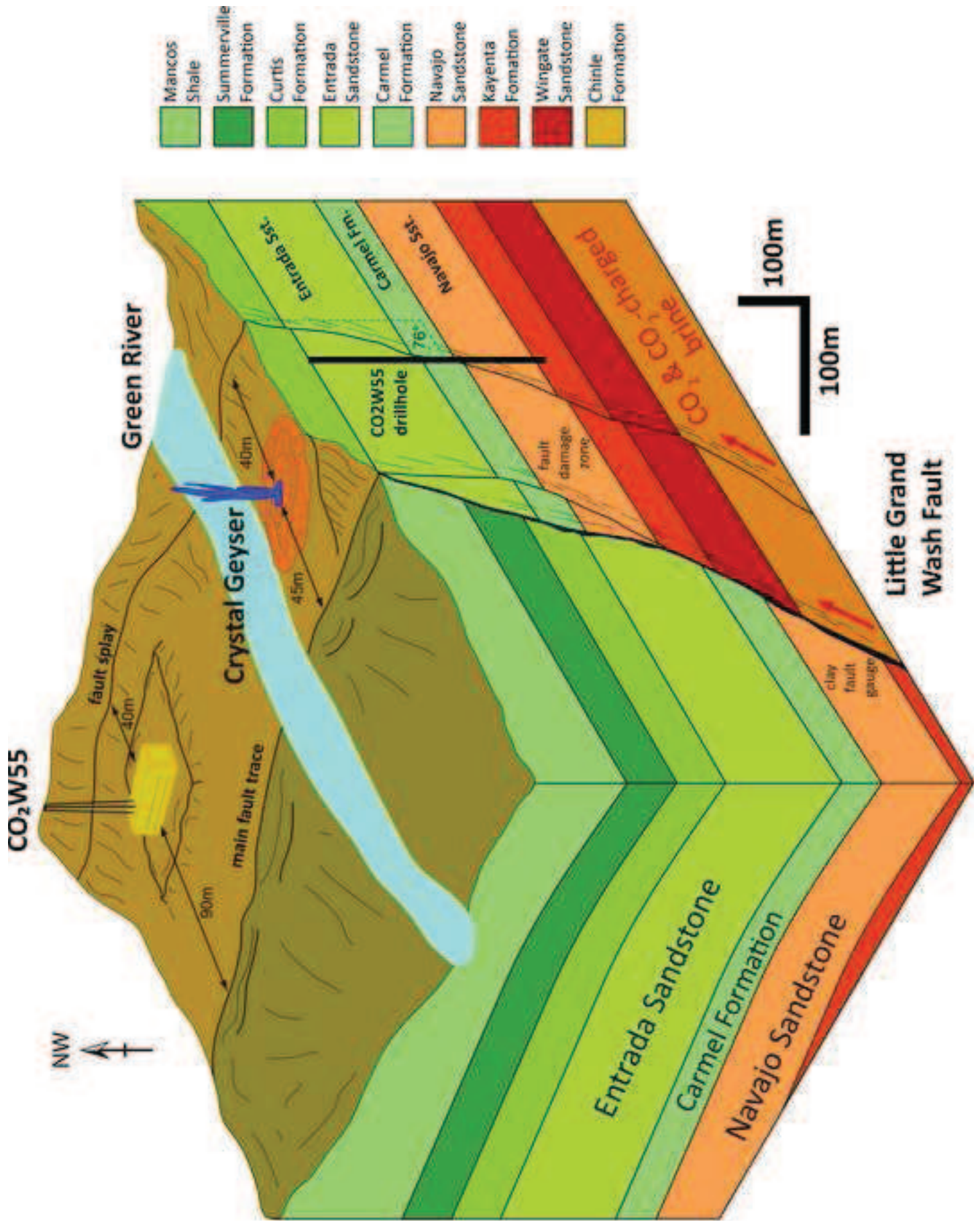
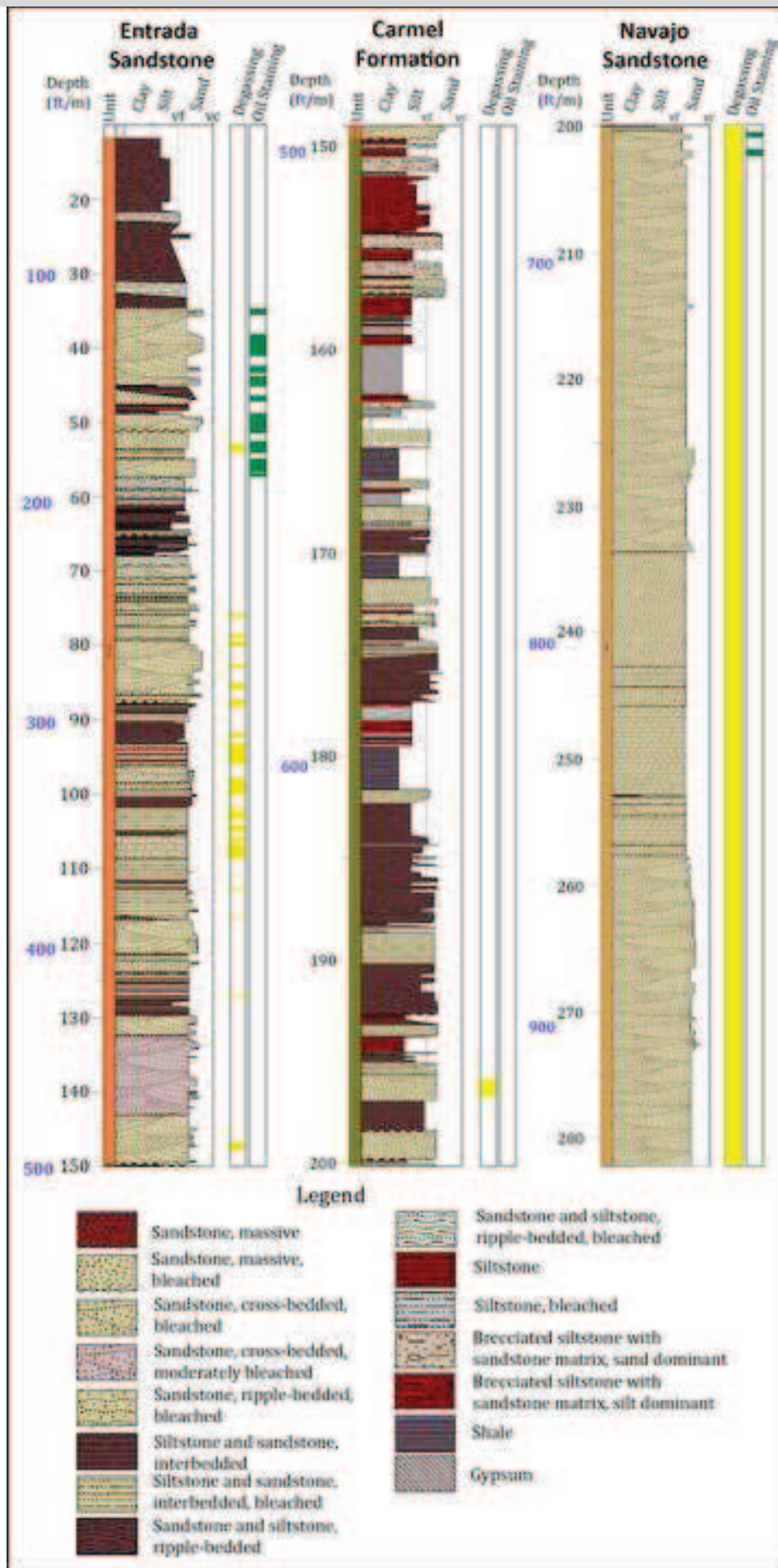


Figure 5



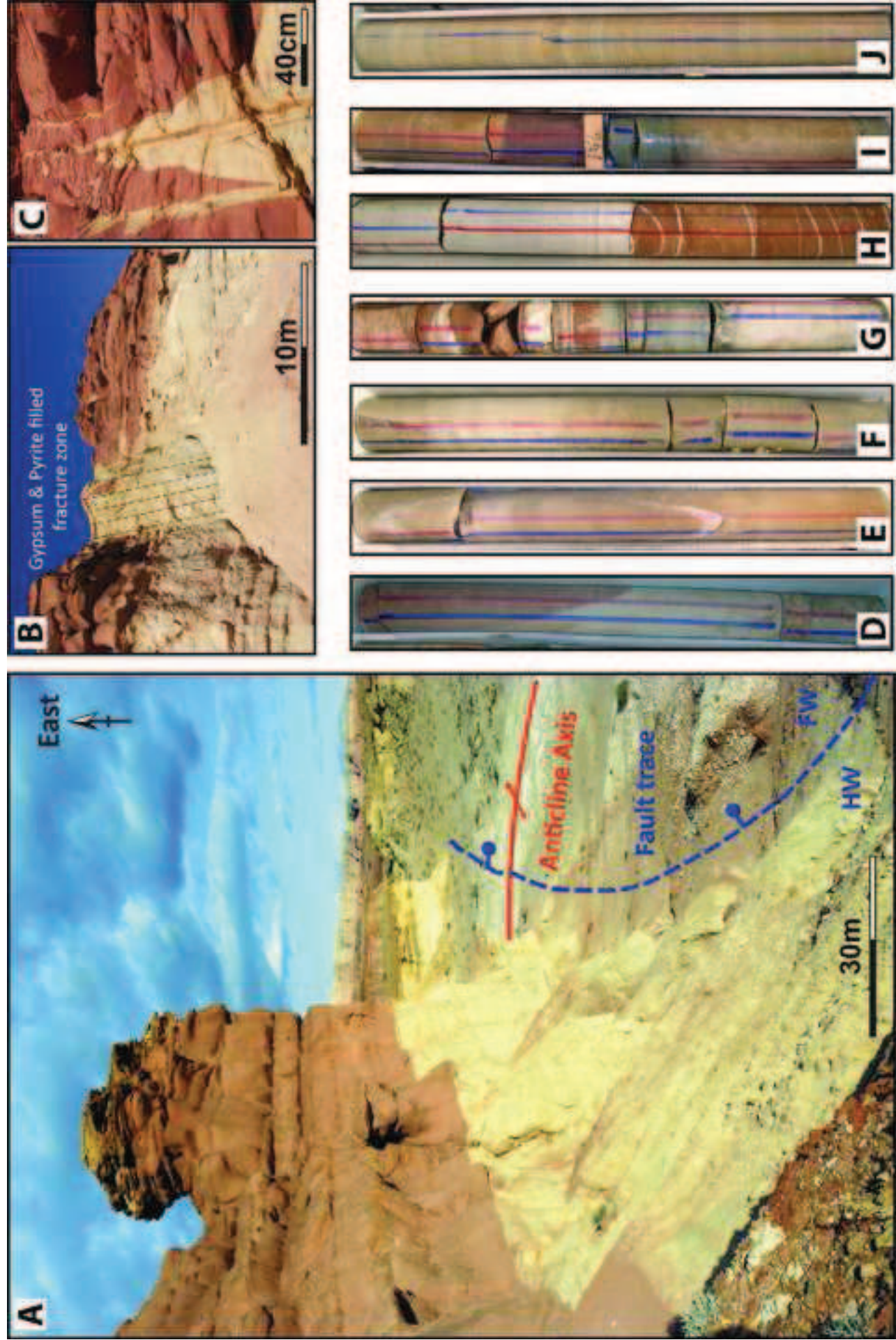


Figure 7

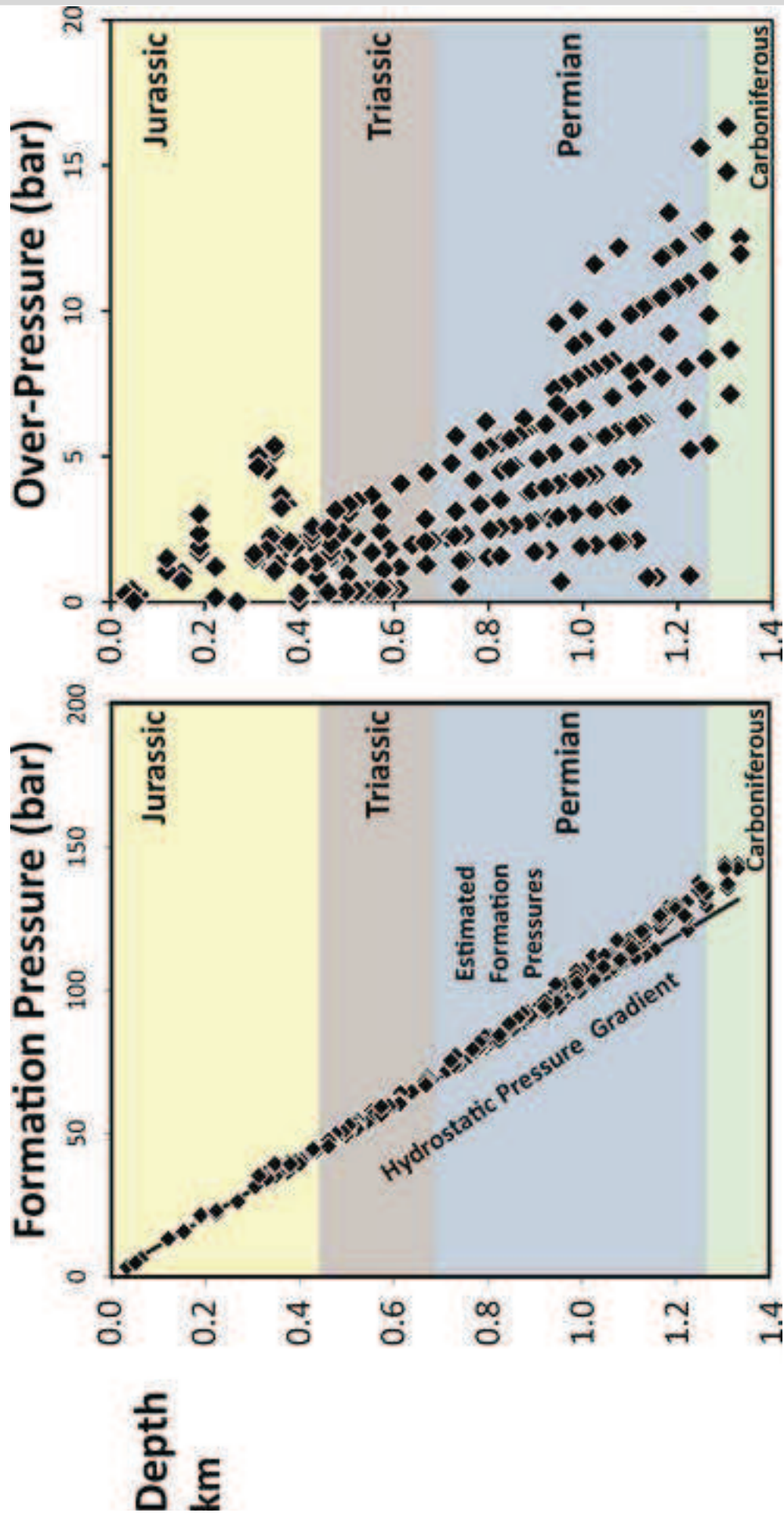
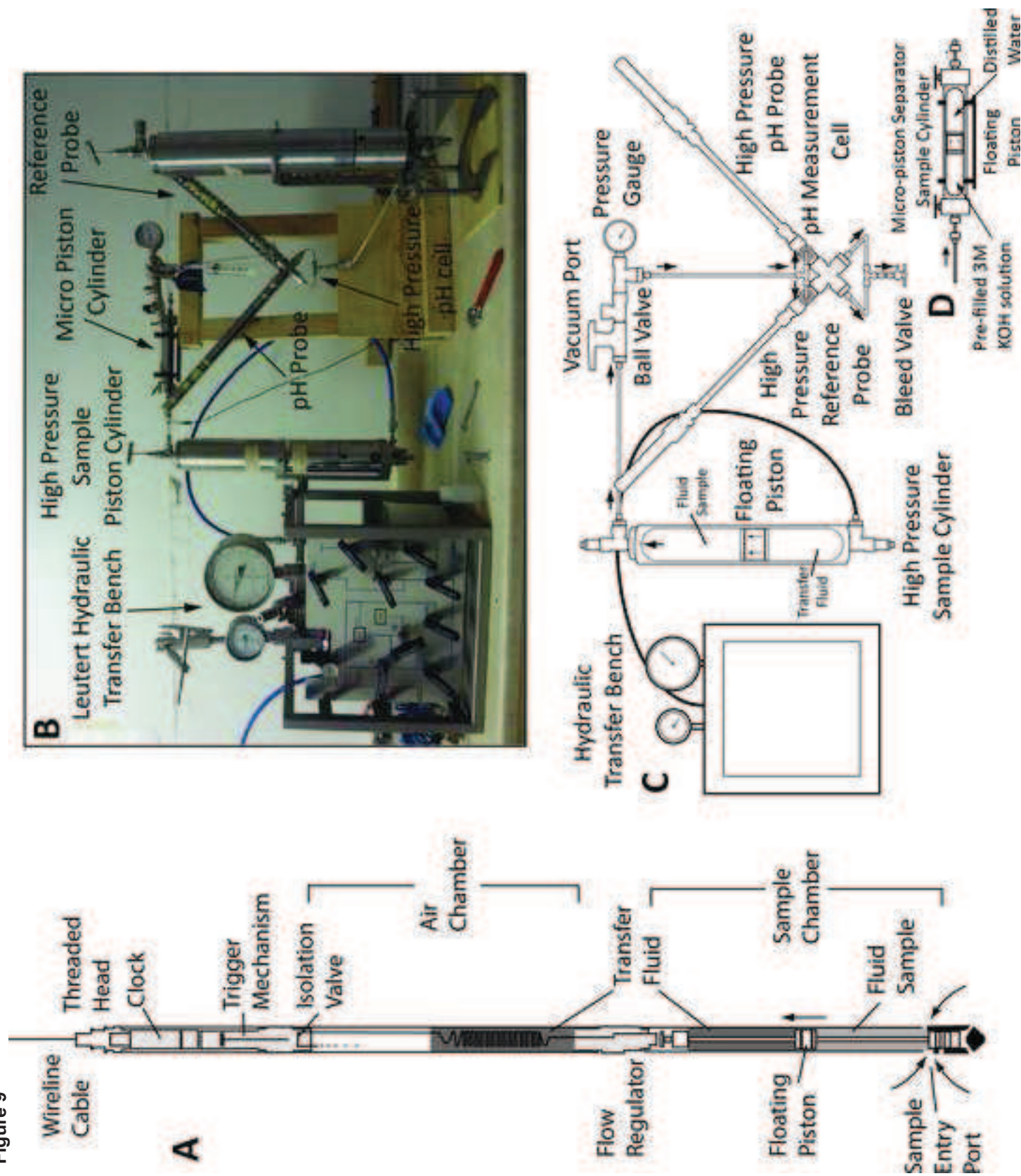


Figure 8

Figure 9



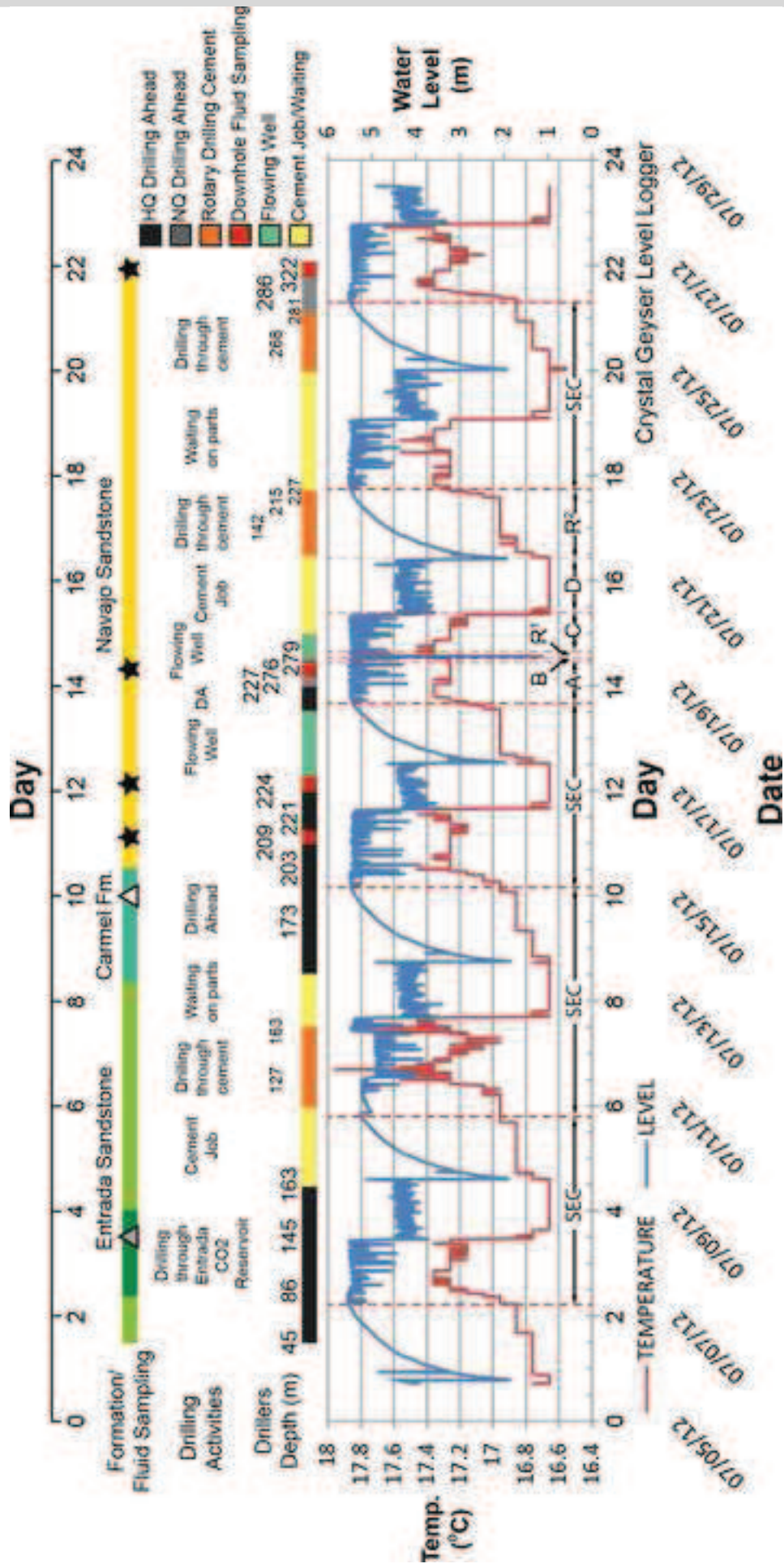
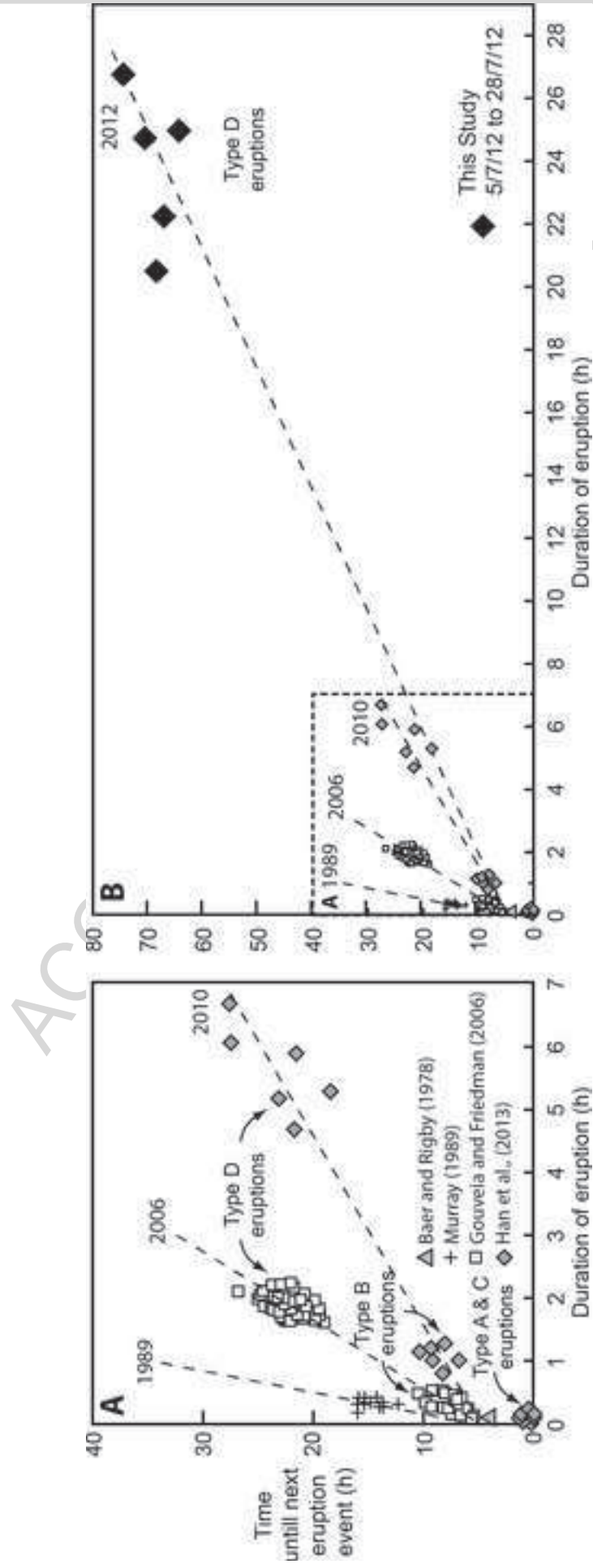


Figure 10

Figure 11



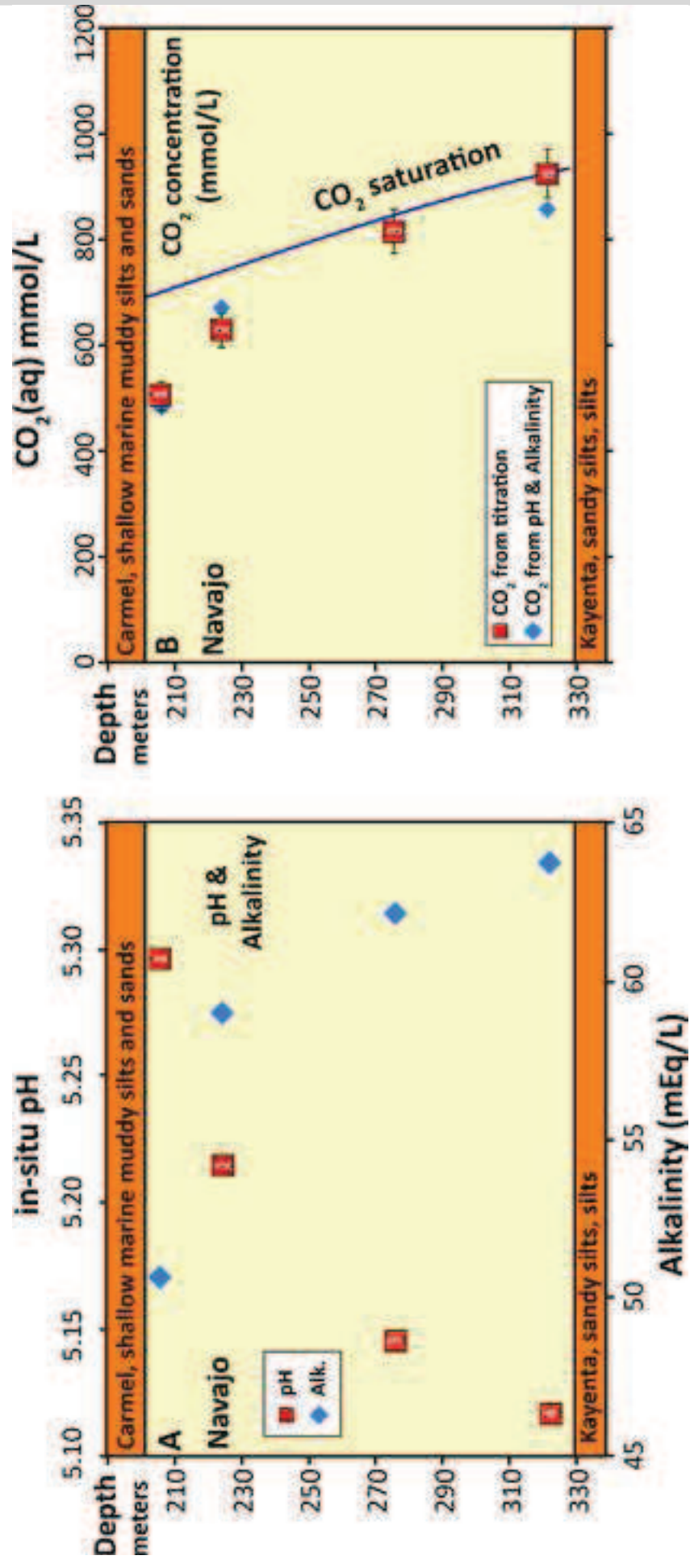


Figure 12

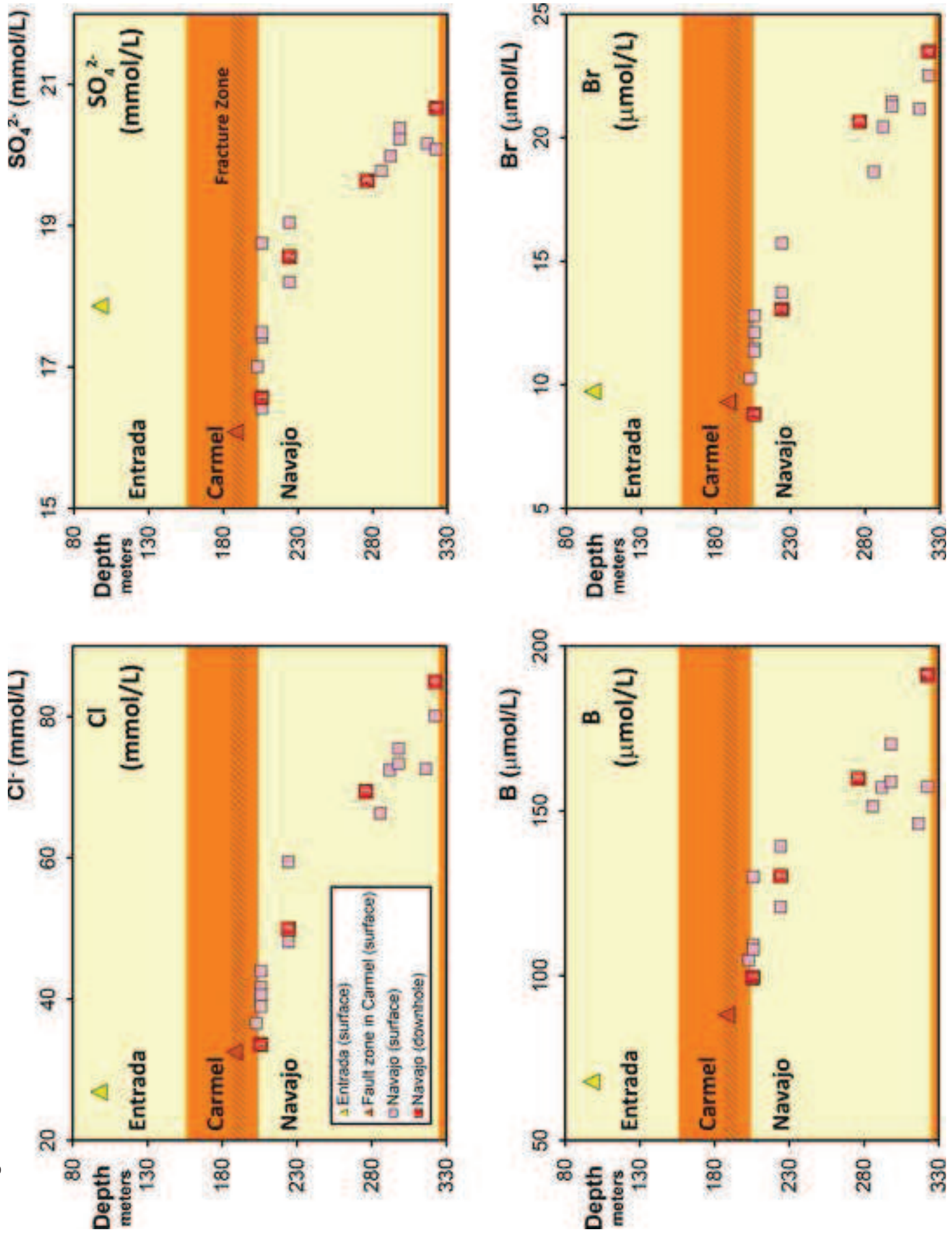


Figure 13

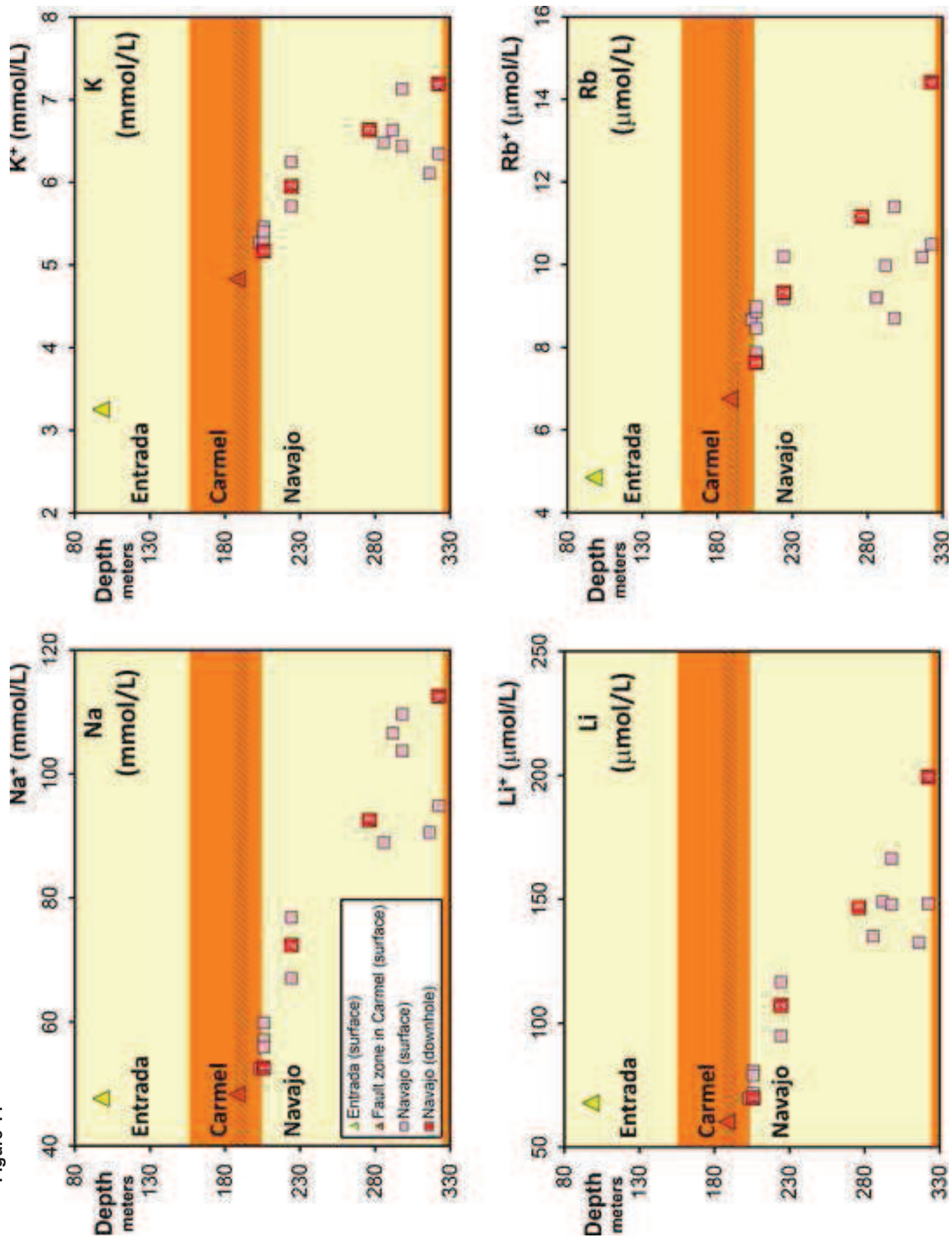


Figure 14

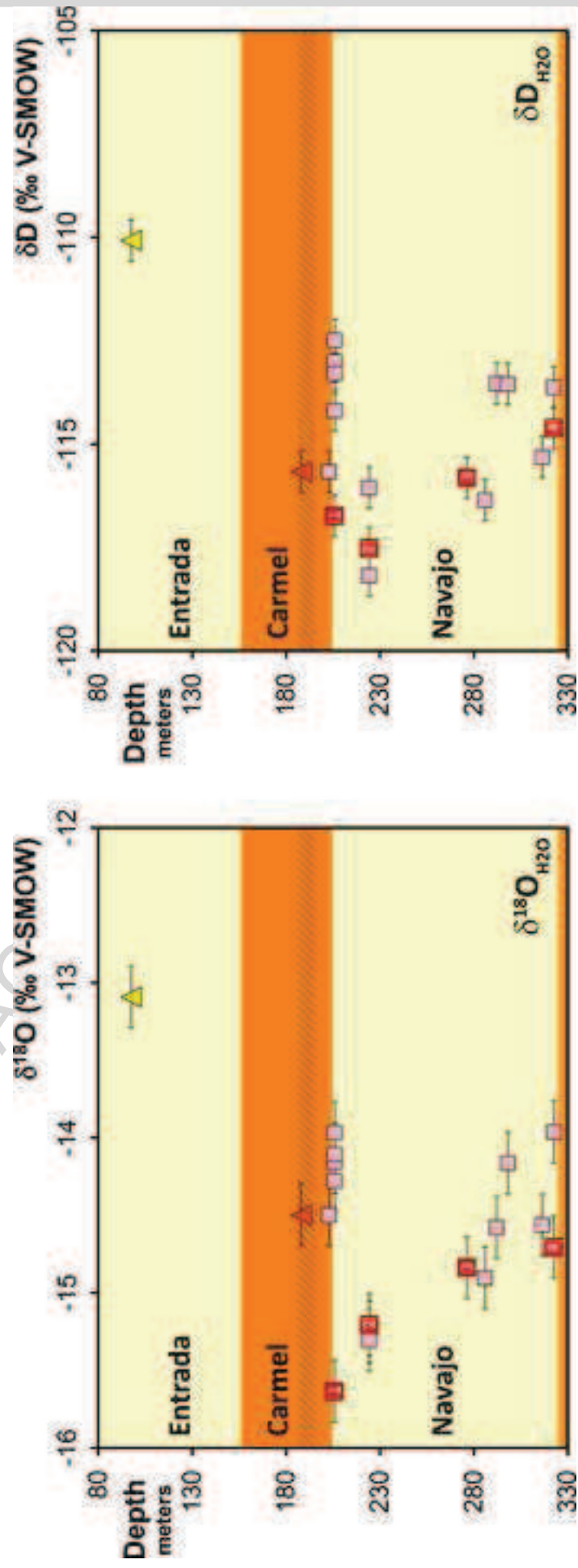


Figure 15

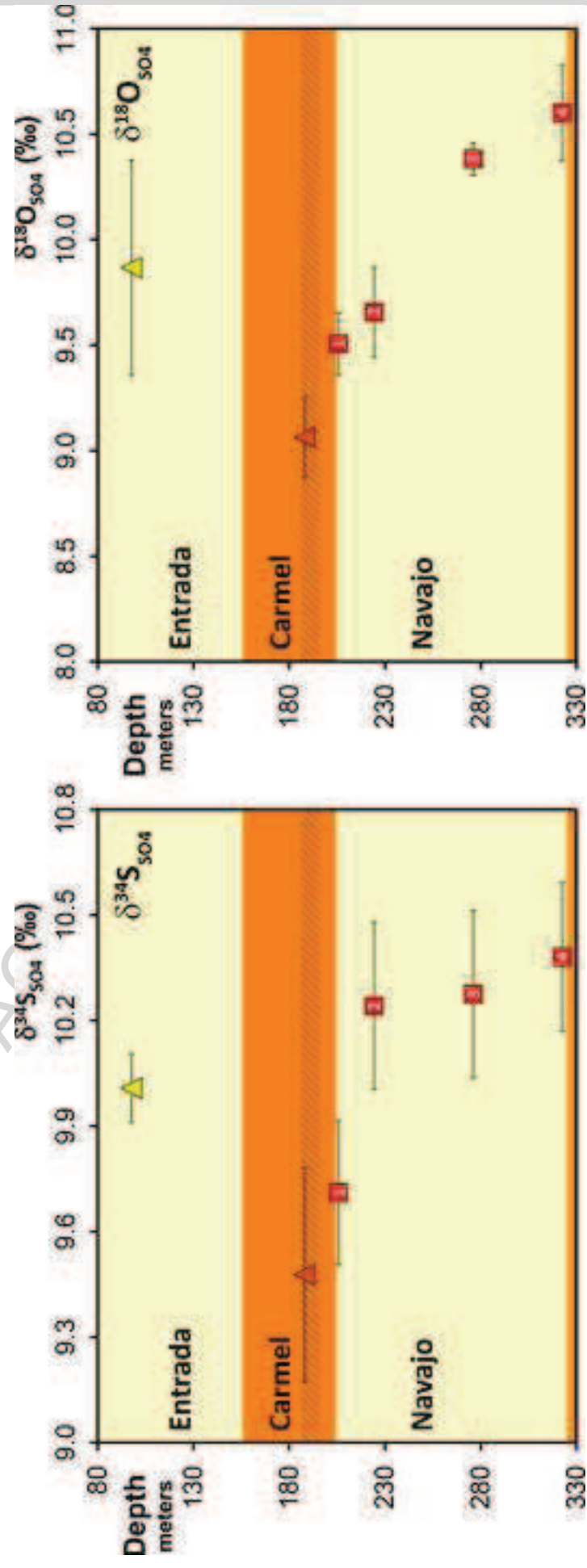


Figure 16

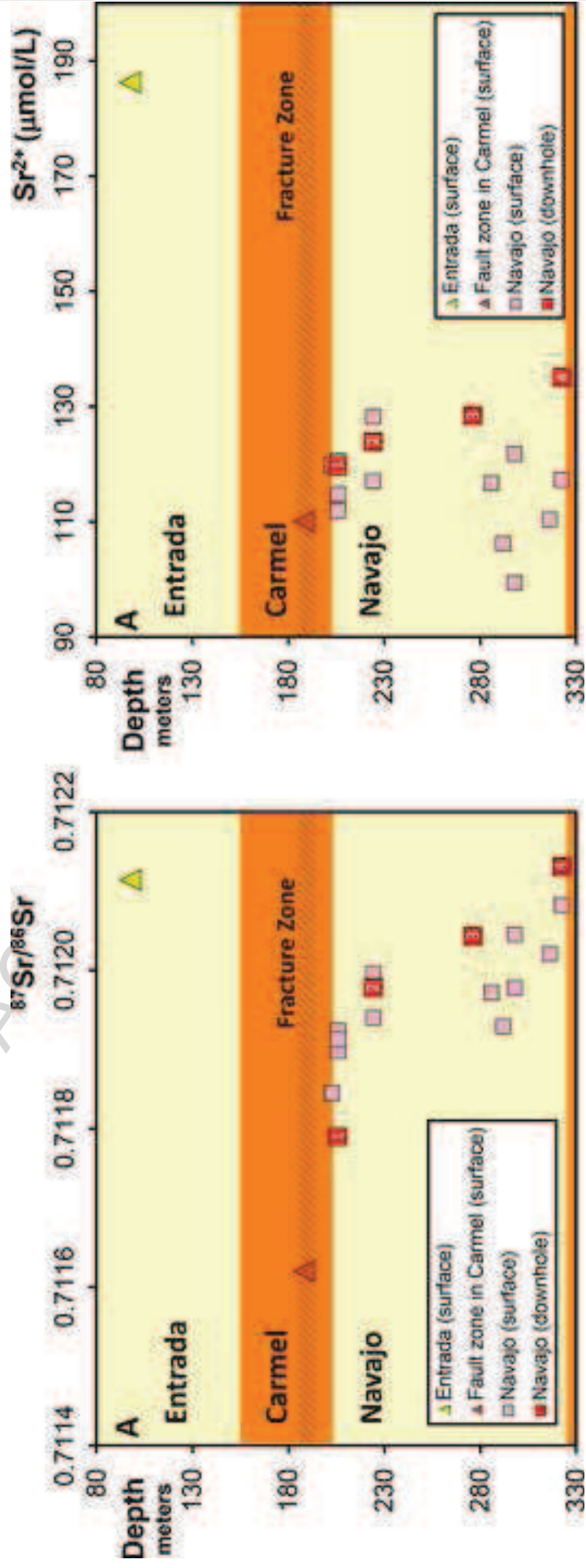
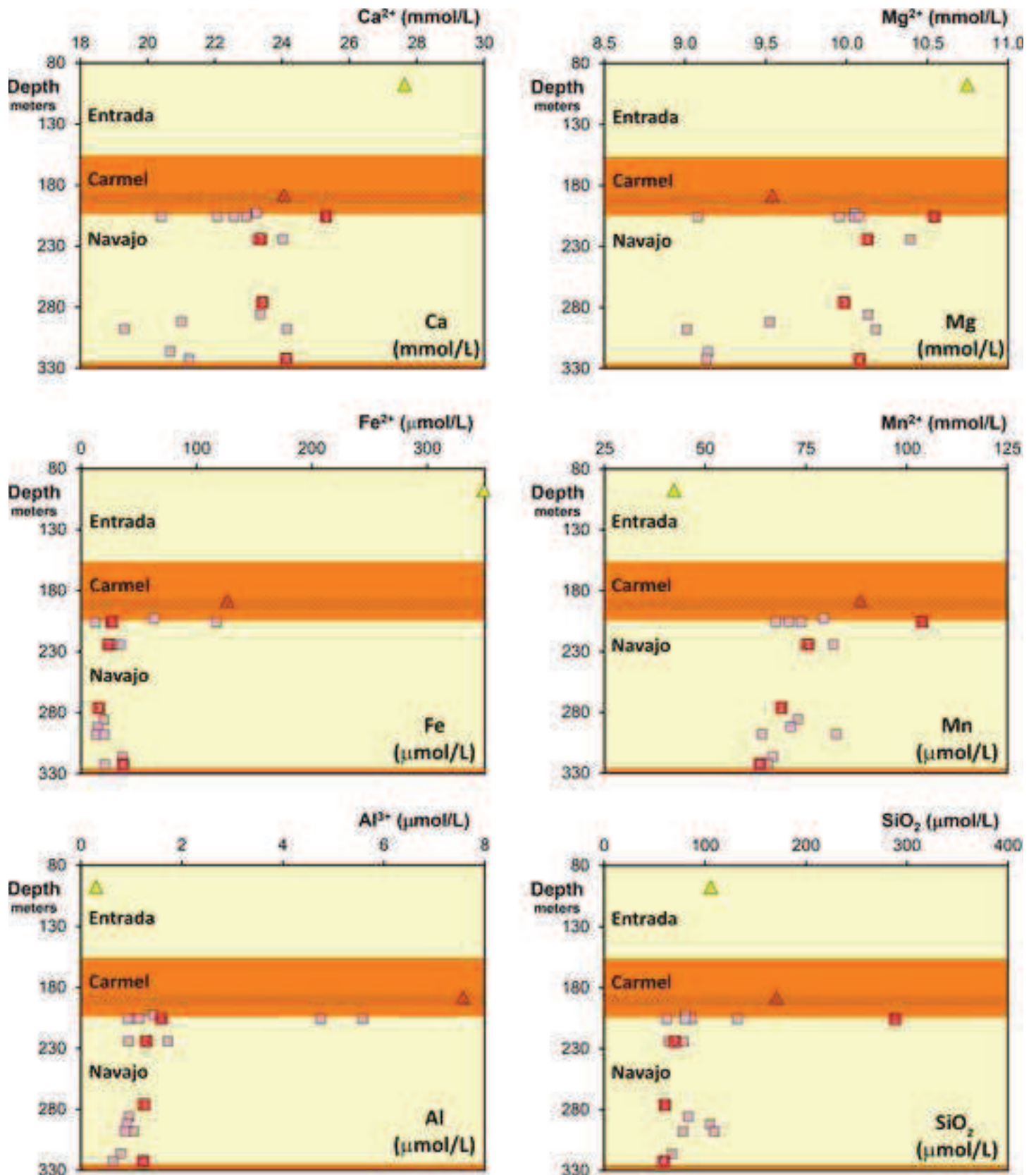


Figure 17

Figure 18



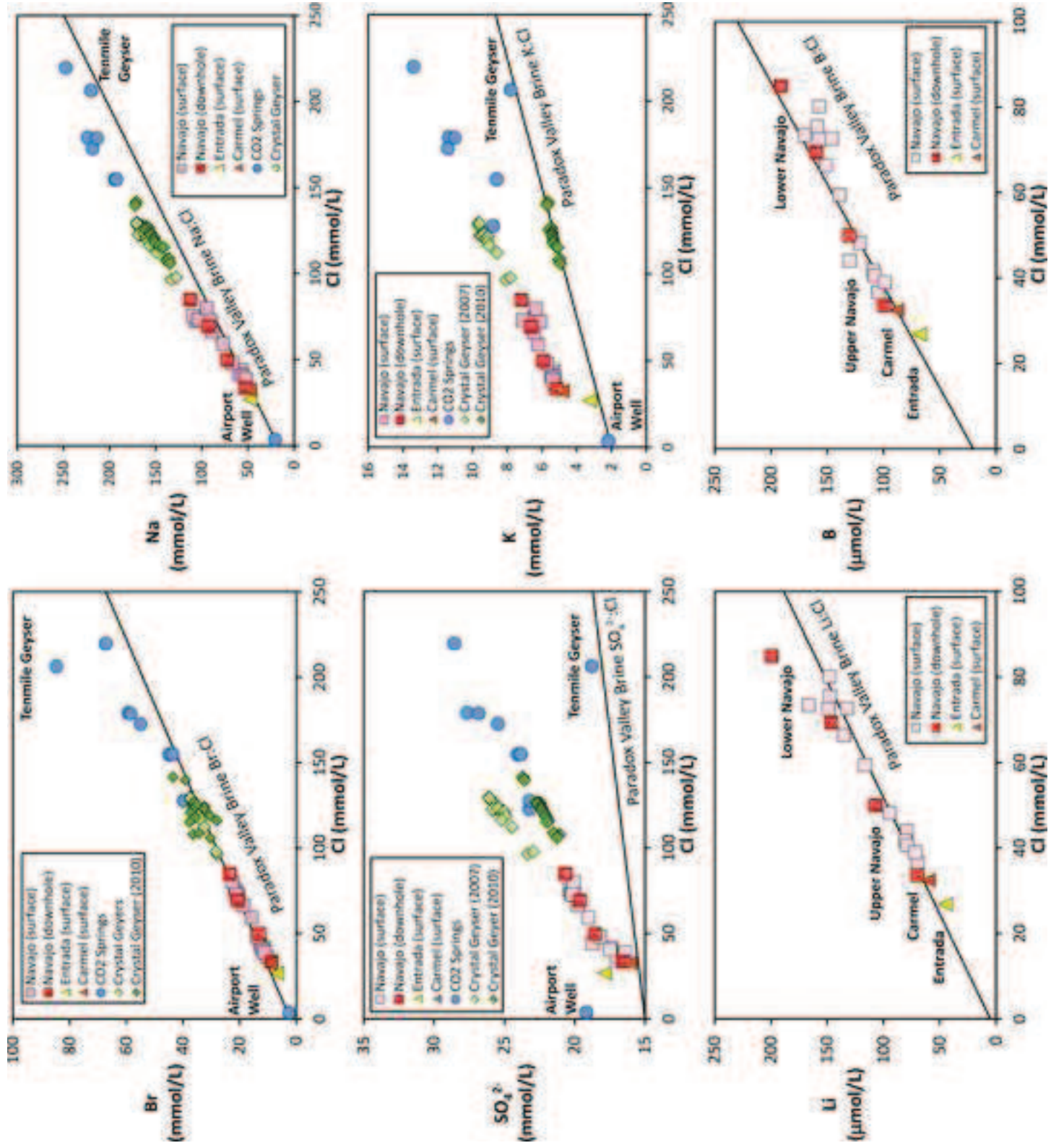


Figure 19

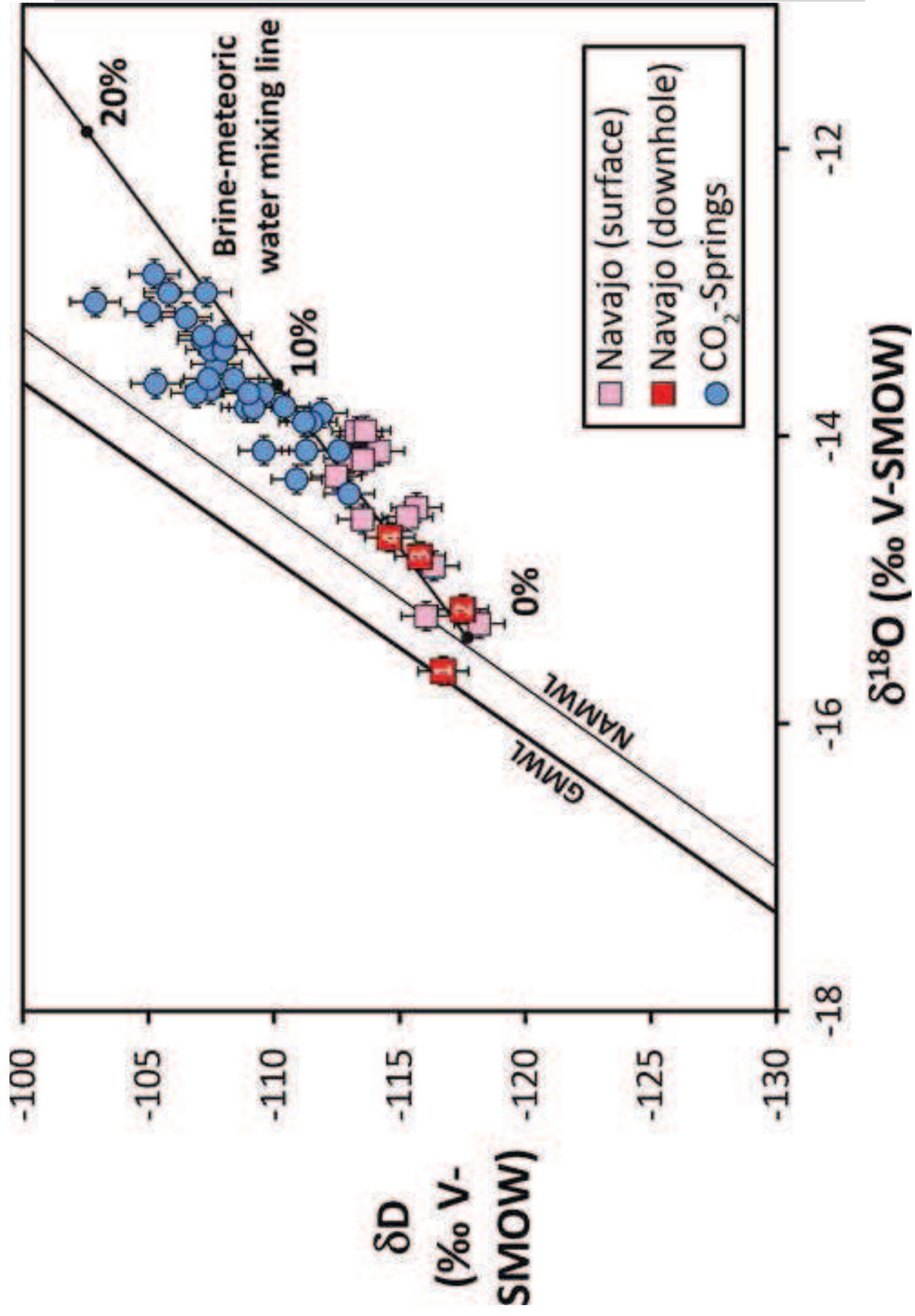
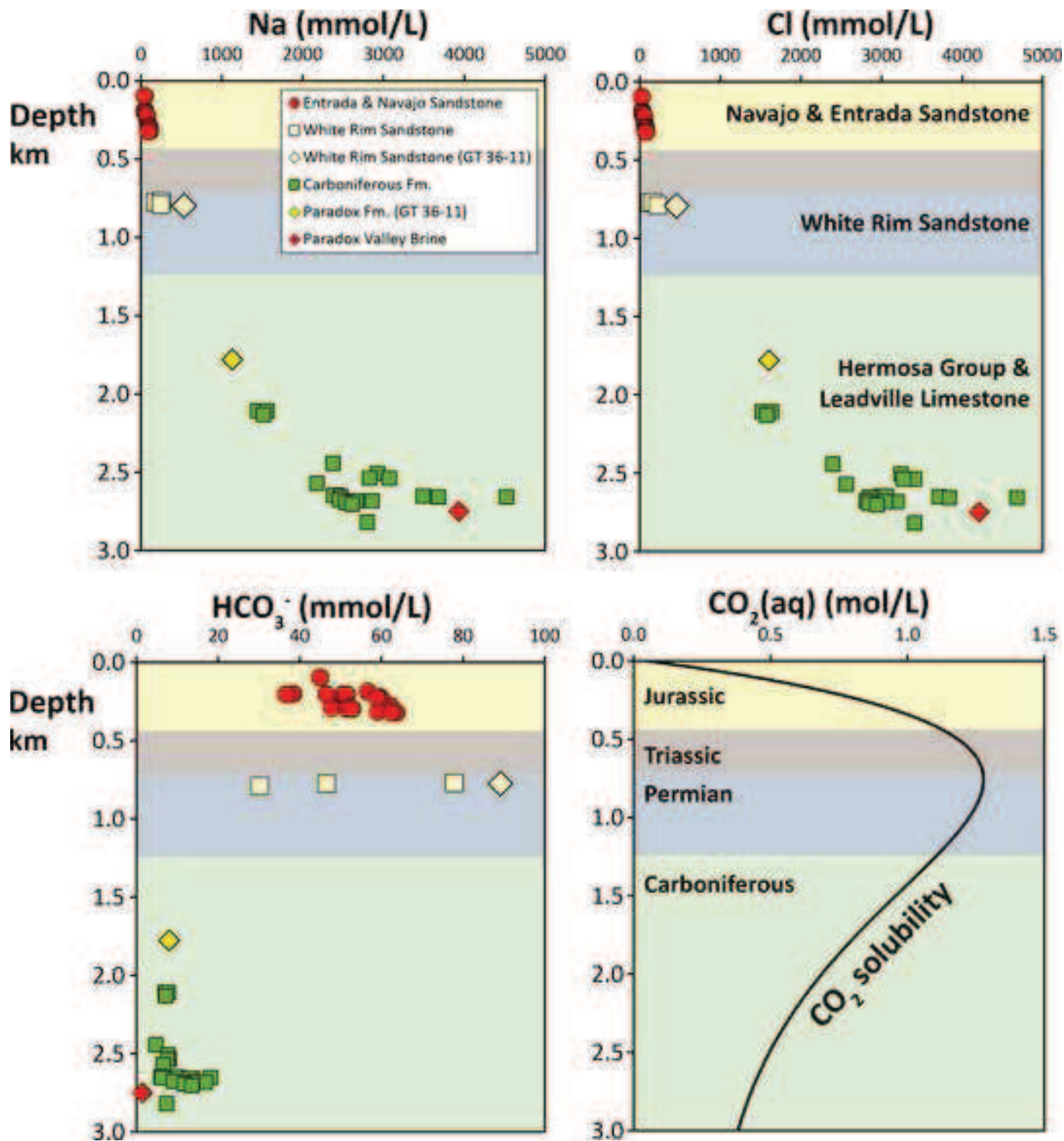


Figure 20

Figure 21



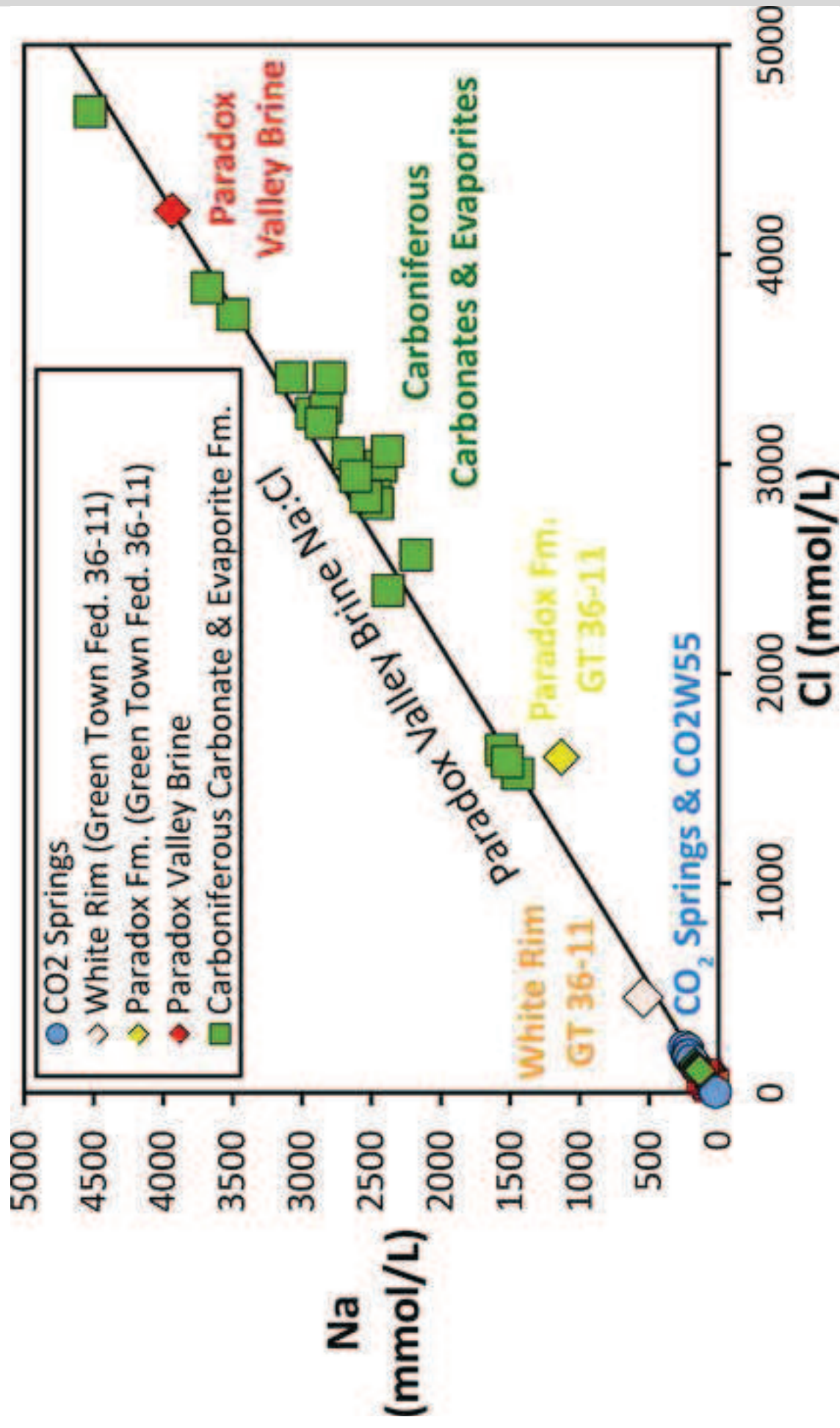
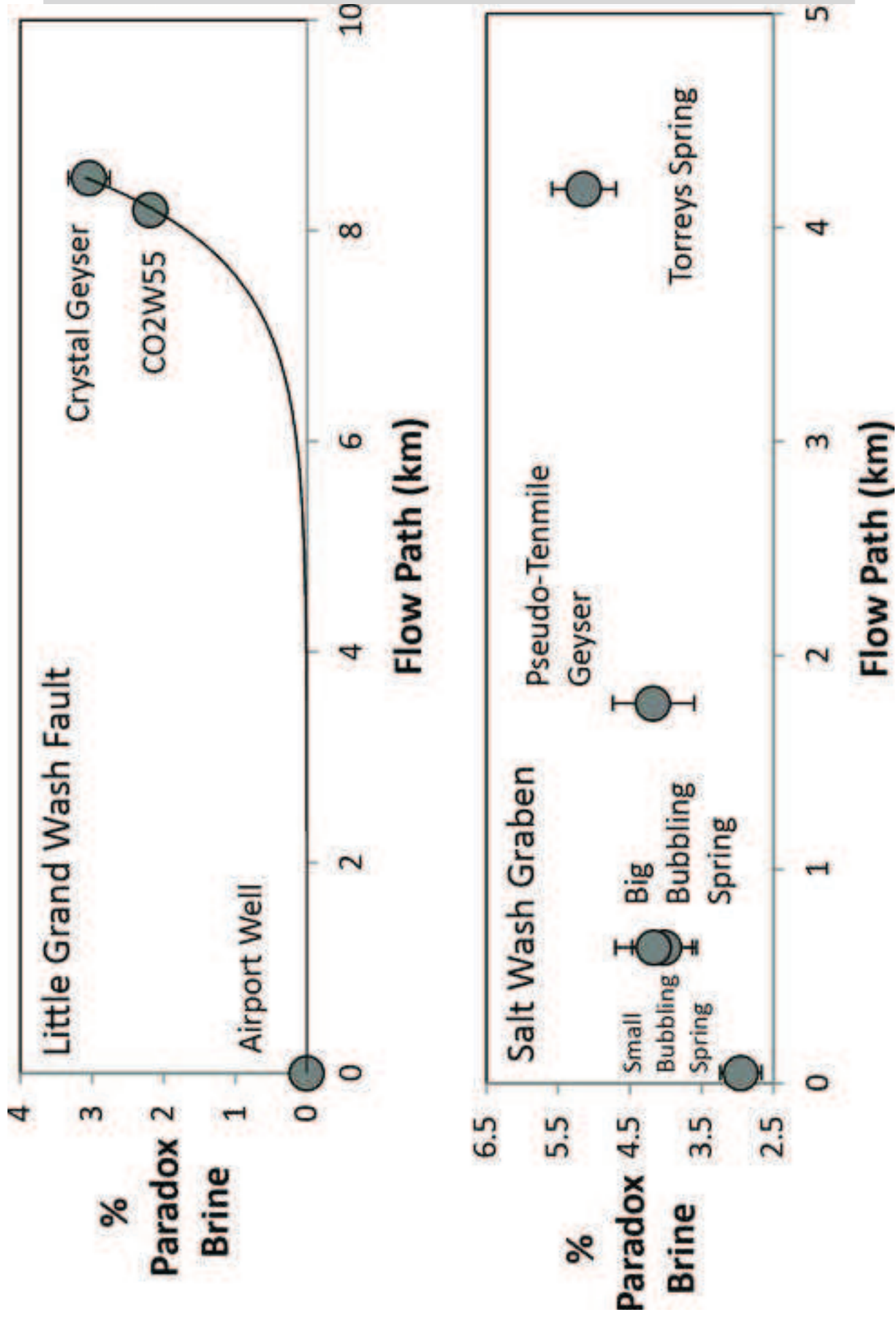


Figure 22

Figure 23



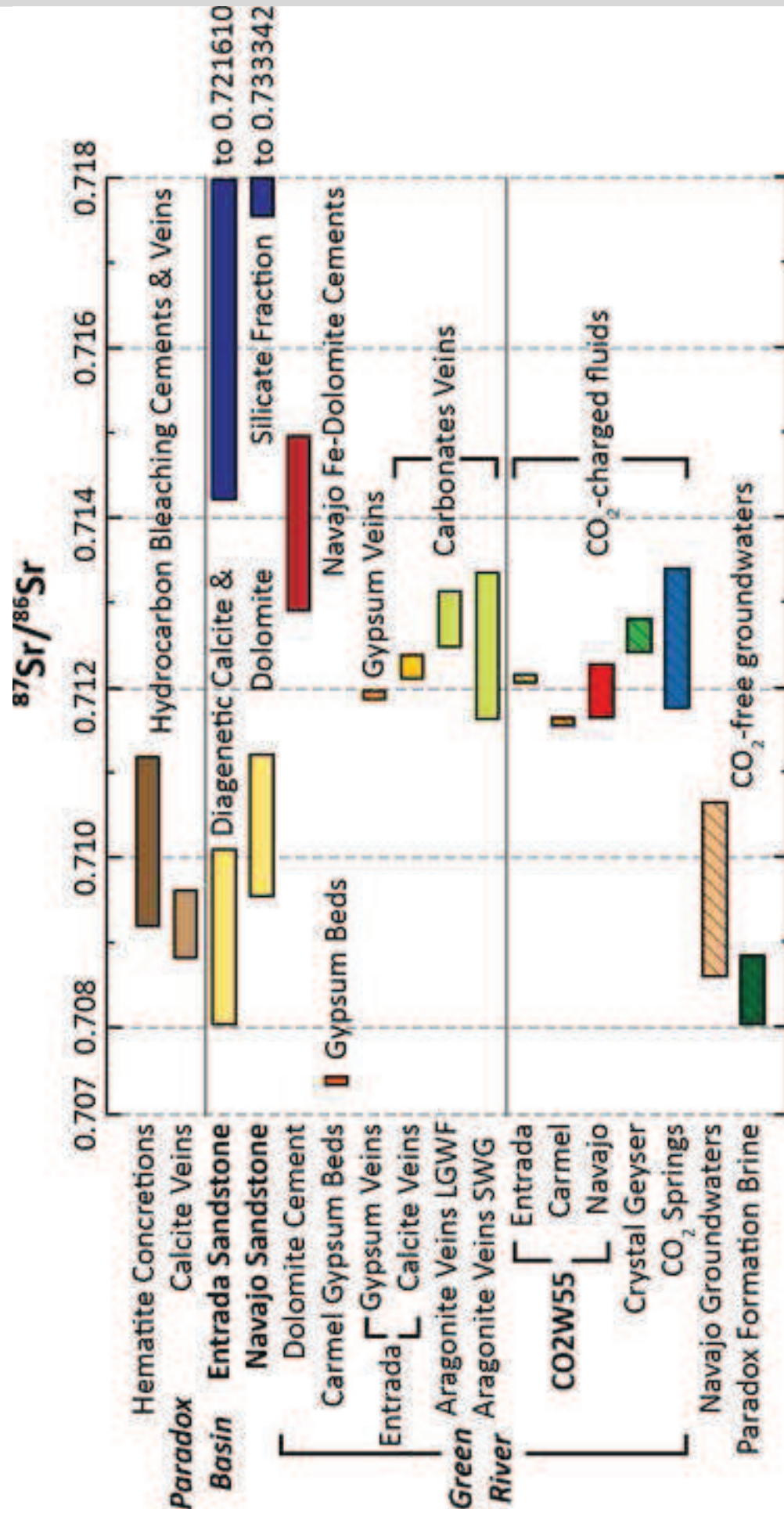
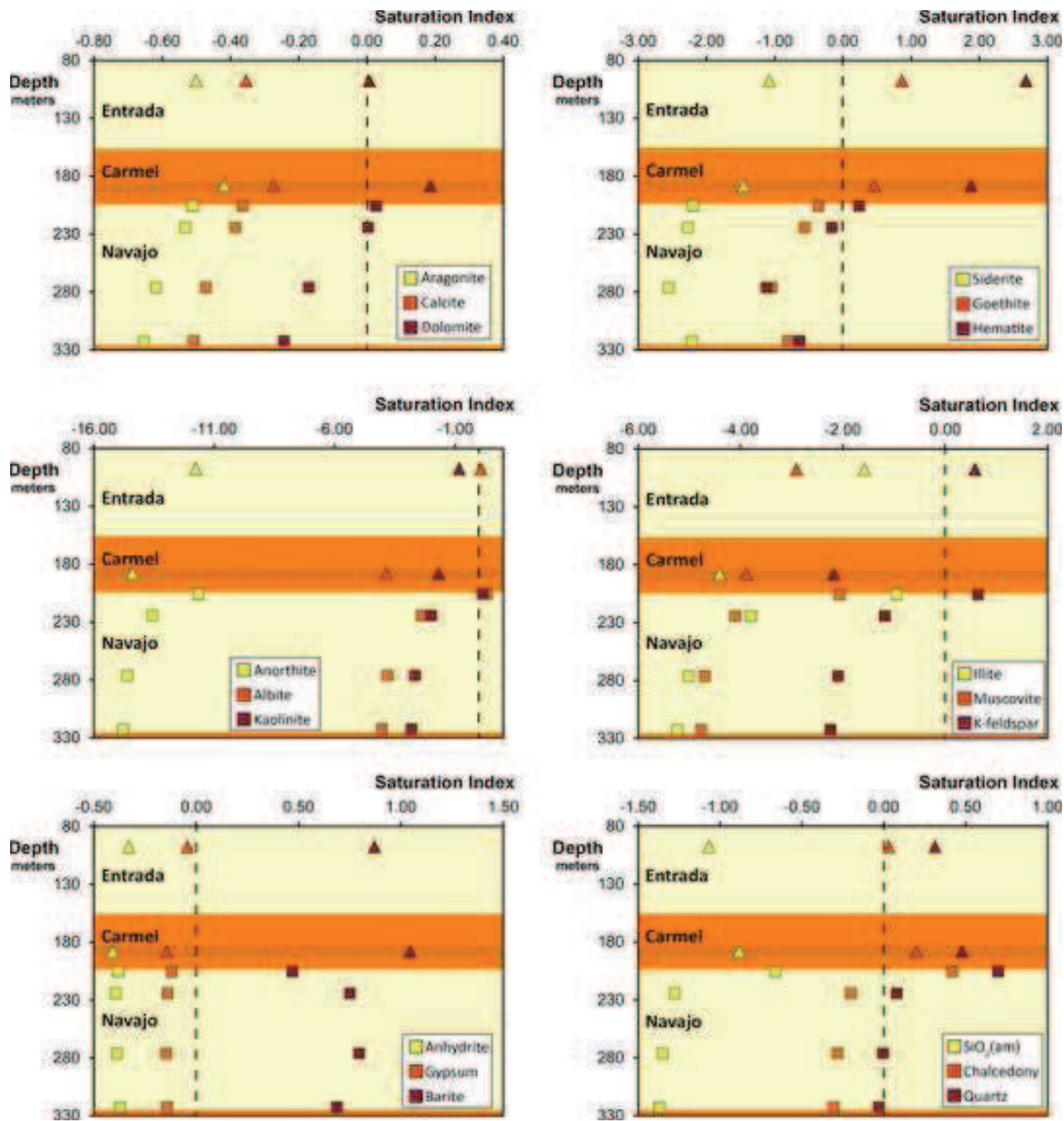
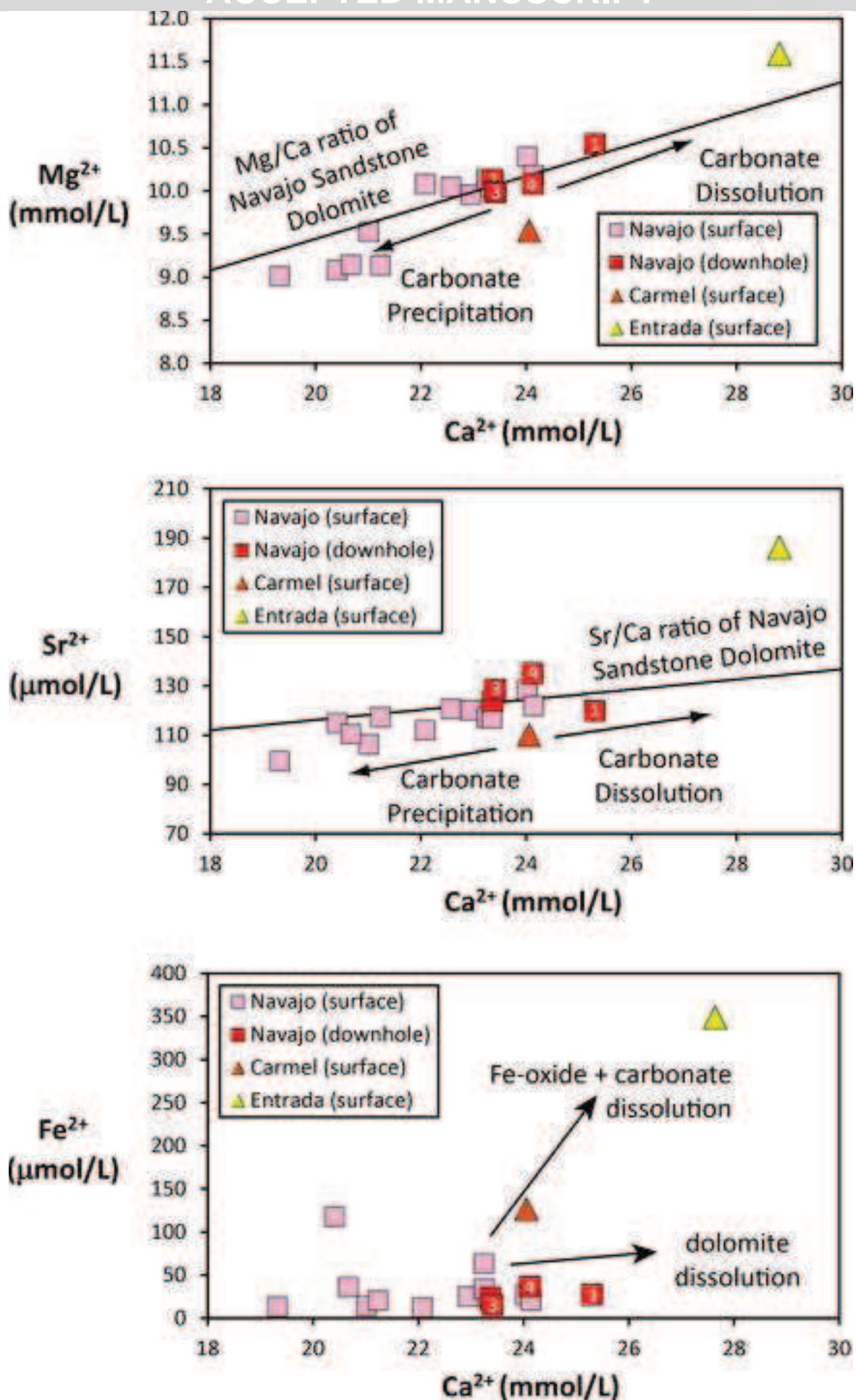


Figure 24

Figure 25





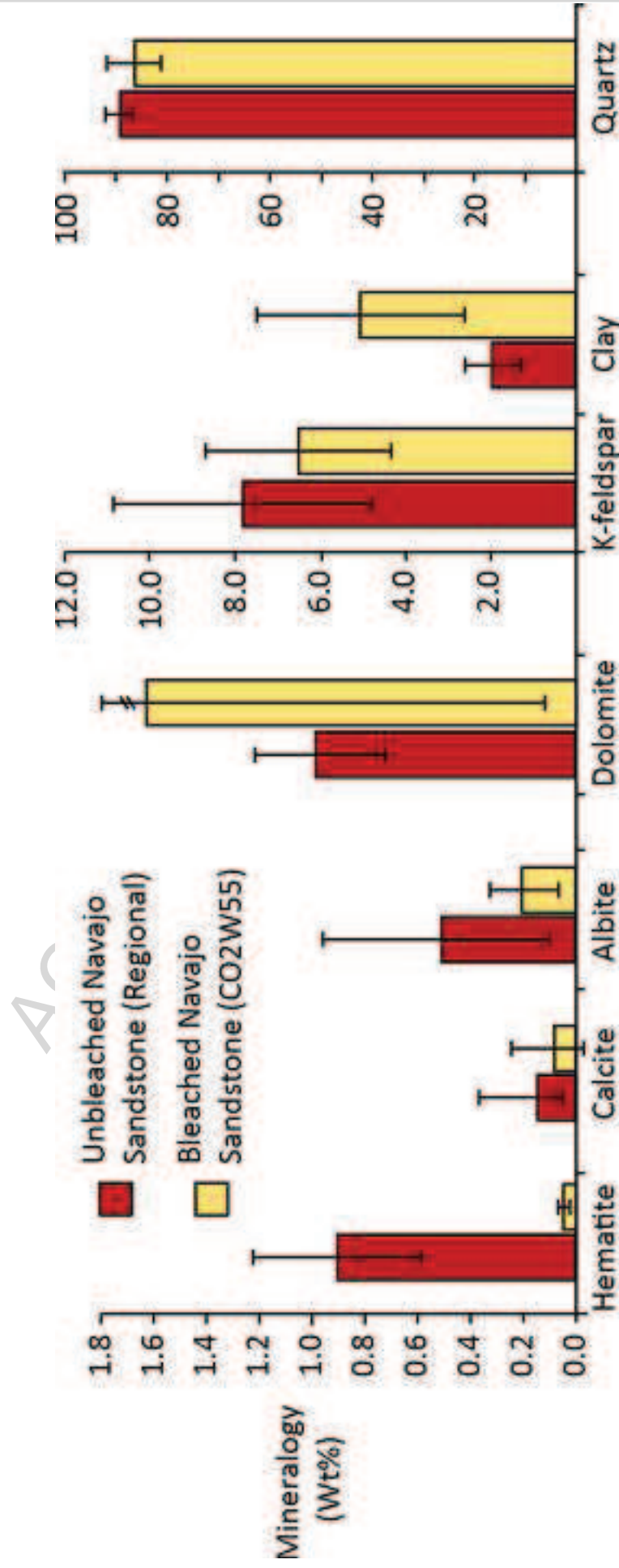


Figure 27

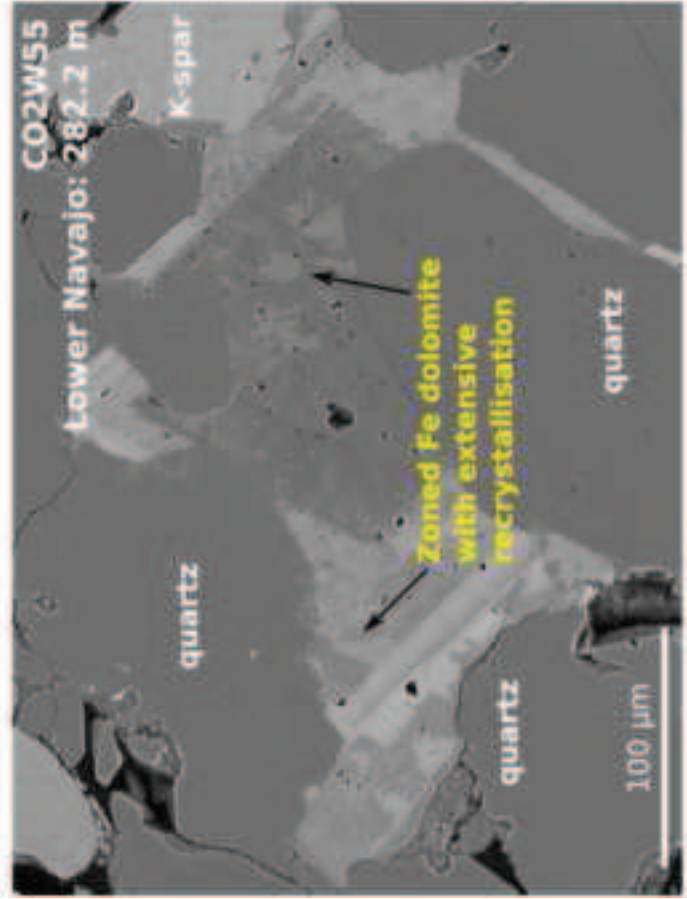
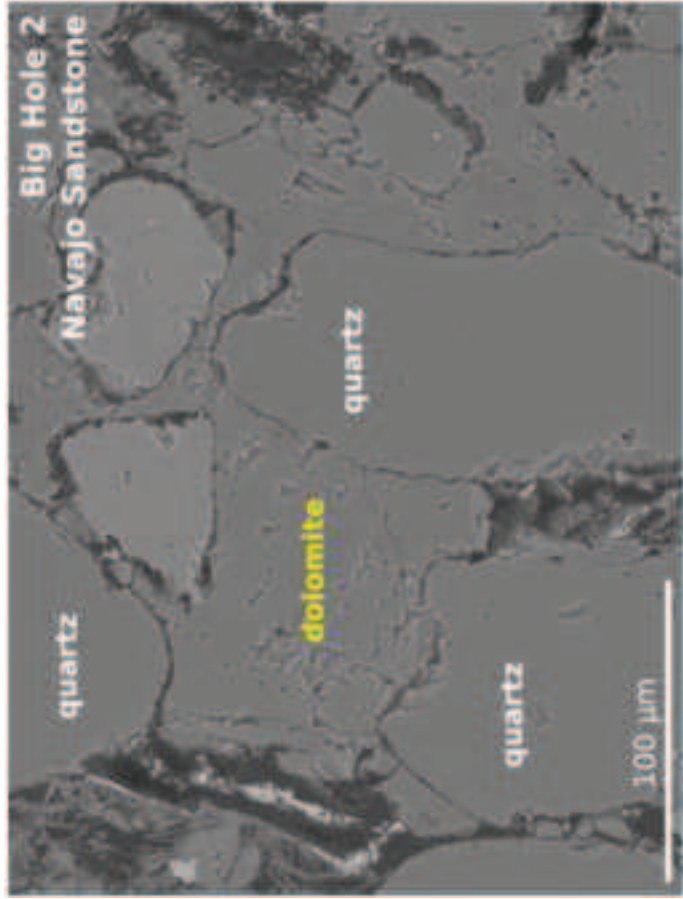
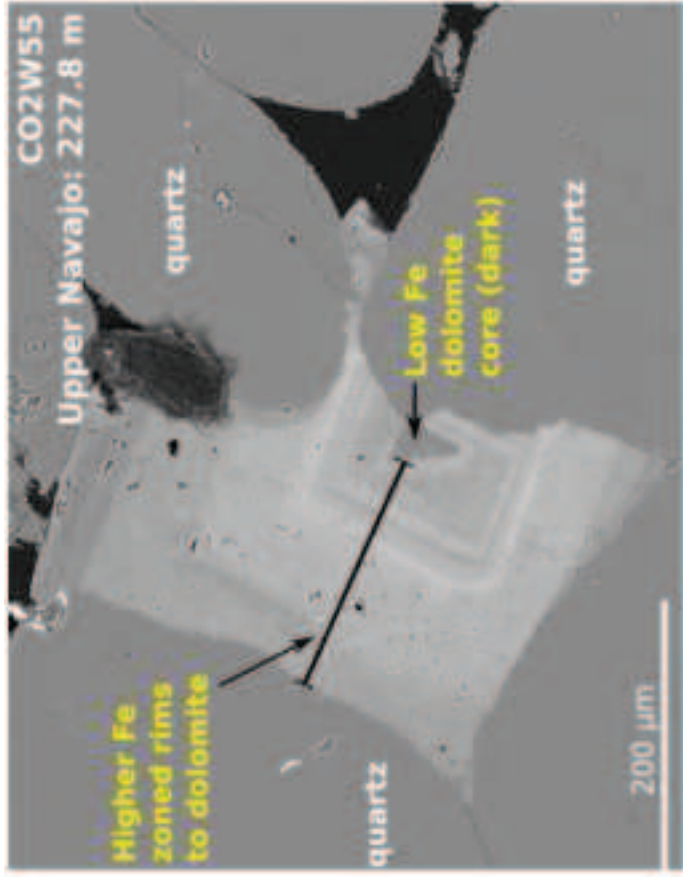


Figure 28

Crystal Geyser 'Type B' Eruption

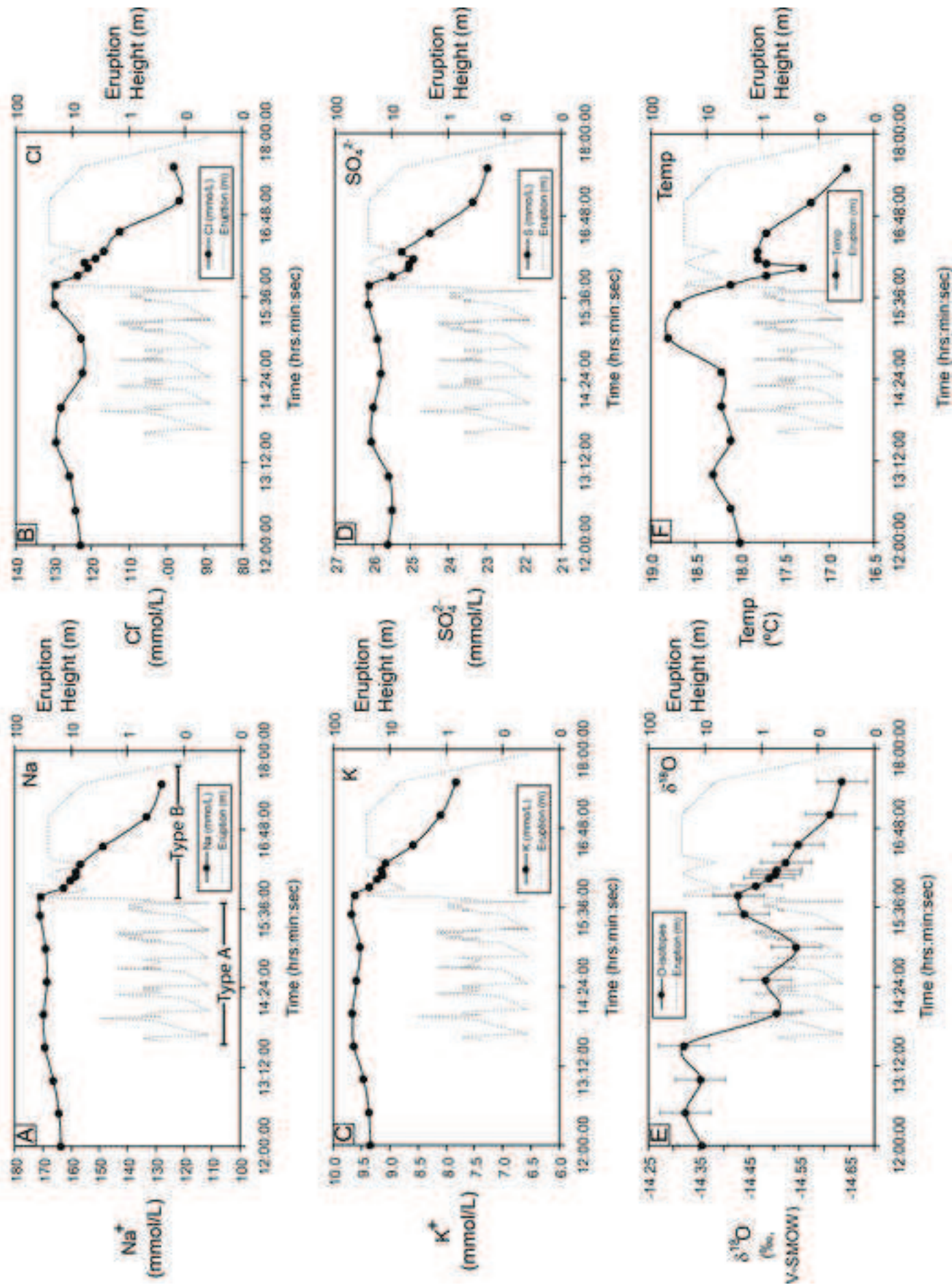


Figure 29

Crystal Geyser 'Type B' Eruption

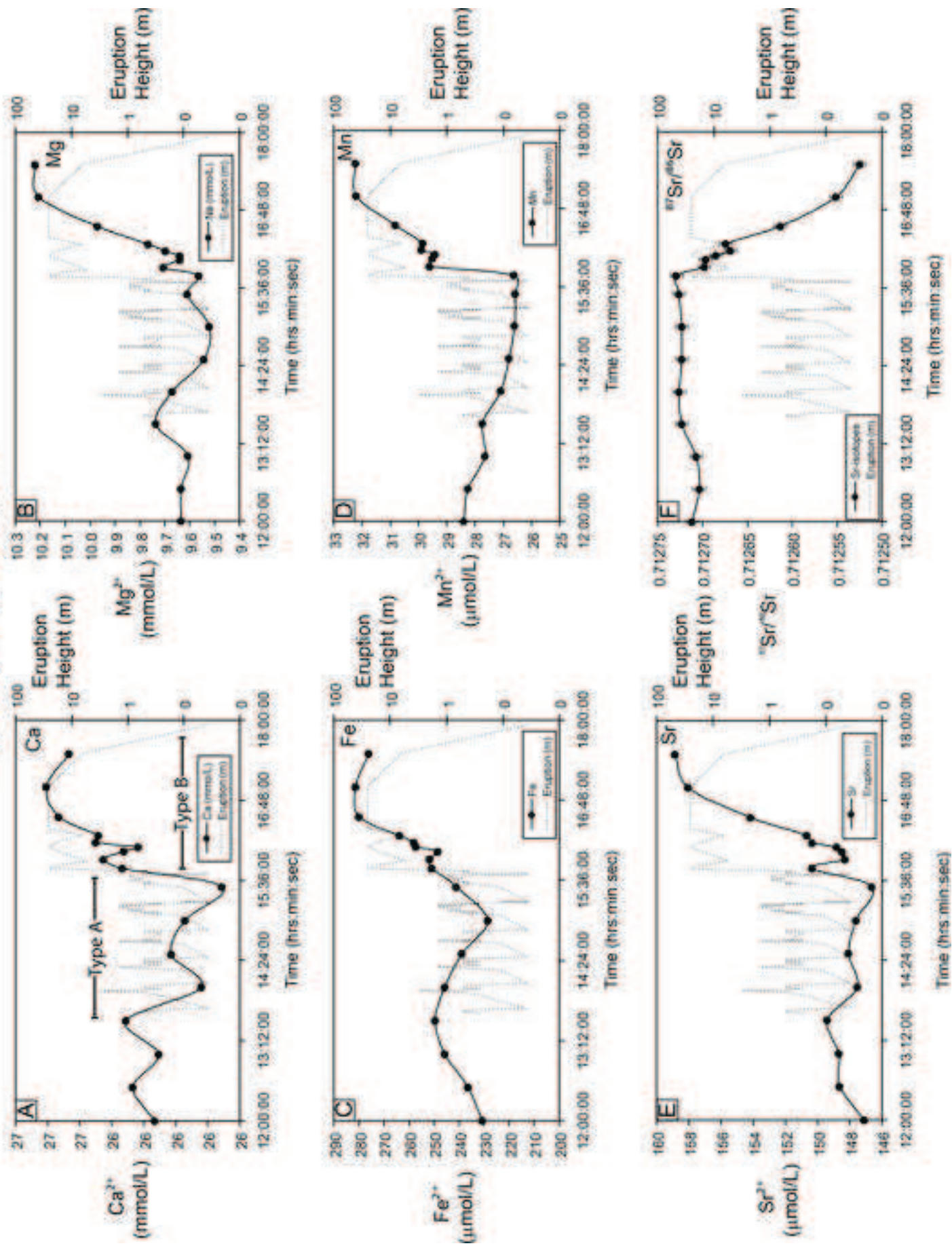
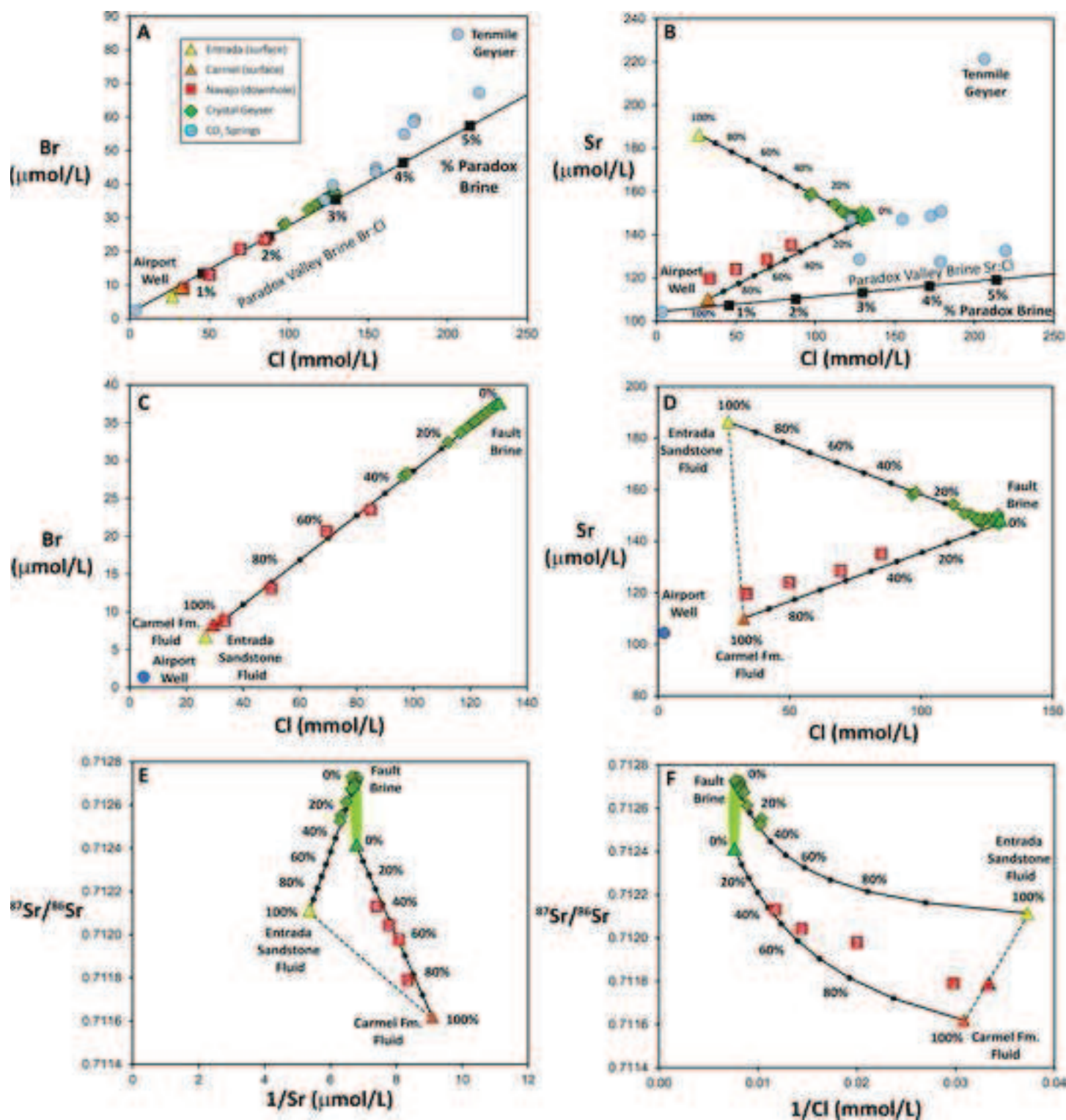


Figure 30

Figure 31



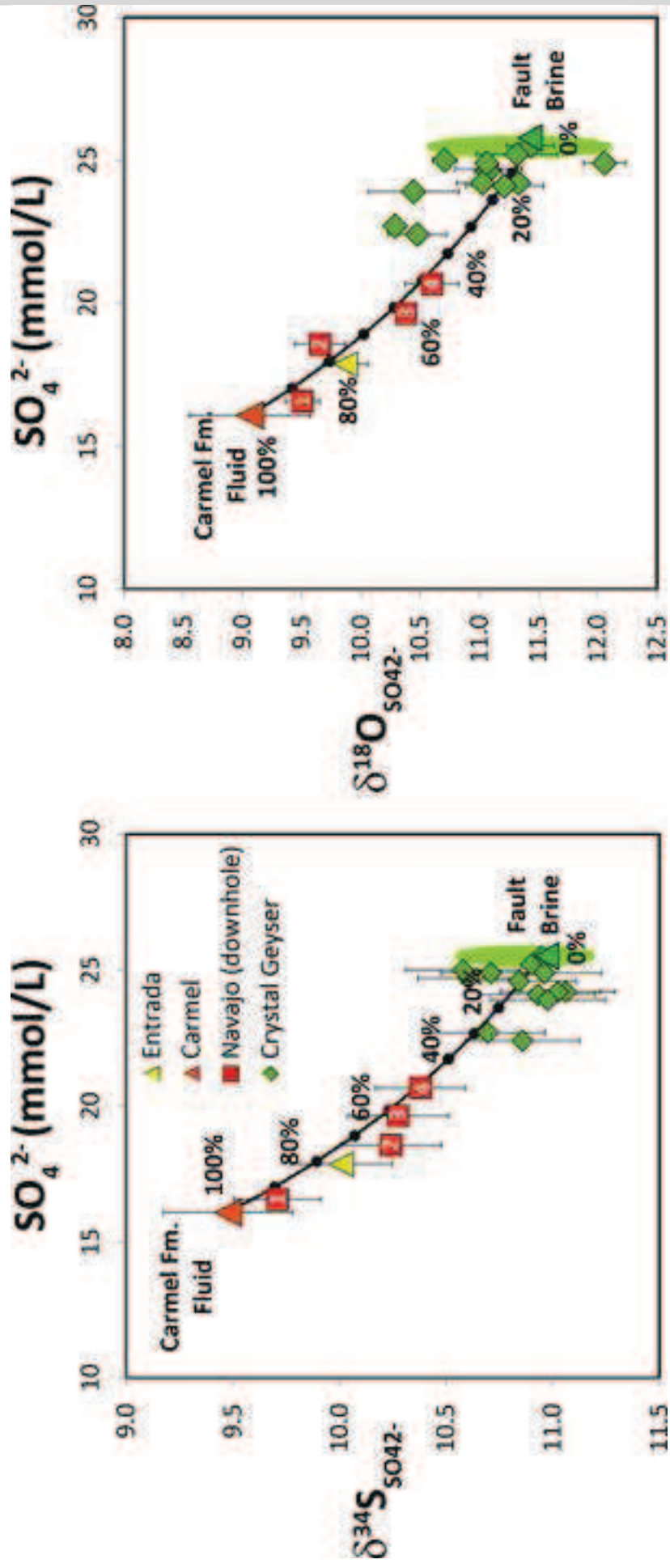


Figure 32

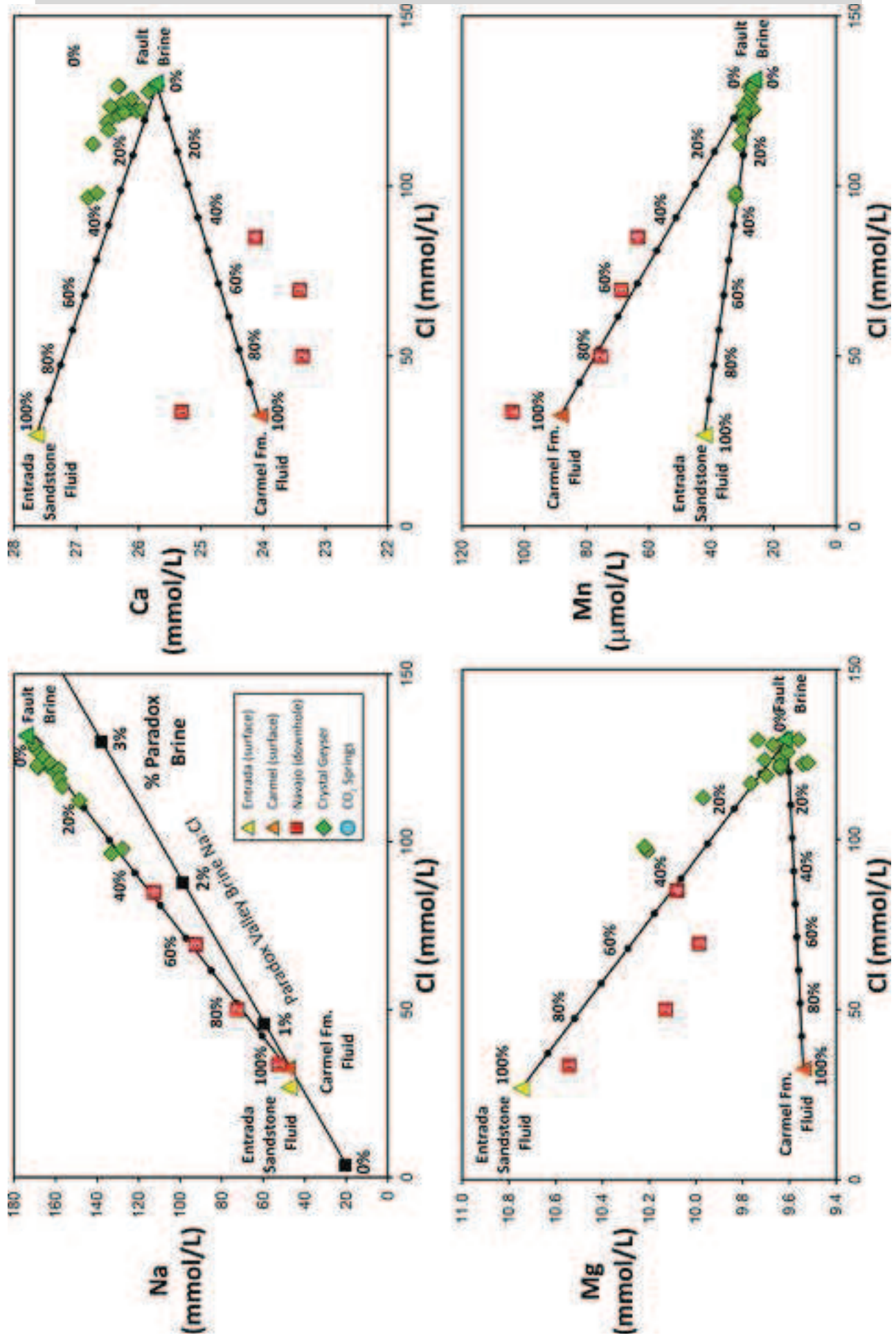


Figure 33

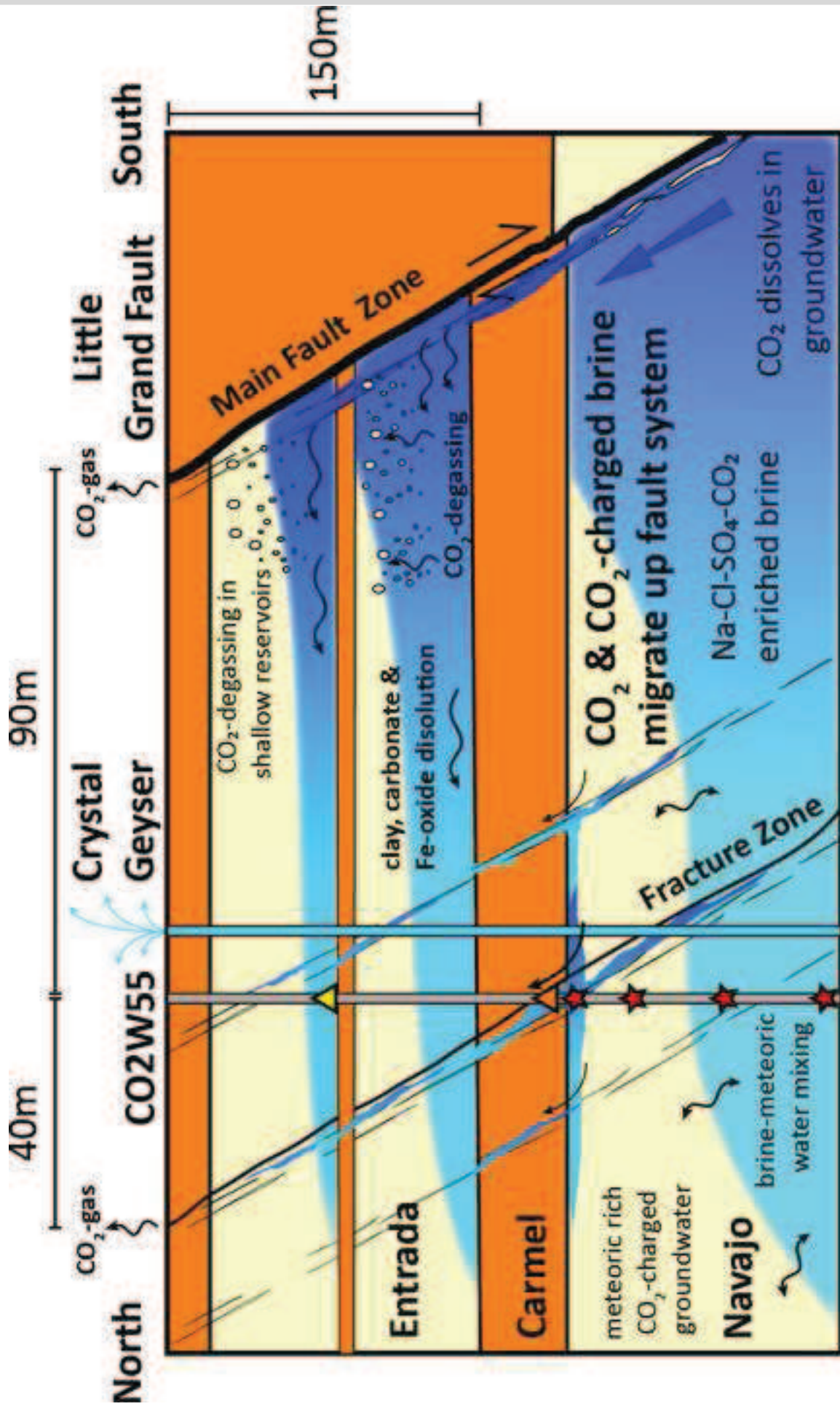


Figure 34

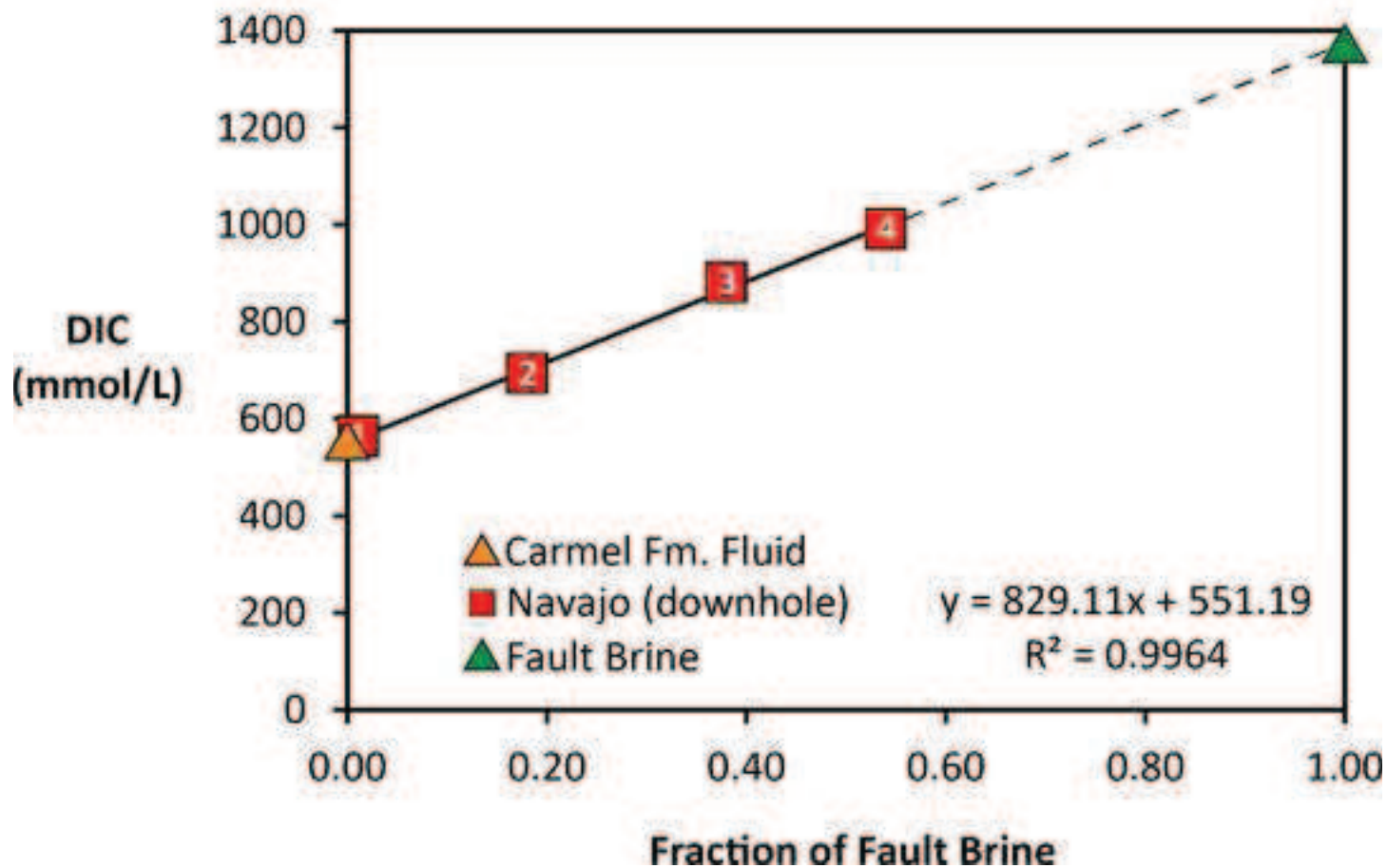
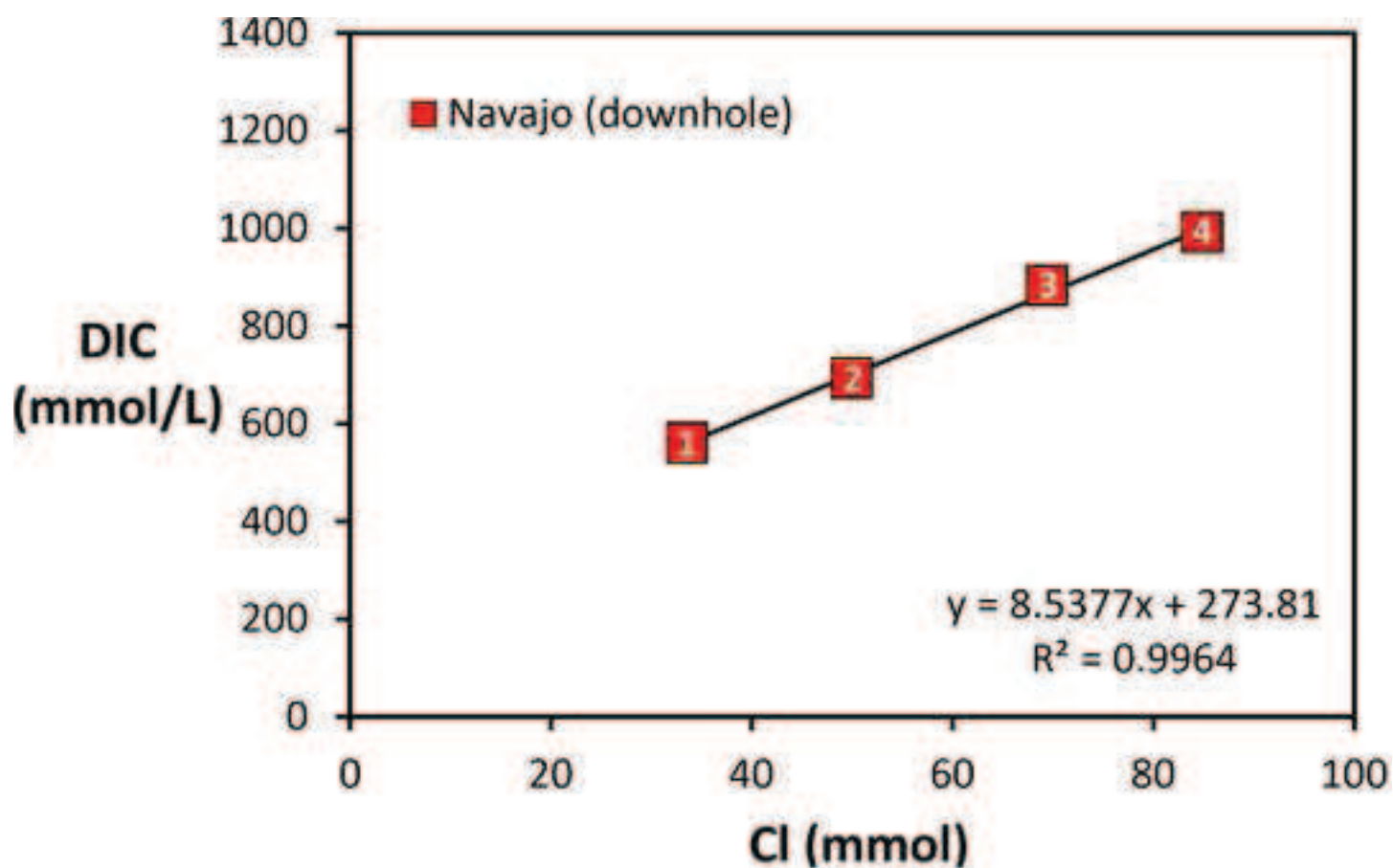


Table 1

Code	Formation	Depth	Temp	pH		DIC	Alkalinity	Al ³⁺	B ⁺	Ba ²⁺
				(surface)	(insitu)					
		m	°C			mmol/l	mEq/L	μmol/l	μmol/l	μmol/l
ENTRADA	Entrada	98	13.6	6.3			45.00	0.3	67.8	0.4
UDP001	Carmel	188	15.5	6.2			56.68	7.6	88.1	0.6
DSF001	Navajo	206	15.9		5.30	561	50.62	1.6	99.5	0.2
DFS002	Navajo	224	16.3		5.21	692	59.24	1.3	130.3	0.3
DFS003	Navajo	276	17.4		5.15	882	62.14	1.3	159.9	0.4
DFS004	Navajo	322	18.3		5.13	991	63.74	1.2	191.2	0.3
UDP002	Navajo	203	15.8	6.43			38.43	1.4	104.7	0.4
UDP003*	Navajo	206	15.9	6.42			80.24	1.2	130.0	0.6
UDP004	Navajo	206	15.9	6.43			36.66	5.6	109.4	0.3
UDP005	Navajo	206	15.9	6.22			46.58	4.8	107.9	0.4
UDP006	Navajo	206	15.9	6.43			51.50	0.9	99.0	0.5
UDP007	Navajo	224	16.3	6.52			59.82	0.9	120.9	0.3
UDP008	Navajo	224	16.3	6.58			58.92	1.7	139.3	0.3
UDP009	Navajo	286	17.6	6.23			52.17	1.0	151.4	0.4
UDP010	Navajo	292	17.7	6.11			47.91	0.9	157.1	0.3
UDP011	Navajo	298	17.8	6.15			51.60	1.0	158.9	0.4
UDP012	Navajo	298	17.8	6.27			52.92	0.9	170.3	0.4
UDP013	Navajo	316	18.2	6.24			59.18	0.8	146.2	0.3
UDP014	Navajo	322	18.3	6.51			62.50	0.6	157.4	0.3

Table 2

Sample Labels	$^{87}\text{Sr}/^{86}\text{Sr}$	%error $\times 10^{-6}$	$\delta^{18}\text{O}$		$\delta^{34}\text{S}$	σ		
			VSMOW	δD		σ	σ	
ENTRADA	0.71211	6	-13.09	-110.1	10.01	0.24	9.87	0.51
UDP001	0.71162	6	-14.50	-115.7	9.48	0.34	9.06	0.19
DSF001	0.71179	8	-15.63	-116.7	9.71	0.21	9.51	0.15
DFS002	0.71198	7	-15.21	-117.5	10.24	0.24	9.66	0.21
DFS003	0.71204	7	-14.84	-115.8	10.28	0.24	10.38	0.08
DFS004	0.71213	7	-14.70	-114.6	10.38	0.21	10.60	0.23
UDP002	0.71185	7	-14.50	-115.7	#N/A	#N/A	#N/A	#N/A
UDP003	0.71192	7	-14.16	-113.0	#N/A	#N/A	#N/A	#N/A
UDP004	#N/A	#N/A	-14.11	-114.2	#N/A	#N/A	#N/A	#N/A
UDP005	0.71190	8	-13.97	-113.3	#N/A	#N/A	#N/A	#N/A
UDP006	0.71191	7	-14.28	-112.5	#N/A	#N/A	#N/A	#N/A
UDP007	0.71194	7	-15.25	-116.1	#N/A	#N/A	#N/A	#N/A
UDP008	0.71200	7	-15.30	-118.2	#N/A	#N/A	#N/A	#N/A
UDP009	0.71197	8	-14.90	-116.4	#N/A	#N/A	#N/A	#N/A
UDP010	0.71193	7	-14.58	-113.5	#N/A	#N/A	#N/A	#N/A
UDP011	0.71198	7	-14.16	-113.5	#N/A	#N/A	#N/A	#N/A
UDP012	0.71205	7	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
UDP013	0.71202	7	-14.56	-115.3	#N/A	#N/A	#N/A	#N/A
UDP014	0.71208	7	-13.96	-113.6	#N/A	#N/A	#N/A	#N/A

Code	Spring	Latitude	Longitude	Eh	pH	Temp	Alkalinity	Al ³⁺	Ba ²⁺
				mV		°C	mEq/L	μmol/l	μmol/l
CG001	Crystal Geyser	38.93900	-110.13550	-5	6.52	18.2	68.86	5.8	0.1
GR07009	Torreys Spring	38.85873	-110.07277	-39.6	6.51	16.4	78.72	5.8	0.0
GR07007	Tenmile Geyser	38.86272	-110.10125	-22.6	6.55	18.5	58.21	5.0	0.1
GR07004	Pseudo-Tenmile Geyser	38.86574	-110.10046	6.44	6.42	15.8	62.06	4.7	0.0
GR07018a	Chaffin Ranch Geyser	38.76350	-110.12744	-35	6.25	16	76.12	5.8	0.0
GR07002	Green River Airport Well	38.96618	-110.22624	-42	6.28	26.8	37.08	4.6	0.1
GR07012a	Big Bubbling Spring	38.87107	-110.11154	-32	6.36	17.7	66.04	5.0	0.0
GR07010	Small Bubbling Spring	38.87265	-110.11662	-7	6.24	19.2	56.54	4.3	0.1
GR07013a	Side Seep, BBS	38.86998	-110.11086	-32	6.25	17.9	59.69	4.3	0.1
GR07019	Tumble Weed Geyser	38.81984	-110.12753	-32	6.3	17.9	62.12	6.0	0.0

Table 4

Code	Spring	Ar	N ₂	CO ₂	CH ₄	δ ¹³ C-CO ₂
		%	%	%	vpm	‰ PVDB
CG001	Crystal Geyser	0.54	3.36	96.1	73	-6.87
GR07009	Torreys Spring	1.91	7.23	90.9	81	-6.23
GR07007	Tenmile Geyser	1.41	18.1	80.5	247	-6.89
GR07004	Pseudo-Tenmile Geyser	0.68	2.27	97.1	98	-7.09
GR07018a	Chaffin Ranch Geyser	0.68	3.6	95.5	108	-6.3
GR07002	Green River Airport Well	0.99	3.91	95.1	171	-6.28
GR07012a	Big Bubbling Spring	1.53	5.45	93	94	-6.99

Code	Time	pH	Temp	Alkalinity	Al ³⁺	Ba ²⁺	Ca ²⁺	Fe ²⁺	K ⁺	Mg ²⁺	Mn ²⁺	Na ⁺
			°C	mEq/L	μmol/l	μmol/l	mmol/l	μmol/l	mmol/l	mmol/l	μmol/l	mmol/l
CG1	12:00:00	6.32	18	75.59	5.82	0.08	26.13	230.60	9.35	9.63	28.40	163.56
CG2	12:30:00	6.38	18.1	69.35	5.38	0.08	26.27	236.41	9.37	9.64	28.25	164.41
CG3	13:00:00	6.38	18.3	68.98	5.56	0.07	26.11	245.59	9.46	9.61	27.63	166.21
CG4	13:30:00	6.38	18.1	64.70	6.07	0.09	26.31	249.52	9.64	9.73	27.75	169.29
CG5	14:00:00	6.38	18.2	74.53	5.39	0.07	25.84	245.61	9.66	9.67	27.08	169.69
CG6	14:30:00	6.37	18.2	62.83	6.17	0.07	26.03	238.93	9.58	9.54	26.80	168.38
CG7	15:00:00	6.31	18.8	62.67	5.31	0.08	25.94	228.53	9.52	9.52	26.60	168.87
CG8	15:30:00	6.38	18.7	68.34	5.95	0.08	25.71	240.97	9.67	9.61	26.58	170.81
CG9	15:47:00	6.57	18.1	68.71	5.99	0.07	26.33	250.77	9.61	9.56	26.62	170.65
CG10	15:55:10	6.57	17.7	71.21	6.09	0.08	26.45	251.78	9.36	9.71	29.62	162.50
CG11	16:02:00	6.55	17.3	62.66	5.75	0.08	26.32	248.30	9.22	9.64	29.51	160.07
CG12	16:06:00	6.57	17.7	69.75	5.78	0.08	26.24	257.15	9.12	9.64	29.42	158.24
CG13	16:10:00	6.55	17.8	72.49	5.85	0.07	26.50	257.88	9.14	9.70	29.89	158.09
CG14	16:16:30	6.55	17.8	58.35	5.98	0.08	26.48	263.72	9.07	9.76	29.84	156.75
CG15	16:33:00	6.55	17.7	66.23	6.47	0.08	26.73	279.75	8.58	9.97	30.81	148.57
CG16	17:00:00	6.53	17.2	64.85	5.43	0.08	26.81	281.12	8.09	10.21	32.19	133.06
CG17	17:30:00	6.56	16.8	61.11	5.49	0.08	26.67	276.02	7.82	10.22	32.23	127.74

Code	Sample Type	Formation	Locality/Drill-hole	Latitude	Longitude	Depth metres
RS 067	Calcite Vein	Entrada	Salt Wash Graben	38.86487	-110.09982	surface outcrop
RS 092	Calcite Vein	Entrada	Salt Wash Graben	38.87023	-110.11190	surface outcrop
RS 073	Gypsum Vein	Entrada	Salt Wash Graben	38.86655	-110.10241	surface outcrop
RS 073	Gypsum Vein	Entrada	Salt Wash Graben	38.86655	-110.10241	surface outcrop
RS 073	Gypsum Vein	Entrada	Salt Wash Graben	38.86655	-110.10241	surface outcrop
525.5	Gypsum Bed	Carmel	CO2W55	38.93792	-110.13892	160.2
NRS053	Sandstone	Navajo	CO2W55	38.93792	-110.13892	227.8
NRS097	Sandstone	Navajo	CO2W55	38.93792	-110.13892	259.7
A638/1	Sandstone	Navajo	Blaze #1-C	38.98117	-109.84936	1419.6
K3B	Siltstone/sandstone	Kayenta	San Rafael Swell	38.92237	-110.44165	surface outcrop
W9	Sandstone	Wingate	San Rafael Swell	38.92374	-110.44413	surface outcrop

Code	Drill-hole	Formation	Depth	Quartz	Albite	K-feldspar	Illite	Calcite	Dolomite
			metres						
							wt. %		
CNH 2A	CO2W55	Navajo	206.94	88.8	0.0	5.5	4.0	0.0	1.7
CNN 9B	CO2W55	Navajo	226.83	93.0	0.1	2.5	4.0	0.2	0.3
CNH-20	CO2W55	Navajo	237.74	80.5	0.2	8.3	6.0	0.0	4.8
CNH-31	CO2W55	Navajo	248.41	80.4	0.4	8.7	7.7	0.4	2.4
CNH-41	CO2W55	Navajo	250.85	92.0	0.3	5.8	1.5	0.0	0.4
CNH-50	CO2W55	Navajo	272.06	88.5	0.1	6.7	3.7	0.0	0.8
CNH-57	CO2W55	Navajo	282.21	82.1	0.3	8.0	8.4	0.0	1.1

Table 8.

Entrada Sandstone	Na	K	Ca	Mg	Sr	Fe	Mn	SO₄	Br	Cl	HCO₃
predicted	41.2	3.7	28.8	11.6	186.2	354.6	44.9	16.4	7.8	26.8	44.9
measured	47.6	3.3	27.6	10.7	186.3	348.9	42.3	17.9	6.7	26.8	45.0
% Difference	-14.0	13.4	4.2	7.8	0.0	1.6	6.2	-8.1	15.3	0.0	-0.3

Fault Brine	Na	K	Ca	Mg	Sr	Fe	Mn	SO₄	Br	Cl	HCO₃
predicted	164.7	8.9	23.1	9.7	148.4	45.1	28.6	24.2	36.2	129.6	75.2
measured	170.8	9.7	25.7	9.6	146.7	241.0	26.6	25.5	37.4	129.6	68.3
% Difference	-3.6	-7.4	-10.2	0.7	1.2	-81.3	7.4	-5.0	-3.2	0.0	10.0

Carmel Formation	Na	K	Ca	Mg	Sr	Fe	Mn	SO₄	Br	Cl	HCO₃
predicted	51.3	5.1	25.3	10.6	119.4	26.7	104.7	16.5	8.5	32.5	50.3
measured	48.3	4.8	24.1	9.5	110.1	126.8	88.5	16.8	9.3	32.5	56.7
% Difference	6.1	6.1	5.3	10.6	8.5	-78.9	18.3	-2.1	-8.6	0.0	-11.2

Highlights

- We discuss drilling of a natural CO₂ reservoir and CO₂-degassing fault.
- Pressurized fluids for geochemistry, pH and CO₂ content were recovered.
- The fluids dissolve hematite and carbonate minerals as they flow away from the fault.
- Fluid geochemistry shows CO₂ is effectively dissolved during migration.
- Switching of reservoir source coincides with eruption onset of a CO₂-geyser