Dual carbonate clumped isotopes (Δ_{47}-Δ_{48}) constrains kinetic effects and timescales in peridotite-associated springs at The Cedars, Northern California

Supplementary Material-1

Modeling Equations and Parameters

Zeeshan A. Parvez[a, b, c,*], Jamie K. Lucarelli[a,b,*], Irvin W. Matamoros[a, b], Joshua Rubi[b, d], Kevin Miguel[b, d], Ben Elliott[a, b], Randy Flores[a, b], Robert N. Ulrich[a, b], Robert A. Eagle[b, e, f], James M. Watkins[g], John N. Christensen[h], Aradhna Tripati[a, b, e, f]

[a] *Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, CA, USA*
[b] *Center for Diversity and Leadership in Science, University of California, Los Angeles, CA, USA*
[c] *Department of Chemistry and Biochemistry, University of California, Los Angeles, CA, USA*
[d] *East Los Angeles College, Los Angeles, CA, USA*
[e] *Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA, USA*
[f] *Institute of Environment and Sustainability, University of California, Los Angeles, CA, USA*
[g] *Department of Earth Sciences, University of Oregon, Eugene, OR, USA*
[h] *Department of Energy Geosciences, Lawrence Berkeley National Laboratory, Berkeley CA, USA*

* *Joint first author.*

S.1 IsoDIC Model Equations

The following numerical values have been assigned to the respective isotopologue: ^{12}C = 2, ^{13}C = 3, ^{16}O = 6, ^{17}O = 7, ^{18}O = 8. For example, $H^{12}C^{18}O^{16}O^{17}O^{-}$ = H2867.

1. 266 + $H_2$6 ⇌ H2666 + H^+
2. 267 + $H_2$6 ⇌ H2667 + H^+
3. 268 + $H_2$6 ⇌ H2668 + H^+
4. 277 + $H_2$6 ⇌ H2677 + H^+
5. 278 + $H_2$6 ⇌ H2678 + H^+
6. 288 + $H_2$6 ⇌ H2688 + H^+
7. 266 + $H_2$7 ⇌ H2667 + H^+
8. 267 + $H_2$7 ⇌ H2667 + H^+
9. 267 + $H_2$7 ⇌ H2678 + H^+
10. 277 + $H_2$7 ⇌ H2777 + H^+
11. 278 + $H_2$7 ⇌ H2778 + H^+
12. 288 + $H_2$7 ⇌ H2788 + H^+
13. 266 + $H_2$8 ⇌ H2668 + H^+
14. 267 + $H_2$8 ⇌ H2678 + H^+
15. 268 + $H_2$8 ⇌ H2688 + H^+
16. 277 + $H_2$8 ⇌ H2778 + H^+
17. 278 + $H_2$8 ⇌ H2788 + H^+
18. 288 + $H_2$8 ⇌ H2888 + H^+
19. 266 + $H_2$6 ⇌ H3666 + H^+
20. 366 + $H_2$6 ⇌ H3667 + H^+

21. $377 + H_26 \rightleftharpoons H3668 + H^+$
22. $378 + H_26 \rightleftharpoons H3677 + H^+$
23. $378 + H_26 \rightleftharpoons H3678 + H^+$
24. $388 + H_26 \rightleftharpoons H3688 + H^+$
25. $366 + H_27 \rightleftharpoons H3667 + H^+$
26. $367 + H_27 \rightleftharpoons H3677 + H^+$
27. $368 + H_27 \rightleftharpoons H3678 + H^+$
28. $377 + H_27 \rightleftharpoons H3777 + H^+$
29. $378 + H_27 \rightleftharpoons H3778 + H^+$
30. $388 + H_27 \rightleftharpoons H3788 + H^+$
31. $366 + H_28 \rightleftharpoons H3668 + H^+$
32. $367 + H_28 \rightleftharpoons H3678 + H^+$
33. $368 + H_28 \rightleftharpoons H3688 + H^+$
34. $377 + H_28 \rightleftharpoons H3778 + H^+$
35. $378 + H_28 \rightleftharpoons H3788 + H^+$
36. $388 + H_28 \rightleftharpoons H3888 + H^+$
37. 266 + 6H ⇌ H2666
38. 267 + 6H ⇌ H2667
39. 268 + 6H ⇌ H2668
40. 277 + 6H ⇌ H2677
41. 278 + 6H ⇌ H2678
42. 288 + 6H ⇌ H2688
43. 266 + 7H ⇌ H2667
44. 267 + 7H ⇌ H2677
45. 268 + 7H ⇌ H2678
46. 277 + 7H ⇌ H2777
47. 278 + 7H ⇌ H2778
48. 288 + 8H ⇌ H2788
49. 266 + 8H ⇌ H2668
50. 267 + 8H ⇌ H2678
51. 268 + 8H ⇌ H2688
52. 277 + 8H ⇌ H2778
53. 278 + 8H ⇌ H2788
54. 288 + 8H ⇌ H2888
55. 366 + 6H ⇌ H3666
56. 367 + 6H ⇌ H3667
57. 368 + 6H ⇌ H3668
58. 377 + 6H ⇌ H3677
59. 378 + 6H ⇌ H3678
60. 388 + 6H ⇌ H3688
61. 366 + 7H ⇌ H3667
62. 367 + 7H ⇌ H3677
63. 368 + 7H ⇌ H3678
64. 377 + 7H ⇌ H3777
65. 378 + 7H ⇌ H3778
66. 388 + 7H ⇌ H3788

67. 366 + 8H ⇌ H3668
68. 367 + 8H ⇌ H3678
69. 368 + 8H ⇌ H3688
70. 377 + 8H ⇌ H3778
71. 378 + 8H ⇌ H3788
72. 388 + 8H ⇌ H3888
73 – 152. $H^iC^jO^kO^lO^- + {}^mOH^- \rightleftharpoons {}^iC^jO^kO^lO^2 + H_2{}^mO$
where i = 12, 13, 16 ≤ j ≤ k ≤ l ≤ 18, m = 16, 17, 18
153 – 155. $H_2{}^mO \rightleftharpoons {}^mOH^- + H^+$
where m = 16, 17, 18

The above reactions and their isotope effects were used by Guo (2020) to calculate intrinsic kinetic clumped isotope fractionation factors (KFFs) associated with CO_2 hydration and hydroxylation and their reverse reactions.

S.2 COAD Model Equations

S.2.1 Hydration and hydroxylation reactions

1. $266 + H_2 6 \rightleftharpoons H2666 + H$ (forward = k_{+1}) (reverse = k_{-1})
2. $266 + 6H \leftrightarrows H2666$ (forward = k_{+4}) (reverse = k_{-4})
3. $366 + H_2 6 \leftrightarrows H3666 + H$ (forward = c_{+1}) (reverse = c_{-1})
4. $366 + 6H \leftrightarrows H3666$ (forward = c_{+4}) (reverse = c_{-4})
5. $266 + H_2 8 \leftrightarrows H2866 + H$ (forward = a_{+1}) (reverse = $1/3a_{-1}$)
6. $286 + H_2 6 \leftrightarrows H2866 + H$ (forward = b_{+1}) (reverse = $2/3b_{-4}$)
7. $266 + 8H \leftrightarrows H2866$ (forward = a_{+4}) (reverse = $1/3a_{-4}$)
8. $286 + 6H \leftrightarrows H2866$ (forward = b_{+4}) (reverse = $2/3b_{-4}$)
9. $366 + H_2 8 \leftrightarrows H3866 + H$ (forward = p_{+1}) (reverse = $1/3p_{-1}$)
10. $386 + H_2 6 \leftrightarrows H3866 + H$ (forward = s_{+1}) (reverse = $2/3s_{-1}$)
11. $366 + 8H \leftrightarrows H3866$ (forward = p_{+4}) (reverse = $1/3p_{-4}$)
12. $386 + 6H \leftrightarrows H3866$ (forward = s_{+4}) (reverse = $2/3s_{-1}$)
13. $286 + H_2 8 \leftrightarrows H2886 + H$ (forward = p'_{+1}) (reverse = $2/3p'_{-1}$)
14. $288 + H_2 6 \leftrightarrows H2886 + H$ (forward = s'_{+1}) (reverse = $1/3s'_{-1}$)
15. $286 + 8H \leftrightarrows H2886$ (forward = p'_{+4}) (reverse = $2/3p'_{-4}$)
16. $288 + 6H \leftrightarrows H2886$ (forward =s'_{+4}) (reverse = $1/3s'_{-4}$)

S.2.2 Governing equations for the reaction-diffusion model

17. $\frac{d[266]}{dt} = D_{CO_2} * \frac{d^2[266]}{dz^2} - k_{+1}[266] + k_{-1}[E2666]\chi[H] - k_{+4}[266][6H] + k_{-4}[E2666]\chi$
18. $\frac{d[366]}{dt} = D_{CO_2} * \frac{d^2[366]}{dz^2} - c_{+1}[366] + c_{-1}[E3666]^{13}\chi[H] - c_{+4}[366][6H] + c_{-4}[E3666]^{13}\chi$
19. $\frac{d[286]}{dt} = D_{CO_2} * \frac{d^2[286]}{dz^2} - b_{+1}[286] + \frac{2}{3}b_{-1}[E2866]^{18}X[H] - b_{+4}[286][6H] + \frac{2}{3}b_{-4}[E2866]^{18}X$
20. $\frac{d[386]}{dt} = D_{CO_2} * \frac{d^2[386]}{dz^2} - p_{+1}[386] + \frac{1}{3}p_{-1}[E3866]^{63}X[H] - s_{+4}[386][6H] + \frac{2}{3}s_{-4}[E3866]^{63}X$

21. $\frac{d[288]}{dt} = D_{CO_2} * \frac{d^2[288]}{dz^2} - s'_{+1}[288] + \frac{1}{3}s'_{-1}[E2886]^{64}X[H] - s'_{+4}[288][6H] + \frac{1}{3}s'_{-4}[E2886]^{64}X$

22. $\frac{d[E2666]}{dt} = D_{CO_2} * \frac{d^2[E2666]}{dz^2} + k_{+1}[266] - k_{-1}[E2666]X[H]k_{+4}[266][6H] - k_{-4}[E2666]X - Sp * J_{CaCO_3}$

23. $\frac{d[E3666]}{dt} = D_{CO_2} * \frac{d^2[E3666]}{dz^2} + c_{+1}[366] - c_{-1}[E3666]^{13}X[H]c_{+4}[366][6H] - c_{-4}[E3666]^{13}X - Sp * J_{CaCO_3} * \frac{[E3666]}{[E2666]} *^{13} \alpha_{CaCO_3-EIC}$

24. $\frac{d[E2866]}{dt} = D_{CO_2} * \frac{d^2[E2866]}{dz^2} + a_{+1}[266]r_w - \frac{1}{3}a_{-1}[E2866]^{18}X[H] + a_{+4}[266][8H] - \frac{1}{3}a_{-4}[E2866]^{18}X + b_{+1}[286] - \frac{2}{3}b_{-1}[E2866]^{18}X[H] + b_{+4}[286][6H] - \frac{2}{3}b_{-4}[E2866]^{18}X - Sp * J_{CaCO_3} * \frac{[E2866]}{[E2666]} *^{18} \alpha_{CaCO_3-EIC}$

25. $\frac{d[E3866]}{dt} = D_{CO_2} * \frac{d^2[E3866]}{dz^2} + p_{+1}[366]r_w - \frac{1}{3}p_{-1}[E3866]^{63}X[H] + p_{+4}[266][8H] - \frac{1}{3}p_{-4}[E3866]^{63}X + s_{+1}[386] - \frac{2}{3}s_{-1}[E3866]^{63}X[H] + s_{+4}[386][6H] - \frac{2}{3}s_{-4}[E3866]^{63}X - Sp * J_{CaCO_3} * \frac{[E3866]}{[E2666]} *^{63} \alpha_{CaCO_3-EIC} *^{13} \alpha_{CaCO_3-EIC} *^{18} \alpha_{CaCO_3-EIC}$

26. $\frac{d[E2886]}{dt} = D_{CO_2} * \frac{d^2[E2886]}{dz^2} + p'_{+1}[286]r_w - \frac{2}{3}p'_{-1}[E2886]^{64}X[H] + p'_{+4}[286][8H] - \frac{2}{3}p'_{-4}[E2886]^{64}X + s'_{+1}[288] - \frac{1}{3}s'_{-1}[E2886]^{64}X[H] + s'_{+4}[288][6H] - \frac{1}{3}s'_{-4}[E2886]^{64}X - Sp * J_{CaCO_3} * \frac{[E2886]}{[E2666]} *^{64} \alpha_{CaCO_3-EIC} *^{18} \alpha_{CaCO_3-EIC} *^{18} \alpha_{CaCO_3-EIC}$

27. $\frac{d[Alk]}{dt} = D_{Alk} * \frac{d^2[Alk]}{dz^2} - 2 * Sp * J_{CaCO_3}$

28. $\frac{d[Ca^{2+}]}{dt} = D_{Ca^{2+}} * \frac{d^2[Ca^{2+}]}{dz^2} - Sp * J_{CaCO_3}$

S.2.3 Governing equations for the box model

29. $\frac{d[266]}{dt} = -k_{+1}[266] + k_{-1}[E2666]X[H] - k_{+4}[266][6H] + k_{-4}[E2666]X + \frac{F_{spr}}{V_{pool}}\left([266]_{spr} - [266]\right) + \frac{F_{cr}}{V_{pool}}([266]_{cr} - [266])$

30. $\frac{d[366]}{dt} = -c_{+1}[366] + c_{-1}[E3666]^{13}X[H] - c_{+4}[366][6H] + c_{-4}[E3666]^{13}X + \frac{F_{spr}}{V_{pool}}\left([366]_{spr} - [366]\right) + \frac{F_{cr}}{V_{pool}}([366]_{cr} - [266])$

31. $\frac{d[286]}{dt} = -b_{+1}[286] + \frac{2}{3}b_{-1}[E2866]^{18}X[H] - b_{+4}[286][6H] + \frac{2}{3}b_{-4}[E2866]^{18}X + \frac{F_{spr}}{V_{pool}}\left([286]_{spr} - [286]\right) + \frac{F_{cr}}{V_{pool}}([286]_{cr} - [266])$

32. $\frac{d[386]}{dt} = -p_{+1}[386] + \frac{1}{3}p_{-1}[E3866]^{63}X[H] - s_{+4}[386][6H] + \frac{2}{3}s_{-4}[E3866]^{63}X + \frac{F_{spr}}{V_{pool}}\left([386]_{spr} - [386]\right) + \frac{F_{cr}}{V_{pool}}([386]_{cr} - [266])$

33. $\frac{d[288]}{dt} = -s'_{+1}[288] + \frac{1}{3}s'_{-1}[E2886]^{64}X[H] - s'_{+4}[288][6H] + \frac{1}{3}s'_{-4}[E2886]^{64}X + \frac{F_{spr}}{V_{pool}}\left([288]_{spr} - [288]\right) + \frac{F_{cr}}{V_{pool}}([288]_{cr} - [266])$

34. $\frac{d[E2666]}{dt} = k_{+1}[266] - k_{-1}[E2666]X[H]k_{+4}[266][6H] - k_{-4}[E2666]X + \frac{J_{atm} * SA_{pool}}{V_{pool}} + \frac{F_{spr}}{V_{pool}}\left([E2666]_{spr} - [E2666]\right) + \frac{F_{cr}}{V_{pool}}([E2666]_{cr} - [E2666]) - Sp * J_{CaCO_3}$

35. $\frac{d[E3666]}{dt} = c_{+1}[366] - c_{-1}[E3666]^{13}X[H]c_{+4}[366][6H] - c_{-4}[E3666]^{13}X\frac{J_{atm}*SA_{pool}}{V_{pool}} * \left(\frac{[E3666]}{[E2666]}\right)_{hydrox} + \frac{F_{spr}}{V_{pool}}(^{13}R_{EIC(spr)}[EIC]_{spr} - [E3666]) + \frac{F_{cr}}{V_{pool}}([E3666]_{cr} - [E3666]) - Sp * J_{CaCO_3}\frac{[E3666]}{[E2666]} *^{13}\alpha_{CaCO_3-EIC}$

36. $\frac{d[E2866]}{dt} = a_{+1}[266]r_w - \frac{1}{3}a_{-1}[E2866]^{18}X[H] + a_{+4}[266][8H] - \frac{1}{3}a_{-4}[E2866]^{18}X + b_{+1}[286] - \frac{2}{3}b_{-1}[E2866]^{18}X[H] + b_{+4}[286][6H] - \frac{2}{3}b_{-4}[E2866]^{18}X + \frac{J_{atm}*SA_{pool}}{V_{pool}} * (\frac{[E2866]}{[E2666]})_{hydrox} + \frac{F_{spr}}{V_{pool}}([E2866]_{spr} - [E2866]) + \frac{F_{cr}}{V_{pool}}([E2866]_{cr} - [E2866]) - Sp * J_{CaCO_3}\frac{[E2866]}{[E2666]} *^{18}\alpha_{CaCO_3-EIC}$

37. $\frac{d[E3866]}{dt} = p_{+1}[366]r_w - \frac{1}{3}p_{-1}[E3866]^{63}X[H] + p_{+4}[266][8H] - \frac{1}{3}p_{-4}[E3866]^{63}X + s_{+1}[386] - \frac{2}{3}s_{-1}[E3866]^{63}X[H] + s_{+4}[386][6H] - \frac{2}{3}s_{-4}[E3866]^{63}X + \frac{J_{atm}*SA_{pool}}{V_{pool}} * (\frac{[E3866]}{[E2666]})_{hydrox} + \frac{F_{spr}}{V_{pool}}([E3866]_{spr} - [E3866]) + \frac{F_{cr}}{V_{pool}}([E3866]_{cr} - [E3866]) - Sp * J_{CaCO_3}\frac{[E3866]}{[E2666]} *^{63}\alpha_{CaCO_3-EIC} *^{13}\alpha_{CaCO_3-EIC} *^{18}\alpha_{CaCO_3-EIC}$

38. $\frac{d[E2886]}{dt} = p'_{+1}[286]r_w - \frac{2}{3}p'_{-1}[E2886]^{64}X[H] + p'_{+4}[286][8H] - \frac{2}{3}p'_{-4}[E2886]^{64}X + s'_{+1}[288] - \frac{1}{3}s'_{-1}[E2886]^{64}X[H] + s'_{+4}[288][6H] - \frac{1}{3}s'_{-4}[E2886]^{64}X + \frac{J_{atm}*SA_{pool}}{V_{pool}} * (\frac{[E2886]}{[E2666]})_{hydrox} + \frac{F_{spr}}{V_{pool}}([E2886]_{spr} - [E2886]) + \frac{F_{cr}}{V_{pool}}([E2886]_{cr} - [E2886]) - Sp * J_{CaCO_3}\frac{[E2886]}{[E2666]} *^{64}\alpha_{CaCO_3-EIC} *^{18}\alpha_{CaCO_3-EIC} *^{18}\alpha_{CaCO_3-EIC}$

39. $\frac{d[Alk]}{dt} = \frac{F_{spr}}{V_{pool}}\left([Alk]_{spr} - [Alk]\right) + \frac{F_{cr}}{V_{pool}}([Alk]_{cr} - [Alk]) - 2 * Sp * J_{CaCO_3}$

40. $\frac{d[Ca^{2+}]}{dt} = \frac{F_{spr}}{V_{pool}}([Ca^{2+}]_{spr} - [Ca^{2+}]) + \frac{F_{cr}}{V_{pool}}([Ca^{2+}]_{cr} - [Ca^{2+}]) - Sp * J_{CaCO_3}$

S.2.4 Post-processing: Isotopologue concentrations to isotope ratios

41. $\delta^{13}C(‰) = \left(\frac{^{13}R}{0.0118} - 1\right) * 1000$,

42. $^{13}R = \frac{[3666]}{[2666]}$.

43. $\delta^{18}O(‰) = \left(\frac{3*^{18}R}{0.0020052} - 1\right) * 1000$,

44. $^{18}R = \frac{[2866]}{[2666]}$.

45. $\Delta_{47} = (\frac{^{47}R}{^{47}R} - 1) * 1000$,

46. $\frac{^{47}R}{^{47}R^*} = \frac{[386][266]}{[366][286]}$,

47. $\Delta_{63} = \left(\frac{^{63}R}{^{63}R^*} - 1\right) * 1000$,

48. $\frac{^{63}R}{^{63}R^*} = \frac{[3866][2666]}{[3666][2866]}$.

49. $\Delta_{48} = \left(\frac{^{48}R}{^{48}R^*} - 1\right) * 1000$,

50. $\frac{^{48}R}{^{48}R^*} = 4 * \frac{[288][266]}{[286][286]}$,

51. $\Delta_{64} = \left(\frac{^{64}R}{^{64}R^*} - 1\right) * 1000,$
52. $\frac{^{64}R}{^{64}R^*} = 3 * \frac{[2886][2666]}{[2866][2866]}$

S.2.5 Adding Δ48 to the model

Homogeneous reactions and clumped isotope definitions:

1. $286 + 286 \rightleftharpoons 288 + 266$
2. $^{48}K_{CO_2} = \frac{[288][266]}{[286][286]}.$
3. $\Delta_{48} = \left(\frac{^{48}R}{^{48}R^*} - 1\right) * 1000,$
4. $^{48}R = \frac{[288]}{[266]}$
5. $^{48}K_{CO_2} = \frac{[288]}{[266]}\frac{[266]}{[286]}\frac{[266]}{[286]} = {}^{48}R * (2 *^{18} r_{CO_2})^{-1} = \frac{1}{4}(\frac{^{48}R}{^{48}R^*})^{eq}_{CO_2}$
6. $\frac{[288]}{[266]} = {}^{48}R^* = {}^{18}r^2_{CO_2}.$
7. $^{48}K_{CO_2} = \frac{[288][266]}{[286][286]} = \frac{1}{4}\left(\frac{^{48}R}{^{48}R^*}\right)^{eq}_{CO_2} = \frac{1}{4}(\frac{\Delta^{eq}_{48,CO_2}}{1000} + 1)$
8. $H2866 + H2866 \rightleftharpoons H2886 + H2666$
9. $2866 + 2866 \rightleftharpoons 2886 + 2666,$
10. $^{64}K_{HCO_3^-} = \frac{[H2886][H2666]}{[H2866][H2866]} = \frac{1}{3}(\frac{^{64}R}{^{64}R^*})^{eq}_{HCO_3^-} = \frac{1}{3}(\frac{\Delta^{eq}_{64,HCO_3^-}}{1000} + 1)$
11. $^{64}K_{CO_3^{2-}} = \frac{[2886][2666]}{[2866][2866]} = \frac{1}{3}(\frac{^{64}R}{^{64}R^*})^{eq}_{CO_3^{2-}} = \frac{1}{3}\left(\frac{\Delta^{eq}_{64,CO_3^{2-}}}{1000} + 1\right).$

Heterogeneous reactions involving Δ48 isotopologues:

12. $286 + H_28 \underset{2/3p'_{-1}}{\overset{p'_{+1}}{\rightleftharpoons}} H2886^- + H^+$
13. $288 + H_26 \underset{1/3s'_{-1}}{\overset{s'_{+1}}{\rightleftharpoons}} H2886^- + H^+$
14. $286 + 8H^- \underset{2/3p'_{-4}}{\overset{p'_{+4}}{\rightleftharpoons}} H2886^-$
15. $288 + 6H^- \underset{1/3s'_{-4}}{\overset{s'_{+4}}{\rightleftharpoons}} H2886^-$
16. $\frac{d[288]}{dt} = -s'_{+1}[288] + \frac{1}{3}s'_{-1}[E2886]^{64}X[H] - s'_{+4}[288][6H] + \frac{1}{3}s'_{-4}[E2886]^{64}X$

$$\frac{d[E2886]}{dt} = p'_{+1}[286]r_w - \frac{2}{3}p'_{-1}[E2886]^{64}X[H] + p'_{+4}[286][8H] - \frac{2}{3}p'_{-4}[E2886]^{64}X + s'_{+1}[288] - \frac{1}{3}s'_{-1}[E2886]^{64}X[H] + s'_{+4}[288][6H] - \frac{1}{3}s'_{-4}[E2886]^{64}X$$

S.3 Model Parameters

Symbol	Expression or value at 25°C	Reference
K_1	$\frac{[H][H2666]}{[266]}$	-

K_2	$\frac{[H][H2666]}{[H2666]}$	-
K_w	[6H][H]	-
k_{+1}	$\ln k_{+1} = 1246.98 - \frac{61900}{T_K} - 183.0 ln T_k$	Uchikawa and Zeebe (2012)
k_{-1}	$k_{-1} = k_{+1}/K_1$	-
k_{+4}	$ln\, k_{+4} = 17.67 - \frac{2790.47}{T_K}$	Uchikawa and Zeebe (2012)
k_{-4}	$k_{-4} = k_{+4}\frac{K_w}{K_1}$	-
χ	$\chi = \frac{1}{1+\frac{K_2}{[H^+]}}$	-
Carbon isotope parameters		
${}^{13}\alpha^{eq}_{HCO_3^- - CO_2}$	$-9.866T^{-1} + 1.02412$	Zhang et al. (1995)
${}^{13}\alpha^{eq}_{HCO_3^- - CO_2}$	$-0.867\ T^{-1} + 1.00252$	Zhang et al. (1995)
${}^{13}\alpha^{KFF}_{c_{+1}}$	0.9872	Yumol et al. (2020)
${}^{13}\alpha^{KFF}_{c_{+4}}$	0.9814	Christensen et al. (2021)
c_{+1}	$c_{+1} = {}^{13}\alpha^{KFF}_{c_{+1}} \cdot k_{+1}$	-
c_{-1}	$c_{-1} = c_{+1} / \left(K_1 \cdot {}^{13}\alpha^{eq}_{HCO_3^- - CO_2}\right)$	-
c_{+4}	$c_{+4} = {}^{13}\alpha^{KFF}_{c_{+4}} \cdot k_{+4}$	-
c_{-4}	$c_{-4} = c_{+4} / \left(\frac{K_1}{K_w} \cdot {}^{13}\alpha^{eq}_{HCO_3^- - CO_2}\right)$	-
${}^{13}\chi$	${}^{13}\chi = \frac{1}{1+\frac{K_2 \cdot {}^{13}\alpha^{eq}_{HCO_3^- - CO_3}}{[H^+]}}$	-
Oxygen isotope parameters		
${}^{18}\alpha^{eq}_{CO_2 - H_2O}$	$\exp(2520\, T_K^{-2} + 0.01212$	Beck et al. (2005)
${}^{18}\alpha^{eq}_{HCO_3^- - H_2O}$	$\exp(2590\, T_K^{-2} + 0.00189$	Beck et al. (2005)
${}^{18}\alpha^{eq}_{CO_3^{2-} - H_2O}$	$\exp(2390\, T_K^{-2} - 0.00270$	Beck et al. (2005)
${}^{18}\alpha^{eq}_{OH^- - H_2O}$	$5.6676 \times 10^{-5}\, T_K + 0.9622$	Zeebe (2020)
${}^{18}\alpha^{KFF}_{a_{+1}}$	1.0000	Yumol et al. (2020)
${}^{18}\alpha^{KFF}_{b_{+1}}$	0.9812	Yumol et al. (2020)
${}^{18}\alpha^{KFF}_{a_{+4}}$	0.971 at 5 °C 0.978 at 25 °C	Watkins and Devriendt (2021)
${}^{18}\alpha^{KFF}_{b_{+4}}$	1.0000	Christensen et al. (2021)
a_{+1}	$a_{+1} = {}^{18}\alpha^{KFF}_{a_{+1}} \cdot k_{+1}$	-

b_{+1}	$b_{+1} = {}^{18}\alpha^{KFF}_{b_{+1}} \cdot k_{+1}$	-
a_{-1}	$a_{-1} = a_{+1}/(K_1 \cdot {}^{18}\alpha_{HCO_3^- - H_2O})$	-
b_{-1}	$b_{-1} = b_{+1}/(K_1 \cdot {}^{18}\alpha_{HCO_3^- - CO_2})$	-
a_{+4}	$a_{+4} = {}^{18}\alpha^{KFF}_{a_{+4}} \cdot k_{+4}$	-
b_{+4}	$b_{+4} = {}^{18}\alpha^{KFF}_{b_{+4}} \cdot k_{+4}$	-
a_{-4}	$a_{-4} = a_{+4}/\left(\frac{K_1}{K_w} \cdot \frac{{}^{18}\alpha_{HCO_3^- - H_2O}}{{}^{18}\alpha^{eq}_{OH^- - H_2O}}\right)$	-
b_{-4}	$b_{-4} = b_{+4}/\left(\frac{K_1}{K_w} \cdot {}^{18}\alpha_{HCO_3^- - CO_2}\right)$	-
${}^{18}\chi$	${}^{18}\chi = \frac{1}{1 + \frac{K_2 \cdot {}^{13}\alpha^{eq}_{CO_3 - HCO_3^-}}{[H^+]}}$	-
***Δ*47 parameters**		
$\left(\frac{{}^{47}R}{{}^{47}R^*}\right)^{eq}_{CO_2}$	$(\Delta^{eq}_{47,CO_2}/1000) + 1$	Hill et al. (2020)
$\left(\frac{{}^{63}R}{{}^{63}R^*}\right)^{eq}_{HCO_3^-}$	$(\Delta^{eq}_{63,HCO_3^-}/1000) + 1$	Hill et al. (2020); Tripati et al. (2015)
$\left(\frac{{}^{63}R}{{}^{63}R^*}\right)^{eq}_{CO_3^{2-}}$	$(\Delta^{eq}_{63,CO_3^{2-}}/1000) + 1$	Hill et al. (2020); Tripati et al. (2015)
${}^{63}\alpha^{eq}_{CO_3^{2-} - HCO_3}$	$\left(\frac{{}^{63}R}{{}^{63}R^*}\right)^{eq}_{CO_3^{2-}} / \left(\frac{{}^{63}R}{{}^{63}R^*}\right)^{eq}_{HCO_3^-}$	-
${}^{63}K_2$	${}^{63}\alpha^{KFF}_{CO_3^{2-} - HCO_3^-} \cdot {}^{13}\alpha^{eq}_{HCO_3^- - CO_3} \cdot {}^{18}\alpha^{eq}_{CO_3^{2-} - HCO_3^-} \cdot K_2$	-
${}^{63}\chi$	$\frac{1}{1 + \frac{{}^{63}K_2 \cdot {}^{63}\alpha^{eq}_{CO_3 - HCO_3^-}}{[H^+]}}$	-
${}^{13-18}KIE_{p+1}$	1-0.146/1000	Guo (2020)
${}^{13-18}KIE_{s+1}$	1-0.219/1000	Guo (2020)
${}^{13-18}KIE_{p+4}$	1-0.016/1000	Guo (2020)
${}^{13-18}KIE_{s+1}$	1-0.175/1000	Guo (2020)
p_{+1}	$\frac{c_{+1} \cdot a_{+1}}{k_{+1} \cdot {}^{47}KIE_{p_1}}$	Uchikawa et al. (2021)
s_{+1}	$\frac{c_{+1} \cdot b_{+1}}{k_{+1} \cdot {}^{47}KIE_{s_1}}$	Uchikawa et al. (2021)
p_{-1}		-
s_{-1}		-
p_{+4}	$\frac{c_{+4} \cdot a_{+4}}{k_{+4} \cdot {}^{13-18}KIE_{p4}}$	Uchikawa et al. (2021)

s_{+4}	$\frac{c_{+4} \cdot b_{+4}}{k_{+4} \cdot {}^{47}KIE_{s4}}$	Uchikawa et al. (2021)
p_{-4}	$p_{+4} / \left[\left(\frac{{}^{63}R}{{}^{63}R^*} \right)^{eq}_{HCO_3^-} \cdot \frac{K_1}{K_w} \cdot {}^{13}\alpha^{eq}_{HCO_3^- - CO_2} \cdot {}^{18}\alpha^{eq}_{HCO_3^- - OH^-} \right]$	-
s_{-4}	$s_{+4} \cdot \left[\left(\frac{{}^{47}R}{{}^{47}R^*} \right)^{eq}_{CO_2} / \left(\frac{{}^{63}R}{{}^{63}R^*} \right)^{eq}_{HCO_3^-} \cdot \frac{K_1}{K_w} \cdot {}^{13}\alpha^{eq}_{HCO_3^- - CO_2} \cdot {}^{18}\alpha^{eq}_{HCO_3^- - CO_2} \right]$	-
***Δ*₄₈ parameters**		
$\left(\frac{{}^{64}R}{{}^{64}R^*} \right)^{eq}_{CO_2}$	$(\Delta^{eq}_{48,CO_2}/1000) + 1$	Hill et al. (2020)
$\left(\frac{{}^{64}R}{{}^{64}R^*} \right)^{eq}_{HCO_3^-}$	$(\Delta^{eq}_{64,HCO_3^-}/1000) + 1$	Hill et al. (2020)
$\left(\frac{{}^{64}R}{{}^{64}R^*} \right)^{eq}_{CO_3^{2-}}$	$(\Delta^{eq}_{64,CO_3^{2-}}/1000) + 1$	Hill et al. (2020)
${}^{64}\alpha^{eq}_{CO_3^{2-} - HCO_3}$	$\left(\frac{{}^{64}R}{{}^{64}R^*} \right)^{eq}_{CO_3^{2-}} / \left(\frac{{}^{64}R}{{}^{64}R^*} \right)^{eq}_{HCO_3^-}$	-
${}^{64}K_2$	${}^{64}\alpha^{KFF}_{CO_3^{2-} - HCO_3^-} \cdot {}^{18}\alpha^{eq}_{CO_3^{2-} - HCO_3^-} {}^{18}\alpha^{eq}_{CO_3^{2-} - HCO_3^-} \cdot K_2$	-
${}^{64}\chi$	$\frac{1}{1 + \frac{{}^{64}K_2 \cdot {}^{64}\alpha^{eq}_{CO_3 - HCO_3^-}}{[H^+]}}$	-
${}^{18-18}KIE_{p'_{+1}}$	1+0.049/1000	Guo (2020)
${}^{18-18}KIE_{s'_{+1}}$	1-0.146/1000	Guo (2020)
${}^{18-18}KIE_{p'_{+4}}$	1-0.144/1000	Guo (2020)
${}^{18-18}KIE_{s'_{+4}}$	1-0.086/1000	Guo (2020)
p'_{+1}	$\frac{a_{+1} \cdot b_{+1}}{{}^{48}KIE_{p'_1} \cdot k_{+1}}$	-
s'_{+1}	$\frac{b_{+1} \cdot b_{+1}}{{}^{48}KIE_{s'_1} \cdot k_{+1}}$	-
p'_{-1}		-
s'_{-1}		-
p'_{+4}	$\frac{a_{+4} \cdot b_{+4}}{{}^{48}KIE_{p'_4} \cdot k_{+4}}$	-
s'_{+4}	$\frac{b_{+4} \cdot b_{+4}}{{}^{48}KIE_{s'_4} \cdot k_{+4}}$	-
p'_{-4}	$p'_{+4} / \left[\left(\frac{{}^{64}R}{{}^{64}R^*} \right)^{eq}_{HCO_3^-} \cdot \frac{K_1}{K_w} \cdot {}^{18}\alpha^{eq}_{HCO_3^- - CO_2} \cdot {}^{18}\alpha^{eq}_{HCO_3^- - OH^-} \right]$	-

s'_{-4}	$s'_{+4} \cdot \left[\left(\frac{{}^{48}R}{{}^{48}R^*} \right)^{eq}_{CO_2} / \left(\frac{{}^{64}R}{{}^{64}R^*} \right)^{eq}_{HCO_3^-} \cdot \frac{K_1}{K_w} \cdot {}^{18}\alpha^{eq}_{HCO_3^- - CO_2} \cdot {}^{18}\alpha^{eq}_{HCO_3^- - CO_2} \right]$	-