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Diagenesis in tephra-rich sediments from the Lesser Antilles Volcanic Arc: Pore fluid constraints

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44 **Abstract**

45
46 We present sediment pore fluid and sediment solid phase results obtained during IODP
47 Expedition 340 from seven sites located within the Grenada Basin of the southern Lesser Antilles
48 Volcanic Arc region. These sites are generally characterized as being low in organic carbon
49 content and rich in calcium carbonate and volcanogenic material. In addition to the typical
50 reactions related to organic matter diagenesis, pore fluid chemistry indicates that the diagenetic
51 reactions fall within two broad categories; (1) reactions related to chemical exchange with
52 volcanogenic material and (2) reactions related to carbonate dissolution, precipitation, or
53 recrystallization. For locations dominated by reaction with volcanogenic material, these sites
54 exhibit increases in dissolved Ca with coeval decreases in Mg. We interpret this behavior as
55 being driven by sediment-water exchange reactions from the alteration of volcanic material that
56 is dispersed throughout the sediment package, which likely result in formation of Mg-rich
57 secondary authigenic clays. In contrast to this behavior, sediment sequences that exhibit
58 decreases in Ca, Mg, Mn, and Sr with depth suggest that carbonate precipitation is an active
59 diagenetic process affecting solute distributions. The distributions of pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ reflect
60 these competitive diagenetic reactions between volcanic material and carbonate, which are
61 inferred by the major cation distributions. From one site where we have solid phase $^{87}\text{Sr}/^{86}\text{Sr}$
62 (site U1396), the carbonate fraction is found to be generally consistent with the contemporaneous
63 seawater isotope values. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ of the non-carbonate fraction ranges from
64 0.7074 to 0.7052, and these values likely represent a mixture of local arc volcanic sources and
65 trans-Atlantic eolian sources. Even at this site where there is clear evidence for diagenesis of
66 volcanogenic material, carbonate diagenesis appears to buffer pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ from the larger
67 changes that might be expected given the high abundance of tephra in these sediments. Part of

68 this carbonate buffering, at this site as well as throughout the region, derives from the fact that
69 the Sr concentration in the non-carbonate fraction is generally low (< 200 ppm), whereas the
70 carbonate fraction has Sr concentrations approaching ~1000 ppm.

71

72 **1.0 INTRODUCTION**

73

74 Explosive volcanism contributes tephra and ash to marine sediments throughout the
75 global ocean. For example, it has been estimated that 15 - 20 wt% of Caribbean Sea sediments
76 are composed of ash (Peters et al. 2000) and, on a larger scale, ~6 - 60 wt% of northwest Pacific
77 sediments may be composed of volcanogenic material (Scudder et al. 2009, 2014). Diagenesis of
78 this material can lead to the release of dissolved constituents, precipitation of new minerals
79 (clays and carbonates), and (re)crystallization of various mineral phases (Elderfield et al., 1982;
80 Fisher and Schmincke, 1984; Gieskes et al., 1986; Gieskes et al., 1987; Gieskes et al., 1990a, b,
81 c). In particular, highly reactive glassy particles can exert a strong influence on diagenetic
82 processes (Kutterfolf et al., 2009; Hesse and Schacht, 2011), and these processes can impact the
83 ocean's elemental budgets (Hart and Staudigel, 1982; Staudigel and Hart, 1982; Aller, 2014).
84 One pertinent example is that these reactions can play an important role in the Earth's carbon
85 cycle by promoting the burial of organic and inorganic carbon, which can ultimately regulate
86 long-term feedbacks between climate and atmospheric CO₂ (Haeckel et al., 2001; Wallmann et
87 al., 2008; Hembury et al., 2012).

88 A large number of Ocean Drilling Program (ODP) and Deep Sea Drilling Project (DSDP)
89 studies have examined the pore fluid geochemistry of deep sea sediments that reflect chemical
90 reaction between pore waters and volcanic material (Gieskes and Lawrence, 1981; Gieskes,
91 1983; Gieskes et al., 1987; Gieskes et al., 1990a, b, c; Lyons et al., 2000). These sediments often

92 exhibit a characteristic pore fluid relationship whereby decreases in Mg correspond to increases
93 in Ca (Gieskes and Lawrence, 1981; Gieskes, 1983; Gieskes et al., 1987; Gieskes et al., 1990a, b;
94 Lyons et al., 2000). The coeval increases in Ca and depletions in Mg are thought to reflect the
95 diagenesis of volcanic material, which are often attributed to reaction with basaltic basement, but
96 may also include dispersed volcanic material within the sediment through exchange reactions
97 that occur during secondary clay formation, particularly smectite (Hein et al., 1979; Gieskes et
98 al., 1987; Gieskes et al., 1990a; Chan and Kastner, 2000; Lyons et al., 2000; Scholtz et al., 2010;
99 Scholtz et al., 2013). The distribution of other elements in pore fluids also show patterns that
100 reflect the alteration of volcanic material, with these alteration products being either a source or a
101 sink of a particular element to the pore fluids (Brumsack and Zuleger, 1992; James and Palmer,
102 2000; Lyons et al., 2000; Teichert et al., 2005; Scholz et al., 2010; Scholz et al., 2013). Pore fluid
103 changes in Ca, Mg, and Sr can also reflect the precipitation or dissolution of carbonate phases,
104 and in many environments these carbonate reactions dominate the geochemical signatures of
105 diagenesis, regardless of the presence of volcanic matter (Gieskes and Lawrence, 1981; Gieskes,
106 1983; Gieskes et al., 1990a; Chan and Kastner, 2000; Lyons et al., 2000; Sample et al., 2017).
107 The current study examines diagenetic reactions occurring within the sediment package of
108 tephra-rich sediments, with an emphasis on identifying the conditions under which volcanic
109 material diagenesis will be expressed in the pore fluids.

110

111 **2.0 STUDY SITE DETAILS**

112 The Lesser Antilles volcanic arc is characterized by the westward subduction of the
113 Atlantic plate beneath the Caribbean plate (Macdonald et al., 2000; Picard et al., 2006). The arc
114 extends 800 km from South America to the Greater Antilles in the north, separating the

115 Caribbean Sea from the Atlantic Ocean (**Figure 1**) (Macdonald et al., 2000; Le Friant et al.,
116 2003). At $2 - 4 \text{ cm y}^{-1}$, convergence of the Atlantic plate and Caribbean plate is slow compared
117 to most active volcanic arcs (Macdonald et al., 2000). To the north of Martinique, the island arc
118 splits into two chains of islands (**Figure 1**) (Macdonald et al., 2000; Le Friant et al., 2003;
119 Boudon et al., 2013). To the south of Dominica, the two volcanic arcs are superimposed with
120 volcanism occurring from the Oligocene to the present day (**Figure 1**) (Germa et al., 2011). To
121 the west of the arc lies the Grenada Basin, formed from the rifting of a back arc (Macdonald et
122 al., 2000). This basin is roughly 150 km wide and 600 km long, ranging from Saba Bank to the
123 Venezuela margin (Picard et al., 2006). Since the time of back arc rifting, the Grenada Basin has
124 been accumulating sediment, a significant portion of which is provided by the volcanic activity
125 of the arc. Sediment thickness ranges from 7 km in the north to 12 km in the south (Macdonald
126 et al., 2000; Picard et al., 2006). Sediments within the basin contain hemipelagic mud, tephra,
127 ash, pumice, volcanoclastic turbidites, and debris flows, with the turbidites and debris flows
128 being a result of flank collapses associated with active volcanoes along the western most arc
129 (**Figure 1**) (Deplus et al., 2001; Le Friant et al., 2003; Picard et al., 2006; Le Friant et al., 2015;
130 Wall-Palmer et al., 2016).

131 Sediment cores were collected in 2012 on IODP Expedition 340 to the Lesser
132 Antilles Volcanic Arc (Expedition 340 Scientists, 2012; Le Friant et al., 2013). Three sites were
133 sampled off the coast of Montserrat and five were sampled to the south of Martinique. There are
134 seven cores of interest to this study, the three located in the northern region, U1394 - U1396 and
135 four sites in the southern region (**Figure 2**). Site descriptions are briefly summarized here from
136 the Expedition 340 reports (Expedition 340 Scientists, 2012; Le Friant et al., 2013; Coussens et
137 al., 2016), which should be consulted for more detailed descriptions. Sites U1394 and U1395

138 consist of hemipelagic mud, bioclastic, volcanoclastic, and mixed turbidites, volcanoclastics, and
139 tephra whereas Site U1396 is composed of hemipelagic sediment, tephra, and volcanoclastic
140 sand. Site U1396 was located on a bathymetric high and contained less of the coarser volcanic
141 materials observed for the other sites, but nevertheless did have ~100 visible layers of tephra as
142 well as cryptotephra (Le Friant et al., 2013; McCanta et al., 2015; Coussens et al., 2016; Palmer
143 et al., 2016). Biostratigraphic analysis notes the abundance of planktic foraminifera through the
144 bioclastic, carbonate-rich deposits (e.g., Wall-Palmer et al., 2014). The southern sites consist of
145 hemipelagic mud containing interbedded tephra, and volcanoclastic turbidites (Expedition 340,
146 2012; Le Friant et al., 2013). Age constraints at these sites are uncertain; however, the base of
147 Hole U1394B dates to ~353 ka, and the base of Hole U1395B dates to > 1 Ma. A detailed
148 stratigraphic reconstruction of sediments from Site U1396 has been undertaken (Wall-Palmer et
149 al., 2014; Fraass et al., 2016). The uppermost 7 m of Hole 1396C dates to ~ 1 Ma with the base
150 of the core dating to 4.5 Ma (Hatfield, 2015; Coussens et al., 2016). For the southern sites, ages
151 are not well defined.

152

153 **3.0 METHODOLOGY**

154 Most of the data and methods described in this manuscript are available from the IODP
155 data repository or through the various post-cruise data reports (Le Friant et al., 2013; Murray et
156 al., 2016). Nevertheless, for completeness we briefly review the methodology here.

157

158 **3.1 Sediment Coring and Sampling**

159 Sediment cores were collected during Expedition 340 in 2012 using the R/V JOIDES
160 Resolution. An advanced piston corer (APC) and an extended core barrel (XCB) were both

161 employed to retrieve cores during the cruise. The APC and XCB characteristics and system
162 functions can be found in Graber et al. (2002). Briefly, the APC method is used to cut through
163 softer deep-sea sediments and is thought to create minimal sedimentary disturbance relative to
164 other IODP coring systems (Expedition 340 Scientists, 2013). The XCB is necessary for more
165 firm or lithified substrate (Expedition 340 Scientists, 2013). Given the nature of some of the
166 material, including coarse-grained volcanic sands and other debris, there are notable gaps in
167 some of the records presented here. Recovery was typically poorer through coarse-grained
168 material, or in instances where recovery was successful the material was often not suitable for
169 pore fluid extraction (Expedition 340 Scientists, 2013).

170 Sampling occurred approximately every 10 meters unless the sediment was unsuitable for
171 pore fluid extraction. A 10 - 15 cm section of whole-round core was removed to begin the
172 squeezing process in the laboratory. Whole-round sections were then processed within a
173 nitrogen-filled bag and then transferred to a hydraulic press for pore fluid extraction (Manheim,
174 1966). Following the hydraulic press, pore fluids were filtered through 0.45 μm filters and
175 subsampled for various dissolved constituents (Expedition 340 Scientists, 2013).

176 **3.2 Pore Fluid ICP-OES and ICP-MS analysis**

177 All pore fluid data for this manuscript were presented within data reports associated with
178 the expedition with the exception of the $^{87}\text{Sr}/^{86}\text{Sr}$ (Expedition 340 Scientists, 2013; Le Friant et
179 al., 2013; Murray et al., 2016). The reader is directed to those communications for full data sets
180 and analytical details; however, Sr and Sr isotope data for the pore fluids are present in
181 Supplemental Table 1 and for the sediment solid phases in Supplemental Tables 2 and 3. Briefly,
182 pore fluid samples were diluted with 1% quartz-distilled nitric acid and analyzed by either ICP-
183 MS or ICP-OES. The minor elements were spiked with an artificial seawater mixture to matrix-

184 match samples to approximate seawater concentrations of Na, Cl, and Mg from ultrapure salts
185 (Sigma Aldrich). The reported uncertainties (1σ) are a combination of the square root of the sum
186 of the squares of the regression uncertainty of the standard curve, calculated from the standard
187 error of regression and the internal uncertainty calculated from the standard deviation of three
188 sample replicates. The analytical detection limit is the point where the measured concentration is
189 $> 3\sigma$ above the analytical zero.

190 **3.3 $^{87}\text{Sr}/^{86}\text{Sr}$ analyses**

191 Pore fluid was processed for Sr isotope analysis using AG-50 and Sr-Spec columns for Sr
192 separation at Oregon State University's W.M. Keck Collaboratory for plasma mass spectrometry
193 (see Joseph et al., 2013). Mass bias is corrected using $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.1194, and instrumental
194 offset corrected using $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710245 (for NBS 987, National Bureau of Standards). The
195 internal reproducibility is ± 0.000018 for NBS 987 ($n = 67$), and our external reproducibility is \pm
196 0.000024 ($n = 55$), which is calculated from runs of an in-house standard (EMD® Sr Standard).
197 Solid phase $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined either at the University of Southampton or at
198 Oregon State University. For samples analyzed at the University of Southampton, the carbonate
199 fraction was separated by dissolution in 6M HCl, and the residual samples were dissolved in HF-
200 HNO_3 for 24 h on a hot plate at 130°C . The solution was then evaporated until dry and
201 redissolved in 3M HNO_3 . The Sr was isolated using Sr resin (Eichrom Industries, Illinois, USA)
202 and the Sr isotope ratios measured on a VG Sector 54 mass spectrometer. Reported values are
203 the average of 150 ratios obtained by measuring ion intensities in multi-dynamic collection mode
204 normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Measured values of NBS SRM-987 were $^{87}\text{Sr}/^{86}\text{Sr} = 0.710297 \pm$
205 0.000029 (2SD, $n = 24$) during the measurement period, with the Sr isotopic data normalized to
206 NBS SRM-987 = 0.710248. Total solid phase $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined on a number of

207 samples at Oregon State University (Supplemental Table 3) following the general approach
208 outlined above for the pore fluids. These samples were digested as described in Muratli et al.
209 (2010 and 2012) and the ancillary data for these digests are available in Murray et al. (2016).

210 211 **4.0 RESULTS**

212 **4.1 Pore fluids**

213 Generally, Site U1394 exhibits larger pore fluid chemical gradients as compared to U1395
214 (**Figures 3 and 4**). NH_4 concentrations reach values as high as 2 mM, alkalinity in excess of 5
215 mM, and sulfate concentrations that decline to as low as ~ 10 mM at site U1394 whereas U1395
216 is similar but with higher sulfate concentrations (**Figures 3A,B and 4A,B**). Dissolved Mn
217 concentrations typically range between ~1 and 2 μM at depth, with slightly elevated
218 concentrations near the surface. At both sites, Ca and Mg concentrations decrease below their
219 seawater values (**Figures 3 and 4C**). At depth, pore fluid Ca concentrations increase whereas
220 Mg concentrations are depleted at depth at both sites. Pore fluids are generally enriched in Si, Li,
221 and Sr relative to their seawater values and depleted in K (**Figures 3 and 4D, E**). $^{87}\text{Sr}/^{86}\text{Sr}$
222 values for site U1395 decrease slightly with depth, with most of the change in $^{87}\text{Sr}/^{86}\text{Sr}$
223 occurring between ~ 10 and 50 meters below the sediment surface. The structure of the
224 dissolved ion pore fluid profiles differs significantly near the bottom of the profiles, in particular
225 for Site U1394 there are larger near-bottom gradients for a number of constituents as compared
226 to U1395.

227 Pore water data for site U1396 are distinct from the other pore fluid profiles from this study
228 (**Figure 5A-E**), with the low NH_4 and high sulfate concentrations indicating that diagenetic
229 conditions were less reducing than at the other northern sites, although dissolved Mn increases
230 with depth throughout the sequence. Alkalinity is depleted relative to its seawater value and Ca

231 increases by roughly a factor of three within the upper 20 meters of the sequence. The Mg
232 depletion mirrors the Ca enrichment. As with U1394 and U1395, $^{87}\text{Sr}/^{86}\text{Sr}$ values decrease with
233 depth, but U1396 achieves significantly lower $^{87}\text{Sr}/^{86}\text{Sr}$ values (~ 0.7083) in the pore waters than
234 at the other sites discussed here. Similar to the other northern sites, generally Li and Si are
235 enriched over their seawater values whereas K is depleted.

236 The southern sites exhibit similarities to the sites from the north, with the more offshore Sites
237 U1398 and U1399 having larger enrichments in NH_4 and alkalinity and larger depletions in
238 sulfate as compared to U1397 and U1400 (**Figures 6 - 9**). At U1398 and 1399 Ca, Mg, Sr, and
239 $^{87}\text{Sr}/^{86}\text{Sr}$ all decrease with depth, with the exception of the deepest data point from U1398,
240 which shows an enrichment in Ca and Sr. Silica increases and Li generally remains near its
241 seawater value with some slight concentration enrichment at the surface and near the base of the
242 core. At U1400, Ca, Mg, and Sr remain close to present day seawater values with a notable
243 increase in Ca, Sr, and Li near the base of the core and a decrease in Mg and a change in the ^{87}Sr
244 $/^{86}\text{Sr}$ gradient toward lower values (**Figure 9**). One additional point of note regarding U1400 is
245 that the core sampled much deeper within the sediment column as compared to the other sites
246 presented here. The behavior of K throughout the sites is characterized by depletions at all of the
247 sites, with the magnitude of those depletions varying considerably.

248 **4.2 Solid phases**

249 **4.2.1 $^{87}\text{Sr}/^{86}\text{Sr}$ in Sediments from U1396**

250 $^{87}\text{Sr}/^{86}\text{Sr}$ in the carbonate fraction from Site U1396 has values close to those of
251 contemporaneous seawater (**Figure 10**), which have increased over time (e.g., Elderfield, 1986;
252 Paytan et al., 1993). The average Sr concentration in this fraction is ~ 775 ppm (Supplemental
253 Table 2). For the de-carbonated (residual) sedimentary fraction, which has an average Sr

254 concentration of ~135 ppm, $^{87}\text{Sr}/^{86}\text{Sr}$ values range between ~ 0.7074 and 0.705. The pore fluid
255 $^{87}\text{Sr}/^{86}\text{Sr}$ has the lowest values of the sites presented here and these values are between those of
256 the carbonate and the non-carbonate fraction, with the average being lower than the carbonate
257 values.

258 We include the bulk solid phase $^{87}\text{Sr}/^{86}\text{Sr}$ values from the other sites for comparison
259 (Table S3). Because these values are total digests, they represent a mixture of phases and Sr
260 isotope values and the values are difficult to interpret in terms of diagenetic processes.
261 Nevertheless these Sr isotope values are all between the carbonate values and the residual values
262 for site U1396.

263

264 **5.0 Discussion**

265 **5.1 Diagenetic processes involving volcanic material**

266 Pore fluid chemistry indicates that the diagenetic reactions fall into two broad categories;
267 (1) reactions related to exchange with volcanogenic matter, and (2) reactions related to carbonate
268 dissolution, precipitation, and/or recrystallization. Reactions within these categories are to be
269 expected because regional sedimentation is dominated by these combined inputs (e.g., Gieskes
270 and Lawrence, 1981; Gieskes et al., 1990a, b, c; Lyons et al., 2000; Le Friant 2013, 2015; Palmer
271 et al., 2016).

272 The reactions between the pore fluids and volcanogenic material are most clear at sites
273 U1395 and U1396 in the north and below ~ 300 m at U1400 in the south. Signatures of these
274 reactions are most strongly observed for the dissolved major elements, Ca and Mg. At site
275 U1395, there is an initial decrease in Ca concentration with sediment depth followed by an
276 increase below 20 meters (**Figure 4**). Below this depth, increases in dissolved Ca generally

277 mirror the decreases in dissolved Mg (**Figures 4, 11**). At site U1396 there is a shift in pore water
278 Ca and Mg concentrations near the sediment surface with a 1:1 offset from their respective
279 seawater values (**Figure 5, 11**). At Site U1400, the increase in Ca with accompanying decrease
280 in Mg appears to be limited to the deeper (~> 300 m) portions of the sediment column (**Figure 9,**
281 **11B**). Similar inverse relationships between Ca and Mg have been noted in other studies and
282 have been attributed to a variety of processes including CaCO₃ dissolution, volcanic glass
283 alteration, diagenesis of carbonate and silicate sediments, and/or alteration of underlying basaltic
284 crust (e.g., Gieskes and Lawrence, 1981; Gieskes, 1983; Gieskes et al., 1987; Gieskes et al.,
285 1990a; Lyons et al., 2000). The most likely interpretation of the inverse Ca-Mg relationship at
286 the sites presented here is exchange reactions associated with authigenic smectite formation
287 (Hein et al., 1979; Gieskes and Lawrence, 1981; Gieskes, 1983; Gieskes et al., 1987; Martin et
288 al., 1996; James and Palmer, 2000; Lyons et al., 2000; Scholz et al., 2013). These exchange
289 reactions arise because volcanic ash and tephra from subduction zone volcanism contain reactive
290 mafic to intermediate minerals: including, olivine [(Mg,Fe²⁺)₂SiO₄], pyroxene
291 [(Ca,Mg,Fe²⁺)₂Si₂O₆], amphibole [(Mg,Fe²⁺)₇Si₈O₂₂(OH)₂], and Ca-rich plagioclase
292 [Ca,Al₂,Si₂O₈] (Gilkes and McKenzie, 1988). For example, in cores from DSDP Legs 35 and 38,
293 where increases in Ca accompany decreases in Mg, the dissolution of plagioclase and volcanic
294 glass is thought to release Ca as Mg is removed from pore fluids to form Mg-smectite (Kastner
295 and Gieskes, 1976; Gieskes et al., 1987). The involvement of smectite in these reactions is also
296 evidenced by its high cation exchange potential and its prevalence in convergent margin settings
297 with volcanic input (Griffin et al., 1968; Gieskes et al., 1987; Scholz et al., 2010).

298 The sites in the Lesser Antilles where pore fluid Ca and Mg concentrations appear to be
299 driven by alteration of volcanic matter (U1395, U1396, U1400) do not show changes that are as

300 large as some of those observed during ODP Leg 110 in the eastern Caribbean (e.g., Gieskes et
301 al., 1990b) or ODP Leg 165 in the western Caribbean (Lyons et al., 2000), where the $\Delta\text{Ca}:\Delta\text{Mg}$
302 shows a range of 0.1 to 4 (**Figure 11A, C**). Data from Leg 110 (site 671), which sampled
303 sediment east of the volcanic arc from the northern Barbados accretionary complex, shows
304 similar $\Delta\text{Ca}:\Delta\text{Mg}$ in the shallower reaches of the sediment package to those observed at sites
305 U1395 and U1396, followed by a trend that is similar to the larger $\Delta\text{Ca}:\Delta\text{Mg}$ changes seen at site
306 1001 (Figure 11C, Gieskes et al., 1990a, b, c). The larger Ca:Mg ratios from cores from both
307 ODP Legs 110 and 165 are thought to be partially a result of alteration of the underlying basaltic
308 basement (Gieskes et al., 1990a, b, c; Lyons et al., 2000), a process that can strongly enrich deep
309 sediment fluids in Ca, which can then lead to deep authigenic carbonate precipitation (e.g.,
310 Torres et al., 2015; Sample et al., 2017). The lack of these larger Ca:Mg ratios in the Grenada
311 Basin suggest that $\Delta\text{Ca}:\Delta\text{Mg}$ at U1395 and U1396 are dominated by alteration of volcanic matter
312 dispersed throughout the sediment column. The $\Delta\text{Ca}:\Delta\text{Mg}$ pattern at site 671, as well as other
313 sites from Leg 110, shows a transition between a ratio of ~ 1 to ~ 4 in sediments from the
314 accretionary complex (Figure 11C, Gieskes et al., 1990a), and is likely driven by fluid reaction
315 within the accretionary prism where tectonics are forcing changes in the hydrology and
316 chemistry of fluid migration (e.g., Gieskes et al., 1990b; Blanc et al., 1991; Vrolijk et al., 1991).

317 Pore water Si, K, and Li distributions could be interpreted to support the hypothesis that
318 alteration of volcanic material is an important reaction in these sediments with Si and Li
319 generally increasing whereas K generally decreases (Sigurdsson et al., 1997; Chan and Kastner,
320 2000; James and Palmer, 2000). Although we recognize that the increases in Si and Li with
321 increasing depth can be attributed to continued alteration of volcanic ash throughout the
322 sediment package (Lyons et al., 2000), these constituents are also influenced by a number of

323 other sedimentary reactions that likely mask specific processes related to tephra diagenesis. For
324 example, Si is also produced in the pore fluids during biogenic silica dissolution and Si and Li
325 are both taken up during authigenic clay formation independent of volcanic material diagenesis
326 (e.g., Aller, 2014). Furthermore, the slightly elevated Li concentration, which is pervasive
327 throughout the sediment column of some of the sites, particularly those rich in NH_4^+ , could be
328 driven by NH_4^+ substitution for Li in clay mineral inter-layer exchange sites (e.g., Gieskes,
329 1983). The decrease in K in nearly all cores is a commonly observed characteristic of that
330 dissolved constituent and is likely driven by authigenic clay formation although alteration of
331 basalt is certainly a possible mechanism for its depletion as well (e.g., Sun et al., 2016). The
332 notable differences between the vertical distributions of Si, Li, and K as compared to Ca, Mg,
333 and Sr suggest that these former constituents are likely to be influenced by other, perhaps more
334 gradual, authigenic chemical changes within the sedimentary package, e.g., biogenic opal
335 dissolution and authigenic precipitation reactions, as compared to Ca, Mg, and Sr, which exhibit
336 more abrupt distribution changes, and which we interpret as being related to direct interactions
337 with fresh volcanic material (e.g., U1396).

338 The $^{87}\text{Sr}/^{86}\text{Sr}$ pore fluid data likely reflect a confluence of processes including carbonate
339 precipitation and dissolution as well as reactions with tephra (**Figure 12**). The gray box in this
340 figure denotes the approximate $^{87}\text{Sr}/^{86}\text{Sr}$ value of seawater over the past ~ 4 Ma and highlights
341 the range in Sr concentration in the upper sediment package, with an accompanying relatively
342 small change in $^{87}\text{Sr}/^{86}\text{Sr}$ with the exception of Sites U1396, U1398, and to a lesser extent
343 U1400. As one example, Site U1395 exhibits a large increase in pore water Sr concentrations,
344 but is accompanied by a relatively small variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the pore fluids
345 (**Figure 12**). We hypothesize that this pattern of Sr isotope systematics is likely driven by

346 carbonate recrystallization reactions (e.g., Baker et al., 1982). These reactions have the net effect
347 of adding Sr to pore fluid, and because the carbonate Sr isotope values are those of
348 contemporaneous seawater, these reactions “buffer” the pore fluid Sr isotope values toward
349 more radiogenic values (e.g., Richter and DePaolo, 1988; Fantle and DePaolo, 2006). Although
350 the magnitude of the $^{87}\text{Sr}/^{86}\text{Sr}$ changes seem somewhat small at most of our sites relative to
351 U1396, they are also small relative to those samples on Leg 110 (Gieskes et al., 1990a).
352 However, many of those samples were taken from much deeper (older) within the sediment
353 column and may have experienced greater reaction with the basalt or volcanic ash.

354 The upper portion of Site U1396 shows the greatest perturbations to the dissolved Ca,
355 Mg, and alkalinity pore water concentrations, the maximum pore water Sr concentration as well
356 as the largest change in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (**Figures 5, 12**). This site is the only site where we have
357 $^{87}\text{Sr}/^{86}\text{Sr}$ data from both the carbonate and non-carbonate fraction of the sediments (**Figure 10**).
358 The $^{87}\text{Sr}/^{86}\text{Sr}$ of the carbonate fraction from Site U1396 is generally consistent with what would
359 be expected from the contemporaneous seawater isotope value (dashed line in **Figure 10**), with
360 small deviations to lower values near the top of the core. These variations could be related to
361 diagenetic exchange between the carbonate and non-carbonate material (**Figure 10**) or
362 potentially are an artifact of leaching of fresh, non-carbonate material. The non-carbonate
363 fraction has lower $^{87}\text{Sr}/^{86}\text{Sr}$ values, which range from 0.707372 to 0.705178 (**Supplemental**
364 **Table 2**). This fraction likely represents a mixture of the regional volcanogenic signature, the
365 more distal atmospheric dust signature, as well as any diagenetic overprinting (clay formation)
366 by more radiogenic seawater Sr isotope values. Indeed for the other sites the bulk sediment ^{87}Sr
367 ^{86}Sr values are generally between the carbonate and non-carbonate values (Supplemental Table
368 3) although we do note here the somewhat surprisingly high Sr concentrations at Site U1395

369 even though the $^{87}\text{Sr}/^{86}\text{Sr}$ values bracket the range of values noted here (Murray et al., 2016).
370 The Sr isotope values of the pore waters at Site U1396 have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values of any of
371 the cores and we infer that this site is the most impacted by reaction with volcanogenic material.
372 This impact is noteworthy in that the Sr pore fluid concentration values change significantly
373 within the upper portion of the sediment package despite the presence of a large carbonate Sr
374 reservoir (e.g., ~ 500 – 1000 ppm Sr). The high concentration of Sr in the carbonate fraction
375 contrasts with the much lower Sr concentrations in the residual material (~100 – 200 ppm), and
376 this residual material will presumably include a volcanic ash fraction that has particularly low
377 $^{87}\text{Sr}/^{86}\text{Sr}$ values (e.g., Gieskes et al., 1990a, b, c). In the deeper sections at this site, between 3
378 and 4 Ma, there is a significant shift in the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the non-carbonate sediment
379 fraction indicating a change in the source of this material. These lower values are consistent with
380 volcanic rocks derived from the Lesser Antilles (0.7039 – 0.7058, Hawkesworth et al., 1979).
381 Neither the pore fluid nor the carbonate values are impacted by this isotopic shift (**Figure 10**),
382 which implies that alteration of the volcanogenic phase is not the primary determinant of the
383 pore fluid composition at this depth, rather the deeper pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ values are likely being
384 dominated by the higher Sr reservoir within the carbonate matrix (e.g., Fantle and DePaolo,
385 2006).

386 For the southern sites, pore water Sr concentrations at Site U1400 are nearly constant
387 throughout the sediment package at a concentration closer to its seawater value as compared to
388 Site U1396 (**Figure 9**), and only the deeper samples have $^{87}\text{Sr}/^{86}\text{Sr}$ pore fluid values which,
389 coupled with the changes in Ca and Mg suggest a significant contribution from a less radiogenic
390 (volcanic) substrate. The $^{87}\text{Sr}/^{86}\text{Sr}$ for this site is also likely being heavily influenced by the
391 large carbonate reservoir via carbonate dissolution and recrystallization processes. It is important

392 to note that there is not a well-defined age model for this core, which makes it impossible to
393 assess the magnitude of the contemporary seawater contribution to dissolved Sr. Site U1398 has
394 a significantly different pattern compared to the other cores with a signature of Sr removal in the
395 upper sediment column followed by an increase in Sr with less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values
396 (**Figure 12**). We suggest that this pattern implies that carbonate precipitation or perhaps other
397 authigenic mineral formation is removing some of the Sr, but that reactions with volcanic
398 material that add Sr (as well as Ca) to the pore fluid can overcome this process deeper in the
399 sediment column. This point is discussed further below in the context of carbonate diagenesis.

400 **5.2 Precipitation and Recrystallization of Carbonate Phases**

401 As mentioned above, carbonate precipitation likely occurs throughout the sedimentary
402 package within the Grenada Basin, but the evidence for this process is particularly strong at Sites
403 U1394 (upper 100 meters) and U1399. Calculations of calcite saturation state in these types of
404 sediments are equivocal as accurate estimates for pH and even for the concentration of alkalinity
405 are difficult to obtain. This difficulty is partly caused by depressurization and degassing artifacts
406 during core and sample recovery. Nevertheless here we utilize saturation state calculations from
407 CO₂calc (version 1.2.1, M. Hansen, L. Robbins, J. Kleyvas, S. Meylan) for estimating aragonite
408 and calcite saturation in the fluids from sites U1394, U1398, and U1399. These calculations
409 suggest that for these sites, the pore fluids are generally supersaturated with respect to calcite
410 (**Figure 13**); however, as noted the uncertainties in the carbonate parameters are potentially large
411 and an offset of + 0.2 pH units could lead to an overestimate of Ω on the order of 1 unit, which,
412 given the limited range in Ω , is significant. In the case of site U1394 (upper 100 meters) the
413 three carbonate-forming cations (Ca, Mg, Mn) also decrease with depth, whereas for Site U1399,
414 four of the divalent cations decrease with depth (Ca, Mg, Mn, Sr). The weaker correlation

415 between Ca and Mg at U1394 ($r^2 = 0.38$) as compared to U1399 ($r^2 = 0.75$) stems from the fact
416 that in the lower 100 meters of U1394, Ca and Mg concentrations suggest that there is a switch
417 in the primary diagenetic mechanism from carbonate precipitation to alteration of volcanic
418 matter and/or dissolution of carbonate phases (**Figures 11A, B**). The cation results from site
419 U1398 are somewhat different from the other sites and we relate this to the competition between
420 carbonate precipitation reactions and reactions that involve tephra diagenesis (**Figure 11A, B**).
421 The competing impact from tephra diagenesis, which will enrich the fluids in Ca and (perhaps)
422 Sr, is most notable in the deeper section of this core where Sr and Ca begin to increase with
423 depth as $^{87}\text{Sr}/^{86}\text{Sr}$ values decline (**Figure 7, 11**). Taken together the calculations and the
424 covariance of Ca and Mg, in particular, with the increases in fluid alkalinity support the notion
425 that these cores are likely undergoing carbonate precipitation reactions. Furthermore, all three of
426 these sites exhibit distinctly different behaviors in their dissolved Ca and Mg profiles compared
427 to sites U1395, U1396, and U1400 (**Figures 11A, B**).

428 Precipitation of authigenic carbonates can occur under a variety of diagenetic conditions
429 from oxic to anoxic and from the pelagic ocean to the coastal ocean (Hein et al., 1979;
430 Sigurdsson et al., 1997; Lyons et al., 2000; Hesse and Schacht, 2011; Joseph et al., 2012; Aller,
431 2014; Sample et al., 2017), but the precipitation of Ca-Mg carbonates is favored under sulfate
432 reducing environments (Warthman et al., 2000; Hesse and Schacht, 2011; Aller 2014; Sample et
433 al., 2017). At sites U1394, U1398, and U1399, sulfate reduction is occurring (**Figures 3, 7, 8**),
434 which increases the alkalinity needed for carbonate precipitation (Hein et al., 1979; Sigurdsson et
435 al., 1997; Lyons et al., 2000; Hesse and Schacht, 2011; Joseph et al., 2012; Aller, 2014).
436 Although dolomite precipitation is normally inhibited in anoxic, low temperature settings,
437 laboratory studies suggest the possibility of dolomite precipitation (Warthman et al., 2000) as

438 well as Mg-calcite precipitation (Van Lith et al., 2003) in the presence of sulfate reducing
439 bacteria, which provides a mechanism for raising alkalinity and pH for formation of these
440 carbonate phases. However, dolomite was not found in any of the samples examined during this
441 study and it is indeed unlikely that this phase would be precipitating in these sediments (Murray,
442 2016). Nevertheless XRD results from select samples from the sulfate reducing sections
443 revealed that Mg-calcite is an important carbonate phase accumulating in U1394 and in several
444 samples from U1399 (Expedition 340 Scientists, 2013; Murray, 2016). These results are not
445 surprising, however, as the presence of Mg-rich carbonate within the sediments is likely to be
446 dominated by depositional processes, rather than authigenic processes. Indeed, we can
447 demonstrate that the accumulation of Ca from authigenic processes will be dwarfed by the
448 sediment depositional processes by considering a comparison between the rate of Ca uptake from
449 pore fluids to the accumulation of Ca as primary carbonate. This calculation is based on a
450 dissolved Ca concentration gradient from Site U1399 ($0.13 \text{ mmol L}^{-1} \text{ m}^{-1}$), a porosity of 0.5 and
451 the diffusion coefficient formulation from Sun et al. (2016), yielding a flux of $4 \times 10^{-5} \text{ mmol cm}^{-2}$
452 y^{-1} . We assume a typical carbonate concentration of 20%, a sediment density of 2 g cm^{-3} , and a
453 sedimentation rate of 0.05 cm y^{-1} , which is based on the sedimentation rate at site U1395. These
454 assumptions yield a Ca accumulation rate of $0.2 \text{ mmol cm}^{-2} \text{ y}^{-1}$. These calculations are crude at
455 best, but it is difficult to envision a three to four order of magnitude change in these assumptions
456 that would bring the rates of carbonate accumulation and authigenic precipitation values closer.
457 Even though both the accumulation of Ca and Mg are driven by delivery rather than authigenic
458 processes, the $\Delta\text{Ca}:\Delta\text{Mg}$ ratio, particularly in U1398 and U1399 does point to uptake by a Mg-
459 rich authigenic carbonate phase, i.e., the net $\Delta\text{Ca}:\Delta\text{Mg}$ ratio is ~ 1 , particularly in U1398 and
460 U1399 (**Figure 11**). In summary, and as can be seen in the data shown in **Figures 11A & B**,

461 there are effectively two sinks for Mg within these sediments, volcanic material alteration, which
462 leads to a ~1:1 exchange in Ca, and Mg-rich carbonate precipitation, which leads to uptake of
463 both constituents.

464 In environments rich in mud and tephra/pumice, other elements are known to compete for
465 sites within the authigenic carbonate structure as well (Hein et al., 1979; Mucci, 1987). At Site
466 U1394 decreases in Ca and Mg also coincide with decreases in dissolved Mn above 100 meters
467 (**Figures 3, 14A**) and at Site U1399 ($r^2 = 0.84$) the decrease occurs below ~40 meters (**Figures 6,**
468 **14B**). Rhodochrosite (MnCO_3) precipitation is one possible explanation for the close coupling
469 between Ca and Mn (Hein et al., 1979; Mucci, 1987). Rhodochrosite can precipitate as coatings
470 on pre-existing carbonate debris or as fine crystals dispersed within the sediment package (Hesse
471 and Schacht, 2011). Although dissolved Mn correlates with Ca at both sites, rhodochrosite was
472 not detected (Murray, 2016); however, it is likely that if this phase is present, it is an
473 undetectable component of the sediment package. For example, using a similar approach for the
474 calculations above for Ca in U1399, and assuming a change in dissolved Mn of $1 \mu\text{M meter}^{-1}$
475 (**Figure 8**) we would expect a sediment concentration of $\sim 0.1 \mu\text{g Mn g}_{\text{sed}}^{-1}$, which is unlikely to
476 be seen in the bulk XRD approach used by Murray (2016).

477 Although the coincident decrease in Sr and Ca at U1399 Ca ($r^2 = 0.94$) (**Figure 14B**).
478 may be attributed to the precipitation of aragonite with depth (Irwin, 1980; Lyons et al., 2000;
479 Tang et al., 2008), we consider this possibility to be unlikely. In terms of aragonite saturation, for
480 a sample with a pH of 7.4 and an alkalinity of 5.9 mM, $\Omega_{\text{arag}} = 0.8$, whereas for a pH of 7.6 and
481 an alkalinity of 10.6 mM, $\Omega_{\text{arag}} = 1.3$. Although these values are representative of those seen at
482 site U1399 and could imply marginally favorable conditions for aragonite precipitation, we view
483 these saturation values to be overestimates given the uncertainty of the pH values as discussed

484 above (i.e., the pH values are likely to be artificially high). We thus consider the authigenic
485 precipitation of aragonite to be unlikely and suggest that the depletions in Sr are most likely
486 caused by the incorporation into calcite or some other Sr-rich phase rather than aragonite
487 (Murray, 2016). The notion that Sr is associated with reprecipitation of a carbonate phase should
488 be taken with caution as recrystallization of calcium carbonate typically results in partitioning of
489 Sr into pore fluid rather than precipitation into the carbonate phase (Baker et al., 1982). This
490 point may imply that the coincidence between the Sr and Ca at U1399 is simply fortuitous and
491 that Sr uptake is being driven by other non-carbonate diagenetic phases or minerals (Elderfield et
492 al., 1982; Gieskes et al., 1986).

493 **6.0 Conclusions**

494 The sediments from the Grenada Basin indicate that sediment diagenesis is governed by
495 solute release and precipitation reactions that are driven by the presence of tephra as well as by
496 reactions involving carbonate. At sites U1395, U1396, and U1400, increases in Ca mirror
497 decreases in Mg, likely reflecting alteration of volcanic matter dispersed within the sediment
498 column to form authigenic smectite. In contrast, Sites U1394 and U1399 show coincident
499 decreases in dissolved Ca, Mg, Mn, and in the case of U1399 Sr as well, likely reflecting a
500 dominance of carbonate precipitation, specifically a Mg-rich calcite, which is occurring under
501 the sulfate reducing conditions prevalent throughout much of the region. The $^{87}\text{Sr}/^{86}\text{Sr}$ data
502 presented here support the conclusions based on the major cation data. In particular, site U1396
503 has the most diagnostic data reflecting pore fluid tephra diagenesis in the upper meters of the
504 sediment column (high Ca, low Mg, low $^{87}\text{Sr}/^{86}\text{Sr}$).

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761 **FIGURE CAPTIONS**

762

763 **Figure 1.** Map of the Lesser Antilles Volcanic Arc, showing arc migration over time,
764 active volcanoes, and flank collapses. Ages of migrating arc are from Macdonald et al.
765 (2000), flank collapses are modified from Le Friant et al. (2015), and volcano locations
766 are from the Smithsonian Institution, Global Volcanism Program. Gridded bathymetry is
767 in meters and courtesy of the British Oceanographic Data Centre (gebco.net).

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769 **Figure 2.** Close up of the study area from Expedition 340 cruise in 2012, showing the
770 core locations of interest for this study (U1394, U1395, U1396, U1397, U1398, U1399, and
771 U1400). Flank collapses are modified from Le Friant et al. (2015), volcano locations are from
772 the Smithsonian Institution, Global Volcanism Program, and core coordinates from Expedition
773 340 Scientists (2012). Gridded bathymetry is in meters and courtesy of the British
774 Oceanographic Data Centre (gebco.net).

775

776 **Figure 3.** Dissolved solute distributions for Site U1394. (A) Alkalinity and NH₄, (B) SO₄²⁻ and
777 Mn, (C) Ca and Mg, (D) K and Li, (E) Si, and (F) Sr. Dashed lines denote bottom water
778 concentrations. Alkalinity, NH₄, Ca, Mg, and SO₄²⁻ data are from Le Friant et al. (2013) and
779 minor ion data is from Murray et al. (2016).

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781 **Figure 4.** Dissolved solute distributions for Site U1395. (A) Alkalinity and NH₄, (B) SO₄²⁻ and
782 Mn, (C) Ca and Mg, (D) K and Li, (E) Si, and (F) Sr. Dashed lines denote bottom water
783 concentrations. Alkalinity, NH₄, Ca, Mg, and SO₄²⁻ data are from Le Friant et al. (2013) and
784 minor ion data is from Murray et al. (2016).

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786 **Figure 5.** Dissolved solute distributions for Site U1396. (A) Alkalinity and NH₄, (B) SO₄²⁻ and
787 Mn, (C) Ca and Mg, (D) K and Li, (E) Si, and (F) Sr. Dashed lines denote bottom water
788 concentrations. Alkalinity, NH₄, Ca, Mg, and SO₄²⁻ data are from Le Friant et al. (2013) and
789 minor ion data is from Murray et al. (2016).

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791 **Figure 6.** Dissolved solute distributions for Site U1397. (A) Alkalinity and NH₄, (B) SO₄²⁻ and
792 Mn, (C) Ca and Mg, (D) K and Li, (E) Si, and (F) Sr and ⁸⁷Sr/⁸⁶Sr. Dashed lines denote bottom
793 water concentrations. Alkalinity, NH₄, Ca, Mg, and SO₄²⁻ data are from Le Friant et al. (2013)
794 and minor ion data is from Murray et al. (2016).

795

796 **Figure 7.** Dissolved solute distributions for Site U1398. (A) Alkalinity and NH₄, (B) SO₄²⁻ and
797 Mn, (C) Ca and Mg, (D) K and Li, (E) Si, and (F) Sr and ⁸⁷Sr/⁸⁶Sr. Dashed lines denote bottom
798 water concentrations. Alkalinity, NH₄, Ca, Mg, and SO₄²⁻ data are from Le Friant et al. (2013)
799 and minor ion data is from Murray et al. (2016).

800

801 **Figure 8.** Dissolved solute distributions for Site U1399. (A) Alkalinity and NH₄, (B) SO₄²⁻ and
802 Mn, (C) Ca and Mg, (D) K and Li, (E) Si, and (F) Sr and ⁸⁷Sr/⁸⁶Sr. Dashed lines denote bottom
803 water concentrations. Alkalinity, NH₄, Ca, Mg, and SO₄²⁻ data are from Le Friant et al. (2013)
804 and minor ion data is from Murray et al. (2016).

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806 **Figure 9.** Dissolved solute distributions for Site U1400. (A) Alkalinity and NH₄, (B) SO₄²⁻ and
807 Mn, (C) Ca and Mg, (D) Si and Li, and (E) Sr and ⁸⁷Sr/⁸⁶Sr. Dashed lines denote bottom water

808 concentrations. Alkalinity, NH_4 , Ca, Mg, and SO_4^{2-} data are from Le Friant et al. (2013) and
809 minor ion data is from Murray et al. (2016).

810

811 **Figure 10.** $^{87}\text{Sr}/^{86}\text{Sr}$ in fluids and solid phases plotted as a function of age from Site U1396.
812 Data are from the carbonate fraction, the residual non-carbonate fraction, and the pore fluids.
813 Age calculations are derived from (Hatfield, 2015; Coussens et al., 2016) and dashed line
814 represents the strontium isotope value of contemporaneous seawater (Elderfield, 1982; Paytan et
815 al., 1993).

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817

818 **Figure 11.** Dissolved Mg and Ca displaying the two dominant diagenetic reactions
819 occurring in the Grenada Basin for the [A] northern sites U1394, U1395, and U1396 [B]
820 southern sites U1399 and U1400. Data from sites 998, 999, 1000, and 1001 are plotted with data
821 from this study for comparison [C, D] and are taken from Lyons et al. (2000). Data from site
822 671, which lies to the east within the northern Barbados accretionary complex are from Gieskes
823 et al., 1990a.

824

825 **Figure 12.** $^{87}\text{Sr}/^{86}\text{Sr}$ plotted as a function of $1/\text{Sr}$ in pore fluids. The gray box indicates Sr
826 isotope compositions characteristic of the most recent ~ 4 Ma (Elderfield, 1986). Data to the
827 right of the figure are those exhibiting removal of Sr from pore fluids, relative to the seawater
828 value. Data to the left of the figure are those samples exhibiting Sr enrichment in the pore fluids.
829 Note that the Sr isotope values of the pore waters at Site U1396 have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values
830 of any of the cores suggesting that this site is the most impacted by reaction with volcanogenic
831 material.

832

833 **Figure 13.** Calcite saturation state calculations for sites U1394, 1398, and 1399. Note that most
834 values are supersaturated with respect to calcite; however, the large uncertainties in these
835 calculations, including the values for pH, likely mean that the relative saturation states are
836 uncertain, as discussed within the text.

837

838 **Figure 14.** Dissolved minor phases that can be incorporated into the carbonate phase; (A) Mn
839 for site U1394 (B) Mn and Sr for site U1399. Note that there is not a correlation between Sr and
840 Ca for site U1394, which may imply that carbonate precipitation is not what is driving the
841 correlation for site U1399.

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Table A1. Sr isotope composition of interstitial pore fluid samples.

	Core	Type	Section	Top Depth (CSF-A)	Bottom Depth (CSF-A)	Sr (μM)	\pm	$^{87}\text{Sr}/^{86}\text{Sr}$	\pm
340-U1395B-									
	1	H	3	4.4	4.5	107.8	0.7	0.709151	0.000006
	2	H	3	10.3	10.4	112.8	0.6	0.709145	0.000007
	3	H	5	22.7	22.8	184.2	1.2	0.709086	0.000004
	4	H	3	29.32	29.42	235.4	4.8	0.709056	0.000007
	4	H	6	33.88	33.98	274.8	5.3	0.709051	0.000006
	5	H	3	38.8	38.9	318.5	5.2	0.709028	0.000008
	6	H	4	49.72	49.82	382.3	5.1	0.709019	0.000008
	6	H	6	52.85	52.95	389.6	5.8	0.709026	0.000007
	7	H	4	59.31	59.41	422.3	5.5	0.709029	0.000006
	9	H	1	72.6	72.7	515.6	5.3	0.709037	0.000006
	10	H	2	82.3	82.4	583.8	4.7	0.709033	0.000007
	10	H	5	86.81	86.91	585.0	5.7	0.709029	0.000007
	11	H	3	92.1	92.2	613.6	6.0	0.709038	0.000008
	12	H	3	101.15	101.25	643.9	6.2	0.709044	0.000009
	12	H	6	105.7	105.8	663.4	5.0	0.709056	0.000006
	13	H	4	112.02	112.12	689.2	5.2	0.709046	0.000009
	14	H	3	117.3	117.4	698.4	6.8	0.709051	0.000009
	24	X	1	185.5	185.6	694.3	7.3	0.709098	0.000007
	25	X	1	195.1	195.2	706.3	4.7	0.709088	0.000008
340-U1396C-									
	1	H	3	4.4	4.5	248.2	5	0.708817	0.000007
	2	H	3	12.8	12.9	242.7	5	0.708669	0.000004
	2	H	6	17.3	17.4	222.9	5	0.708593	0.000033
	3	H	3	22.2	22.3	206.7	5	0.708577	0.000006
	3	H	6	26.8	26.9	194.0	5	0.708514	0.000013
	4	H	3	31.8	31.9	180.8	0.9	0.708467	0.000019
	4	H	5	34.8	34.9	182.7	0.9	0.708481	0.000008
	5	H	4	42.8	42.9	166.4	1.5	0.708423	0.000008
	5	H	6	45.8	45.9	163.7	0.6	0.708412	0.000009
	6	H	3	50.7	50.8	158.3	0.7	0.708376	0.000010
	6	H	6	55.3	55.4	154.9	1.7	0.708376	0.000012
	7	H	3	60.3	60.4	155.0	1.0	0.708353	0.000012
	7	H	6	64.8	64.9	148.1	1.0	0.708327	0.000010

	Core	Type	Section	Top Depth (CSF-A)	Bottom Depth (CSF-A)	Sr (μM)	\pm	$^{87}\text{Sr}/^{86}\text{Sr}$	\pm
	8	H	3	69.8	69.9	144.9	0.9	0.708302	0.000013
	8	H	6	74.35	74.45	144.4	0.9	0.708295	0.000012
	9	H	3	79.3	79.4	142.6	0.7	0.708303	0.000009
	9	H	5	82.3	82.4	141.3	0.6	0.708289	0.000008
	10	H	3	88.82	88.92	142.2	0.6	0.708275	0.000009
	10	H	6	93.35	93.45	142.1	0.9	0.708333	0.000007
	11	H	3	98.3	98.4	142.8	0.6		
	11	H	6	102.71	102.81	140.6	0.6	0.708310	0.000010
	12	H	3	107.83	107.93	139.7	0.6	0.708325	0.000009
	12	H	6	112.1	112.2	139.0	0.7	0.708317	0.000009
	13	H	2	115.81	115.91	138.5	0.6	0.708318	0.000007
	14	H	5	127.49	127.59	135.7	0.8	0.708347	0.000008
	15	H	3	134.33	134.43	132.1	0.7	0.708356	0.000008
	15	H	6	138.8	138.9	133.8	1.0	0.708327	0.000033
340-U1397B-									
	1	H	3	4.4	4.5	85.7	0.4	0.709165	0.000007
	2	H	3	10.82	10.92				
	2	H	6	15.32	15.42	86.8	1.0	0.709138	0.000006
	3	H	2	19	19.1	88.3	0.4	0.709126	0.000006
	3	H	5	23.36	23.46	94.5	1.9	0.709124	0.000007
	5	H	2	37	37.1	105.0	1.3	0.709084	0.000008
	5	H	6	42.55	42.65	105.3	0.9	0.709098	0.000006
	6	H	2	46.5	46.6	106.8	1.0	0.709072	0.000007
	6	H	6	52.5	52.6	106.3	1.0	0.709094	0.000008
	9	H	4	75.55	75.65	119.1	1.1	0.709092	0.000008
	23	X	2	164.02	164.12	108.6	0.9	0.709092	0.000009
	23	X	5	168.52	168.62	110.8	1.0	0.709088	0.000007
	24	X	2	173.6	173.7	113.7	1.1	0.709102	0.000006
	25	X	1	181.6	181.7	113.9	0.9	0.709091	0.000008
340-U1398B-									
	9	H	3	62.5	62.6	60.9	0.4	0.709017	0.000008
	9	H	5	65.5	65.6	58.8	0.4	0.709044	0.000007
	11	H	2	76.7	76.8	57.1	0.6	0.709030	0.000008
	12	H	2	85.8	85.9	55.7	0.4	0.708993	0.000005
	14	H	3	100.3	100.4	57.9	0.5	0.708947	0.000006
	14	H	5	103.3	103.4	58.2	0.5		

	Core	Type	Section	Top Depth (CSF-A)	Bottom Depth (CSF-A)	Sr (μM)	\pm	$^{87}\text{Sr}/^{86}\text{Sr}$	\pm
	15	H	3	109.79	109.89	60.7	0.5		
	15	H	5	112.71	112.81	61.7	0.4		
	18	H	3	130.9	131	67.9	0.4		
	18	H	6	134.97	135.07				
	19	H	2	138.9	139	73.4	0.4		
	19	H	3	140.4	140.5	75.2	0.6		
	20	H	2	148.36	148.46	80.2	0.6	0.708634	0.000018
	20	H	6	154.24	154.34	84.9	0.4	0.708655	0.000017
	22	H	2	160.22	160.32	94.0	0.5	0.708593	0.000017
	22	H	4	163.15	163.25	98.6	0.5	0.708564	0.000031
	23	H	1	166.3	166.4	99.8	0.6	0.708641	0.000021
	27	X	1	187.47	187.57				
	34	X	1	254.08	254.19	161.8	1.1	0.708558	0.000030
340-U1399B-									
	1	H	2	2.9	3	99.4	0.9	0.709161	0.000007
	2	H	3	10.1	10.2	86.1	1.2	0.709153	0.000008
	3	H	3	19.62	19.72	85.2	1.0	0.709123	0.000007
	3	H	5	22.6	22.7				
	4	H	2	27.6	27.7	82.1	1.0	0.709098	0.000009
	4	H	4	30.6	30.7	78.9	0.9	0.709068	0.000006
	5	H	3	38.6	38.7	77.2	0.9	0.709064	0.000008
	5	H	5	41.6	41.7	75.4	0.8	0.709060	0.000008
	6	H	2	46.5	46.6	72.1	1.1	0.709055	0.000007
	6	H	4	49.45	49.55	72.0	0.8	0.709086	0.000008
	8	H	1	64.12	64.22	68.3	0.8	0.709070	0.000009
	8	H	3	67.07	67.17	66.6	0.8	0.709081	0.000007
	9	H	3	76.32	76.42	63.2	0.8	0.709068	0.000010
	12	H	1	95.72	95.82	66.0	0.8	0.709041	0.000009
	13	H	3	107.1	107.2	62.4	0.9	0.709012	0.000007
	15	H	5	122.13	122.24	60.6	0.9	0.709000	0.000008
	18	H	2	131.83	131.93	61.1	0.8	0.708984	0.000006
	24	H	1	160.7	160.8	62.9	0.9	0.708944	0.000010
	25	H	1	167.8	167.9	61.6	0.8	0.708985	0.000010
340-U1400B-									
	7	H	4	31.24	31.34	87.7	0.9	0.709230	0.000008

	Core	Type	Section	Top Depth (CSF-A)	Bottom Depth (CSF-A)	Sr (μM)	\pm	$^{87}\text{Sr}/^{86}\text{Sr}$	\pm
	8	H	5	42.4	42.5	87.5	0.9	0.709200	0.000041
	9	H	1	45.9	46	88.5	0.9	0.709193	0.000029
	10	H	3	52.91	53.01	90.9	1.0	0.709175	0.000008
	10	H	6	57.42	57.52	93.5	1.0	0.709143	0.000001
	11	H	4	63.92	64.02	93.3	0.8	0.709139	0.000021
	12	H	2	70.08	70.18	92.8	0.8	0.709155	0.000011
	13	H	5	81.4	81.5	98.4	0.8	0.709137	0.000010
	14	H	3	87.85	87.95	96.6	0.9		
	15	H	4	98.8	98.9	98.0	1.1	0.709087	0.000011
	17	H	4	111.53	111.63	100.1	0.9	0.709049	0.000012
	18	H	4	121	121.1	101.5	0.9	0.709039	0.000009
	19	H	2	127.52	127.62	103.4	0.8	0.709030	0.000011
	20	H	3	133.21	133.31	101.7	1.0	0.709063	0.000012
	21	H	5	143.82	143.92	105.3	0.8	0.709042	0.000006
	22	H	4	151.83	151.93	104.3	0.9	0.709004	0.000013
	23	H	4	161.35	161.45	124.1	1.2	0.709030	0.000008
	24	H	4	170.88	170.98	105.4	1.0	0.709027	0.000011
	25	H	4	180.34	180.44	103.2	0.9		
	26	H	4	189.78	189.88	103.3	1.1		
	27	H	5	200.79	200.89	104.1	0.9		
	28	H	3	207.3	207.4	103.9	1.0		
340-U1400C-									
	27	X	4	231.2	231.3	101.0	0.8		
	29	X	2	247.4	247.5	104.5	0.9		
	30	X	2	257	257.1	104.4	0.8		
	31	X	3	268.1	268.2	108.6	1.0	0.708986	0.000014
	32	X	2	276.2	276.3	111.8	1.1	0.709004	0.000027
	33	X	2	285.8	285.9	111.4	1.0	0.708987	0.000013
	35	X	4	298.4	298.5	112.4	1.1	0.708948	0.000008
	36	X	3	306.5	306.6	113.9	1.0	0.708915	0.000013
	37	X	1	313.12	313.22	116.0	0.9	0.708937	0.000015
	38	X	5	328.3	328.4	113.1	1.2		
	39	X	5	337.71	337.81	116.2	1.2	0.708937	0.000014
	40	X	1	341.5	341.6	113.7	1.1	0.708916	0.000015
	41	X	1	351.1	351.2	114.5	0.9	0.708938	0.000013
	42	X	2	362.2	362.3	114.3	1.5	0.708920	0.000013

	44	X	1	379.75	379.85	115.0	1.0	0.708900	0.000014
	45	X	3	392.45	392.55	113.6	0.9	0.708829	0.000012
	49	X	1	427.48	427.58	131.0	1.3	0.708677	0.000014

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Table A2. Sr isotope composition of solid phase samples from Site U1396.

Sample	Top Depth (cm)	Age Ma	Sr (ppm)				^{87/86} Sr	
			Carbonate	±	Non-Carbonate	±	Carbonate	Non-Carbonate
Modern Sea Water	0	0						
1 H 3	440	0.3	1801		134		0.709031	0.707372
2 H 3	1280	0.78	803		124		0.708868	
2 H 6	1730	0.99	709		180		0.709025	
3 H 3	2220	1.2	958		93		0.709099	
3 H 6	2680	1.5	858		101		0.709069	0.707296
4 H 3	3180	1.77	765		127		0.708997	
4 H 5	3480	1.86			168			
5 H 4	4280	2.15	915	26	108	0	0.709053	
5 H 6	4580	2.25	1001		112		0.708995	
6 H 3	5070	2.5	710		125		0.708970	0.707055
6 H 6	5530	2.56	735		113		0.708877	
7 H 3	6030	2.7	779		150		0.709041	
7H 6	6480	2.8	487		172	19	0.709046	
8 H 3	6980	3	869	24	102	12	0.709051	
8 H 6	7435	3.11	840		120		0.709042	
9 H 3	7930	3.27	1024		110		0.709022	
9 H 5	8230	3.33	996		114		0.709019	0.707380
10 H 3	8882	3.5	625		127		0.709021	
10 H 6	9335	3.58	782	1	129	9	0.709025	
11 H 3	9830	3.7	519	12	175	28	0.709020	
11 H 6	10271	3.8	471		190		0.709020	
12 H 3	10783	3.9	413		200		0.709000	0.705320
12 H 6	11210	4	410	1	176	7	0.709030	
13 H 2	11581	4.05	610		160		0.709010	
14 H 5	12749	4.18	765		105		0.709020	
15 H 3	13433	4.4	524		131		0.709010	
15 H 6	13880	4.48			149	149		0.705178

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Table A3. Sr isotope composition and concentrations of bulk digests.

Sample ID	Core	Type	Section	Top Depth (CSF-A)	Bottom Depth (CSF-A)	Corrected ^{87/86} Sr	±	Sr (ppm) ¹	±
40-1395-									
McM313_02	1	H	3	4.4	4.5	0.707997	0.000007	2272	8
McM313_03	6	H	4	49.72	49.82	0.708198	0.000007	1772	10
McM313_04	13	H	4	112.02	112.12	0.708251	0.000011	2042	10
McM313_05	14	H	3	117.3	117.4	0.707282	0.000007	547	3
McM313_12	14	H	3	117.3	117.4	0.707159	0.000009	555	3
McM313_06	24	X	1	185.5	185.6	0.708299	0.000011	2533	10
McM313_07	25	X	1	195.1	195.2	0.707982	0.000008	2267	14
340-1397-									
McM313_19	1	H	3	4.4	4.5	0.707749	0.000009	715	8
McM313_20	2	H	6	15.32	15.42	0.707553	0.000010	605	3
McM313_23	2	H	6	15.32	15.42	0.707521	0.000006	603	4
McM313_24	6	H	2	46.5	46.6	0.707273	0.000012	460	2
McM313_25	6	H	6	52.5	52.6	0.708124	0.000010	865	7
McM313_26	24	X	2	173.6	173.7	0.708110	0.000008	961	8
McM313_27	25	X	1	181.6	181.7	0.708170	0.000008	1204	9
340-1398-									
McM313_28	9	H	3	62.5	62.6	0.708736	0.000009	446	3
McM313_29	9	H	5	65.5	65.6	0.708009	0.000010	418	3
McM313_30	20	H	6	154.24	154.34	0.708373	0.000009	891	8
McM313_31	22	H	4	163.15	136.25	0.708338	0.000011	320	2
McM313_34	22	H	4	163.15	136.25	0.708278	0.000007	319	2
McM313_35	34	X	1	254.08	254.19	0.708240	0.000008	713	7
340-1399B-									
McM313_36	1	H	2	2.9	3	0.707091	0.000005	275	2
McM313_37	2	H	2	10.1	10.2	0.708917	0.000006	723	8
McM313_38	6	H	2	46.5	46.6	0.708422	0.000009	563	3
McM313_39	6	H	4	49.45	49.55	0.708466	0.000008	976	9
McM313_52	6	H	4	49.45	49.55	0.708099	0.000012	977	9
McM313_40	18	H	2	131.83	131.93	0.707584	0.000007	550	2
McM313_41	24	H	1	160.7	160.8	0.707875	0.000006	561	3
McM313_42	25	H	1	167.8	167.9	0.708690	0.000009	844	9
340-1400B-									
McM313_45	7	H	4	31.24	31.34	0.708060	0.000009	1049	7
McM313_46	8	H	5	42.4	42.5	0.708140	0.000009	785	7
McM313_47	27	H	5	200.79	200.89	0.707315	0.000006	402	2
McM313_48	28	H	3	207.3	207.4	0.707799	0.000008	428	2
340-1400C-									
McM313_49	33	X	2	285.8	285.9	0.707942	0.000014	977	8
McM313_50	41	X	1	351.1	351.2	0.708491	0.000008	676	7
McM313_51	49	X	1	427.48	427.58	0.708325	0.000007	514	5

¹Sr concentration data from Murray et al. (2016)