Oxygen isotopes of calcite precipitated at high ionic strength: $CaCO_3$-DIC fractionation and carbonic anhydrase inhibition

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Supplement

S1. DIC speciation

Although DIC speciation is primarily a function of pH, factors such as temperature, pressure, and solution composition are also important. DIC speciation is well known for seawater solutions (Millero et al., 2006), but our solutions ($CaCl_2$ + NH_4Cl + NaCl) are substantially simpler in composition. The stoichiometric equilibrium constants (pK) have been determined for similar NaCl solutions (Millero et al., 2007), and while this may provide an accurate description of DIC speciation in our system, the stoichiometric solubility product (K_{sp}) for simple NaCl solutions is unknown. Hence, even with an accurate description of solution speciation, it is not straightforward to relate speciation to the degree of supersaturation with respect to calcite in non-seawater solutions. Consequently, we chose to use PHREEQC to model our solution speciation and degree of supersaturation in a self-consistent way using the Pitzer ionic activity database and our exact solution compositions as inputs (Charlton and Parkhurst, 2011; De Lucia and Kühn, 2013).

Differences in speciation between seawater solutions and NaCl solutions are shown in Fig. S1.1 for three different [NaCl] (0, 0.52, 1.37 M). For both seawater and NaCl solutions, increasing salinity shifts pK_1 and pK_2 to lower pH so that at a fixed pH of 8.3 the [CO_3^{2-}] increases while [HCO_3^-] and [CO_2] decrease. Increasing salinity has a greater effect on pK_2 than on pK_1 for both solution types. Overall DIC speciation differs between seawater and NaCl solutions, as increasing salinity in seawater dramatically shifts speciation so that CO_3^{2-} becomes the dominant DIC species at approximately 1 M NaCl (salinity ~75 g/kg) at a pH of 8.3 (Fig. S1.1b). Speciation shifts in NaCl solutions are more moderate, with CO_3^{2-} increasing from 1.8% of total DIC in freshwater solutions to 6.7% of total DIC in highly saline solutions. It is important to note that the PHREEQC speciation for our solution closely matches the DIC speciation based on pure NaCl solutions (Fig S1.1e, Millero et al., 2007).

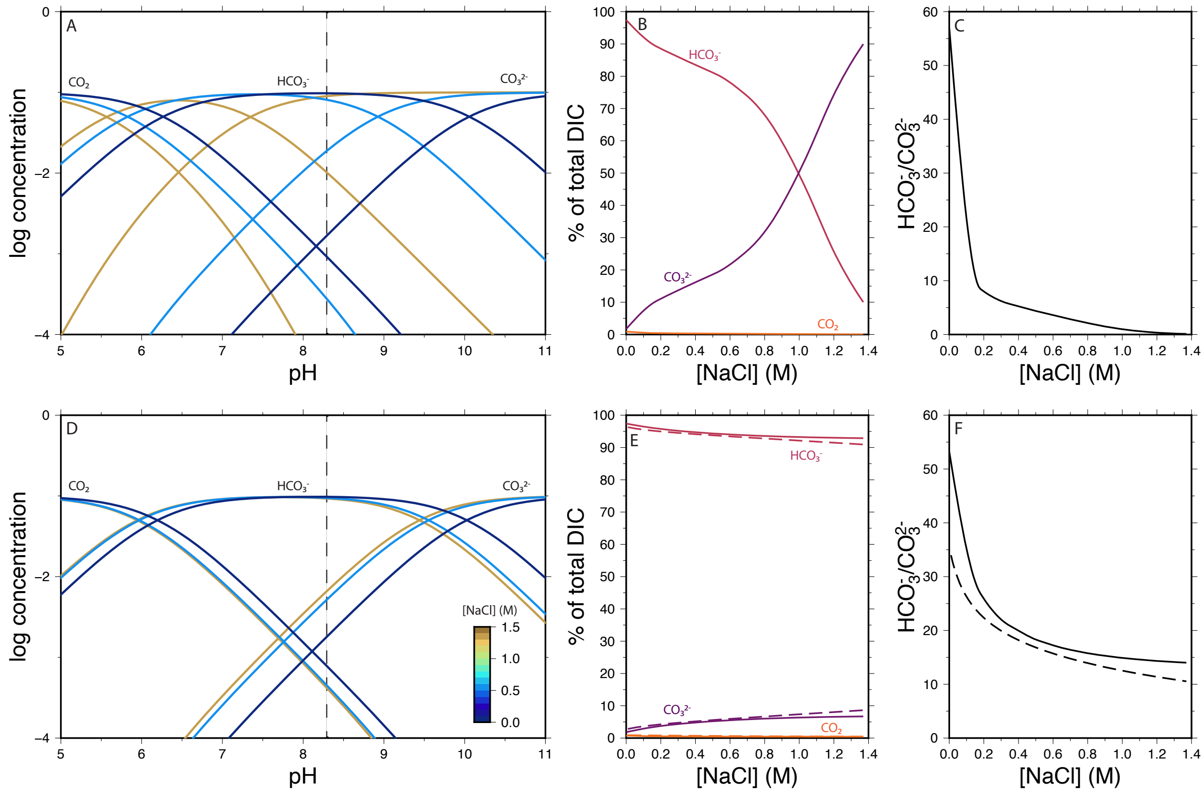

Figure S1.1. Solution speciation in seawater solutions (a-c; Millero et al., 2006) versus NaCl solutions (d-f; solid lines: Millero et al., 2007; dashed lines: PHREEQC, R-package Pitzer database) at 25°C. [NaCl] 0, 0.52, and 1.37 M span the range of this study (a, d). Proportion of each DIC species and HCO_3^-/CO_3^{2-} for solutions at pH 8.3 (b-c, e-f).

S2. Sensitivity of the kinetic isotope effects to the $\delta^{18}O$ of CO_2 gas.

To assess the sensitivity of $1000\ln\alpha_{c/w}$ to the isotopic composition of gas used, we simulated the uncatalyzed case ([bCA] = 0) for different $\delta^{18}O$ values of input CO_2. The results shown in Fig. S2.1 reveal a simple linear relationship between the $\delta^{18}O$ of CO_2 and $\delta^{18}O$ of EIC at steady state (all other parameters fixed) and show that a large 10‰ shift in the $\delta^{18}O$ of CO_2 translates to a much smaller 2‰ shift in the $\delta^{18}O$ of EIC (and calcite). This is attributed to the hydration reaction being bi-directional ($R_b/R_f \sim 0.8$; Fig. 5g of the main text). The sensitivity of $1000\ln\alpha_{c/w}$ to $\delta^{18}O$ of CO_2 decreases as more bCA is added, because bCA pushes R_b/R_f closer to unity.

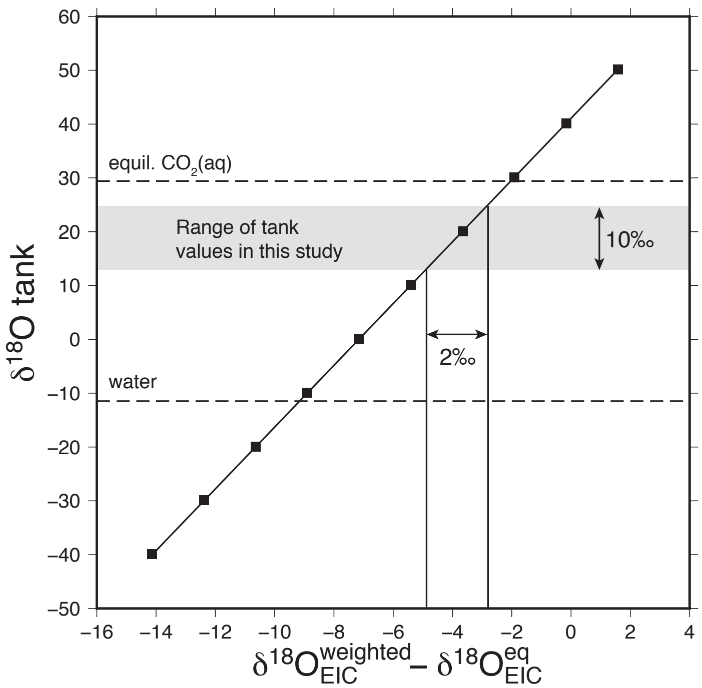

Figure S2.1. Modeled sensitivity of the steady state EIC composition to the δ^{18}O of CO_2 gas.

S3. Research data

Table S3.1. Additional parameters and isotopic data for experiments of this study

Experiment	Salinity (g/kg)	Molality	I	Time (total) (h)	Time (precip) (h)	$\delta^{13}C_c$ (VPDB)	$1000\ln\alpha_{c/DIC}$ (VPDB)	Ω_{peak}	Ω_{ss}
S2	35	0.5542	0.633	51.9	28.4	-44.00	-0.16	5.59	4.20
S3	35	0.5542	0.633	44.3	27.9	-45.56	-0.42	8.46	4.02
S4	15	0.2134	0.274	62.4	42.9	-46.26	-0.97	5.86	2.38
S5	25	0.3843	0.452	41.6	23.3	-45.08	-0.47	7.78	2.52
S6[a]	3.5	-	-	72.8	52.6	-46.06	-	-	-
S7	15	0.2132	0.274	47.7	29.4	-45.29	-0.40	6.85	3.61
S8	3.5	0.0365	0.094	52.2	34.2	-45.37	-0.59	8.46	3.34
S9	25	0.3854	0.453	47.6	32.0	-45.22	-0.40	8.01	3.71
S10	45	0.7275	0.820	66.0	40.7	-45.28	-0.13	8.09	3.70
S11	25	0.3852	0.452	66.9	34.8	-44.32	0.31	10.89	3.68
S12	85	1.4121	1.603	45.9	27.7	-24.00	0.61	7.52	4.09
S13	65	1.0692	1.203	93.2	64.2	-25.13	-0.02	5.14	2.22
S14	55	0.8992	1.010	52.4	36.6	-24.25	-0.33	7.24	2.99
S15	75	1.2414	1.401	61.3	37.5	-23.35	0.41	8.66	5.34
CA1	35	0.5566	0.634	65.2	37.6	-23.78	0.06	8.34	3.48
CA2	35	0.5565	0.634	48.5	33.9	-23.79	-0.05	7.76	3.93
CA3	35	0.5566	0.634	47.5	34.5	-24.29	-0.19	5.66	2.73
CA4	3.5	0.0368	0.094	30.6	21.5	-25.44	-0.54	7.19	3.77
CA5	35	0.5565	0.634	62.2	37.5	-22.86	0.62	8.74	2.79
CA6	35	0.5570	0.634	61.2	40.5	-22.38	0.55	8.12	3.55
CA7	20	0.2999	0.363	61.5	37.1	-21.59	0.61	10.65	3.89
CA9	60	0.9847	1.106	60.3	43.3	-43.55	0.41	8.55	3.62
CA12	45	0.7280	0.820	66.9	51.0	-43.52	-0.38	7.49	2.46
CA13	65	1.0697	1.203	66.0	41.0	-43.35	0.09	7.06	2.25
CA14	15	0.2143	0.274	50.2	36.1	-43.24	-0.44	5.23	2.54
CA15	25	0.3856	0.453	52.0	37.5	-42.59	0.05	6.33	2.64
CA18	3.5	0.0387	0.095	42.7	35.5	-17.67	-0.30	9.03	5.11
CA20	3.5	0.0376	0.094	46.8	40.3	-34.77	-1.27	7.80	3.82

Ionic strength (I), Ω_{peak}, and Ω_{ss} were calculated using the PHREEQC R-package Pitzer database. Ω_{peak} represents the highest degree of supersaturation during an experiment, which occurs at the onset of calcite precipitation. Ω_{ss} represents the average degree of supersaturation for an experiment during the “steady state” calcite growth period.

[a]S6 lacks DIC measurements

Table S3.2. Experiment measurements

Experiment	Time (h)	TA (mEq/L)	[DIC] (mM)	$\delta^{13}C_{DIC}$ (VPDB)	$\delta^{18}O_w$ (VSMOW)	pCO_2 (ppm)
S2	0.00	-	0.07	-35.52	-	206
-	7.40	0.65	0.36	-43.65	-	141
-	22.65	0.92	0.45	-43.49	-	192
-	26.40	0.73	0.32	-43.16	-11.65	170
-	31.97	0.68	0.38	-43.61	-	148
-	44.98	0.65	0.32	-44.52	-	140
-	51.45	0.65	0.33	-44.64	-	142
S3	3.05	0.54	0.24	-44.45	-	70
-	16.65	0.94	0.68	-44.93	-	129
-	21.78	0.73	0.48	-44.78	-	102
-	26.78	0.70	0.40	-45.13	-	97
-	40.47	0.62	0.27	-45.86	-	92
-	43.97	0.69	0.31	-45.81	-11.52	93
S4	4.18	-	0.10	-44.77	-	60
-	12.33	-	0.22	-45.37	-	76
-	18.35	0.62	0.36	-45.73	-	91
-	20.50	-	0.34	-45.37	-	90
-	24.28	0.63	0.16	-45.02	-	70
-	28.60	0.61	0.13	-44.90	-	66
-	39.02	0.63	0.15	-44.54	-	67
-	44.02	0.63	0.15	-46.07	-	68
-	50.77	0.64	0.13	-45.85	-	65
-	62.33	0.80	0.15	-45.80	-11.42	60
S5	4.38	0.53	0.24	-43.30	-	79
-	15.55	0.80	0.51	-44.66	-	131
-	18.98	0.87	0.57	-44.81	-	141
-	25.05	0.69	0.31	-44.04	-	165
-	30.97	0.48	0.23	-45.28	-	194
-	39.35	0.52	0.15	-45.50	-	210
-	41.42	0.54	0.17	-44.81	-11.32	209
S6	3.85	0.46	-	-	-	-
-	18.82	0.69	-	-	-	-
-	26.83	0.61	-	-	-	-
-	41.45	0.51	-	-	-	-
-	45.78	0.53	-	-	-	-
-	52.75	0.52	-	-	-	-
-	63.75	0.50	-	-	-	-
-	66.63	0.50	-	-	-	-

-	72.78	0.50	-	-	-11.31	-
S7	3.83	0.48	0.22	-44.33	-	67
-	13.92	0.71	0.37	-45.16	-	105
-	20.65	0.71	0.42	-44.65	-	117
-	27.57	0.55	0.28	-44.80	-	83
-	38.83	0.55	0.21	-44.47	-	82
-	45.00	0.55	0.24	-45.50	-	89
-	48.00	0.52	0.15	-45.47	-11.34	184
S8	3.65	0.47	0.14	-43.66	-	97
-	11.80	0.65	0.37	-44.47	-	142
-	19.07	0.66	0.26	-44.18	-	143
-	26.07	0.49	0.15	-44.60	-	103
-	34.97	0.50	0.17	-45.47	-	104
-	47.22	0.49	0.13	-45.70	-	102
-	52.15	0.60	0.13	-45.55	-11.39	91
S9	3.22	0.55	0.17	-44.63	-	72
-	14.05	0.85	0.48	-44.68	-	172
-	16.22	0.85	0.59	-44.25	-	179
-	20.40	0.63	0.30	-44.18	-	123
-	25.95	0.62	0.25	-45.22	-	118
-	37.83	0.64	0.25	-45.47	-	124
-	47.38	0.60	0.29	-45.48	-11.40	118
S10	3.08	0.35	-	-	-	78
-	11.67	0.63	-	-	-	142
-	16.90	0.84	-	-	-	171
-	24.42	0.97	-	-	-	198
-	26.50	0.99	0.69	-44.22	-	192
-	34.65	0.63	0.29	-44.45	-	136
-	39.30	0.60	0.27	-45.24	-	129
-	46.10	0.60	0.36	-45.53	-	128
-	59.03	0.59	0.34	-45.76	-	136
-	66.13	0.61	0.31	-45.74	-11.39	132
S11	4.83	0.61	-	-	-	107
-	14.50	0.90	0.59	-44.36	-	189
-	22.10	1.08	0.61	-43.72	-	218
-	28.07	1.15	0.80	-43.03	-	235
-	38.32	0.68	0.34	-43.34	-	139
-	44.27	0.65	0.22	-45.10	-	130
-	50.52	0.63	0.27	-45.51	-	130
-	60.68	0.66	0.25	-45.85	-	131
-	66.98	0.63	0.28	-46.02	-11.62	127
S12	4.55	0.57	-	-	-	131

-	14.03	0.85	0.56	-24.53	-	171
-	20.20	0.92	0.62	-23.87	-	176
-	28.00	0.64	0.34	-24.38	-	127
-	37.50	0.61	0.35	-24.94	-	127
-	45.50	0.62	0.31	-25.23	-11.57	124
S13	4.05	0.46	0.14	-24.15	-	194
-	12.20	0.63	0.27	-24.89	-	221
-	20.13	0.80	0.37	-24.76	-	226
-	28.58	0.88	0.44	-24.53	-	237
-	37.10	0.61	0.22	-24.18	-	219
-	44.32	0.58	0.20	-24.71	-	216
-	51.98	0.58	0.19	-25.08	-	217
-	60.97	0.57	0.20	-25.35	-	210
-	68.32	0.59	0.21	-25.74	-	208
-	76.02	0.58	0.16	-25.83	-	209
-	86.78	0.58	0.18	-26.05	-	204
-	92.95	0.57	0.20	-26.00	-11.72	206
S14	3.52	0.61	0.21	-23.69	-	89
-	10.62	0.90	0.63	-23.82	-	138
-	21.80	0.67	0.25	-23.74	-	98
-	26.72	0.61	0.25	-24.53	-	94
-	34.52	0.64	0.25	-24.39	-	96
-	45.13	0.62	0.22	-24.83	-	95
-	52.00	0.63	0.32	-22.45	-11.82	98
S15	3.37	0.59	0.19	-24.27	-	85
-	13.27	0.95	0.60	-24.32	-	142
-	19.47	1.24	0.71	-23.73	-	172
-	26.03	1.26	0.73	-23.00	-	178
-	36.60	0.96	0.50	-22.96	-	136
-	44.47	0.82	0.55	-23.34	-	122
-	50.45	0.74	0.43	-23.84	-	111
-	61.12	0.67	0.34	-24.53	-11.82	97
CA1	5.15	0.43	0.10	-23.32	-	54
-	14.25	0.56	0.31	-23.96	-	83
-	21.65	0.90	0.67	-23.73	-	148
-	31.08	0.89	0.50	-22.91	-	149
-	39.38	0.68	0.26	-23.68	-	110
-	47.20	0.65	0.33	-24.26	-	108
-	55.07	0.65	0.30	-24.36	-	109
-	64.80	0.66	0.24	-24.49	-11.83	106
CA2	7.63	0.72	0.42	-23.58	-	127
-	14.78	0.95	0.63	-22.89	-	162

-	22.12	0.67	0.34	-23.30	-	105
-	29.22	0.65	0.33	-23.96	-	101
-	38.82	0.64	0.35	-24.20	-	93
-	48.33	0.63	0.24	-24.49	-11.86	97
CA3	2.40	0.48	0.17	-24.53	-	76
-	11.70	0.95	0.46	-23.61	-	146
-	23.03	0.72	0.24	-23.30	-	103
-	26.47	0.65	0.25	-24.24	-	102
-	35.83	0.64	0.21	-24.38	-	99
-	47.05	0.65	0.18	-24.54	-11.91	96
CA4	3.22	0.74	0.14	-24.50	-	134
-	8.38	0.95	0.31	-24.88	-	165
-	21.25	0.70	0.14	-25.12	-	121
-	25.38	0.72	0.19	-25.04	-	138
-	30.22	0.71	0.16	-25.05	-11.68	124
CA5	4.07	0.69	0.24	-23.50	-	94
-	13.15	-	0.48	-23.32	-	159
-	21.82	1.23	0.64	-22.53	-	195
-	24.68	1.29	0.71	-22.26	-	200
-	37.20	0.73	0.25	-23.27	-	131
-	44.22	0.70	0.23	-24.03	-	132
-	51.25	0.69	0.22	-24.25	-	130
-	61.87	0.67	0.20	-24.58	-11.17	128
CA6	4.00	0.60	0.27	-23.19	-	85
-	13.68	-	0.54	-22.54	-	169
-	18.03	1.09	0.66	-21.94	-	191
-	23.15	0.99	0.56	-21.49	-	167
-	29.03	0.79	0.33	-22.30	-	118
-	39.12	0.78	0.29	-23.36	-	107
-	45.95	0.77	0.28	-23.63	-	103
-	51.73	0.73	0.27	-23.75	-	105
-	60.92	0.74	0.27	-24.00	-11.18	102
CA7	3.17	0.58	0.23	-23.19	-	81
-	13.12	0.92	0.55	-22.00	-	173
-	19.50	1.04	0.73	-21.09	-	203
-	26.85	1.02	0.56	-20.41	-	191
-	37.43	0.68	0.27	-22.09	-	113
-	43.67	0.64	0.27	-22.66	-	112
-	50.35	0.65	0.29	-22.87	-	109
-	61.13	0.65	0.23	-23.20	-11.33	104
CA9	3.52	0.55	0.22	-44.09	-	34
-	12.45	0.91	0.57	-43.99	-	126

-	16.98	1.04	0.74	-43.55	-	154
-	25.58	0.68	0.29	-43.29	-	97
-	35.37	0.67	0.29	-44.15	-	95
-	42.58	0.68	0.31	-44.13	-	94
-	49.20	0.68	0.40	-44.03	-	92
-	59.87	0.65	0.28	-44.27	-11.57	90
CA12	3.83	0.63	0.32	-42.02	-	102
-	16.93	0.96	0.64	-42.92	-	184
-	22.37	0.97	0.63	-42.54	-	168
-	29.78	0.79	0.18	-42.25	-	128
-	40.15	0.63	0.24	-43.45	-	96
-	47.15	0.60	0.21	-43.67	-	87
-	53.40	0.60	0.21	-43.93	-	84
-	66.82	0.63	0.21	-44.46	-11.76	83
CA13	2.57	0.63	0.34	-43.70	-	67
-	14.40	0.93	0.54	-43.22	-	171
-	20.68	1.05	0.61	-42.61	-	194
-	26.35	1.00	0.51	-42.13	-	184
-	37.92	0.61	0.22	-43.38	-	103
-	44.25	0.63	0.20	-43.82	-	103
-	50.88	0.62	0.16	-43.87	-	102
-	60.17	0.60	0.18	-43.89	-	105
-	65.75	0.60	0.22	-44.36	-11.65	106
CA14	3.67	0.59	0.17	-42.28	-	87
-	16.05	0.84	0.32	-41.79	-	155
-	23.38	0.63	0.17	-42.22	-	96
-	30.77	0.59	0.15	-43.02	-	94
-	38.28	0.60	0.16	-43.29	-	98
-	44.03	0.62	0.16	-43.66	-	100
-	49.97	0.64	0.15	-43.43	-11.85	97
CA15	4.40	0.63	0.19	-42.63	-	98
-	14.92	0.95	0.46	-42.75	-	179
-	21.23	1.00	0.46	-41.89	-	169
-	29.10	0.79	0.24	-41.90	-	112
-	38.80	0.75	0.18	-42.91	-	98
-	45.10	0.72	0.18	-43.19	-	95
-	51.80	0.68	0.18	-43.19	-11.86	88
CA18	3.20	0.77	0.39	-17.44	-	220
-	13.93	0.71	0.31	-16.77	-	214
-	19.78	0.64	0.24	-17.40	-	192
-	26.93	0.64	0.22	-17.53	-	186
-	36.45	0.65	0.20	-17.66	-	188

-	42.28	0.64	0.22	-17.45	-11.88	191
CA20	6.22	0.74	0.34	-35.65	-	161
-	15.95	0.63	0.23	-35.59	-	127
-	22.50	0.63	0.22	-34.74	-	124
-	29.92	0.61	0.19	-32.34	-	115
-	39.62	0.60	0.16	-31.50	-	102
-	46.50	0.59	0.15	-31.45	-11.95	99