B systematics in cbsyst

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June 15, 2017

Contents

1 B systematics

From Zeebe and Wolf-Gladrow [2001], Eqns. 4.3.43–3.4.46:

$$
\begin{aligned}
B_T &= [\mathrm{B(OH)_3}] + [\mathrm{B(OH)_4}^-] && (1)\\
K_B &= \frac{[\mathrm{B(OH)_4}^-][\mathrm{H}^+]}{[\mathrm{B(OH)_3}]} && (2)\\
[\mathrm{B(OH)_4}^-] &= \frac{\mathrm{B_T}}{1 + [\mathrm{H}^+]/K_B} && (3)\\
[\mathrm{B(OH)_3}] &= \frac{\mathrm{B_T}}{1 + K_B/[\mathrm{H}^+]} && (4)\\
& && (5)
\end{aligned}
$$

The concentration of a B species can also be expressed as a mol fraction of B_T (χ_B), as a function of pH and K_B. From (4), when $[B_T] = 1$:

$$
\begin{aligned}
\chi &= \frac{1}{1 + \frac{K_B}{[\mathrm{H}^+]}} && (6)\\
&= \frac{[\mathrm{H}^+]}{[\mathrm{H}^+] + K_B} \qquad \text{thus:} && (7)\\
[\mathrm{B(OH)_3}] &= \chi[\mathrm{B_T}] && (8)\\
[\mathrm{B(OH)_4}^-] &= (1-\chi)[\mathrm{B_T}] && (9)
\end{aligned}
$$

Note: χ may also be operationally defined for individual species:

$$
\begin{aligned}
\chi_{BO3} &= \frac{[\mathrm{B(OH)_3}]}{\mathrm{B_T}} && (10)\\
\chi_{BO4} &= \frac{[\mathrm{B(OH)_4}^-]}{\mathrm{B_T}} && (11)
\end{aligned}
$$

1.1 On Isotope Notation

B isotope values are most commonly reported as ‰ $\delta^{11}B$:

$$
\delta^{11}B = \left(\frac{\frac{^{11}B}{^{10}B}sample}{\frac{^{11}B}{^{10}B}standard} - 1 \right) \times 1000 \qquad (12)
$$

Where the most commonly used standard is NIST951 (=4.04367). This notation is used for convenience when comparing small offsets driven by natural fractionation processes, but introduces a small (0.08%) error in calculations [Zeebe and Wolf-Gladrow, 2001, pg. 220].

To avoid this error, B isotopes can also be expressed in terms of the ratio of ^{11}B to ^{10}B, and in terms of the fractional abundance of ^{11}B.

$$^{11}R = \frac{[^{11}\mathrm{B}]}{[^{10}\mathrm{B}]} \tag{13}$$

$$^{11}A = \frac{[^{11}\mathrm{B}]}{[\mathrm{B}]} = \frac{[^{11}\mathrm{B}]}{([^{10}\mathrm{B}] + [^{11}\mathrm{B}])} \tag{14}$$

Where:

$$^{11}A = \frac{\frac{[^{11}B]}{[^{10}B]}}{\frac{[^{10}B]}{[^{10}B]} + \frac{[^{11}B]}{[^{10}B]}} = \frac{^{11}R}{1 +^{11} R} \tag{15}$$

$$^{11}R = \frac{^{11}A}{1 -^{11} A} \tag{16}$$

To avoid the slight error inherent in $\delta^{11}B$ calculations, *cbsyst* does all calculations using ^{11}A. It is possible to provide $\delta^{11}B$ values as inputs, and they are automatically provided as outputs, but all calculations use ^{11}A. When performing mixing calculations involving B isotopes, it is most appropriate to use the ^{11}A values because ratios (and by extension, delta values) do not mix linearly. The results of the mixing calculation can then be converted to $\delta^{11}B$ using one of several convenience functions, which convert between $\delta^{11}B$, ^{11}A and ^{11}R.

1.2 Approximate Isostope Systematics

These are the equations commonly used in the δ^{11}B literature, after [Zeebe and Wolf-Gladrow, 2001].

$$[^{11}\mathrm{B(OH)_3}] + [^{10}\mathrm{B(OH)_4}^-] \Leftrightarrow [^{10}\mathrm{B(OH)_3}] + [^{11}\mathrm{B(OH)_4}^-] \tag{17}$$

$$\alpha_B = \frac{[^{11}\mathrm{B(OH)_3}][^{10}\mathrm{B(OH)_4}^-]}{[^{10}\mathrm{B(OH)_3}][^{11}\mathrm{B(OH)_4}^-]} \tag{18}$$

$$\epsilon_B = 1000(\alpha_B - 1) \tag{19}$$

$$\delta^{11}\mathrm{B(OH)_4}^- = \frac{\delta^{11}B_T[B_T] - \epsilon_B[\mathrm{B(OH)_3}]}{[\mathrm{B(OH)_4}^-] + \alpha_B[\mathrm{B(OH)_3}]} \tag{20}$$

$$\delta^{11}\mathrm{B(OH)_3} = \delta^{11}\mathrm{B(OH)_4}^- - \epsilon_B \tag{21}$$

1.3 Exact Isotope Systematics

cbsyst works entirely in ^{11}A, avoiding the approximations inherent in $\delta^{11}B$. Following eqns. 17 and 18:

$$\alpha_B = \frac{\frac{[^{11}\mathrm{B(OH)_3}]}{[^{10}\mathrm{B(OH)_3}]}}{\frac{[^{11}\mathrm{B(OH)_4}^-]}{[^{10}\mathrm{B(OH)_4}^-]}} = \frac{^{11}R_{\mathrm{B(OH)_3}}}{^{11}R_{\mathrm{B(OH)_4}^-}} \tag{22}$$

Thus,

$$\alpha_b = \frac{\frac{^{11}A_{\mathrm{B(OH)_3}}}{1-^{11}A_{\mathrm{B(OH)_3}}}}{\frac{^{11}A_{\mathrm{B(OH)_4{}^-}}}{1-^{11}A_{\mathrm{B(OH)_4{}^-}}}} \tag{23}$$

$$= \frac{^{11}A_{\mathrm{B(OH)_3}}(1 -^{11} A_{\mathrm{B(OH)_4{}^-}})}{^{11}A_{\mathrm{B(OH)_4{}^-}}(1-^{11}A_{\mathrm{B(OH)_3}})} \tag{24}$$

And the ^{11}A of each species can be expressed in terms of α_B, and the ^{11}A of the other species:

$$^{11}A_{\mathrm{B(OH)_3}} = \frac{\alpha_B \ ^{11}A_{\mathrm{B(OH)_4{}^-}}}{(1 -^{11} A_{\mathrm{B(OH)_4{}^-}} + \alpha_B \ ^{11}A_{\mathrm{B(OH)_4{}^-}})} \tag{25}$$

$$^{11}A_{\mathrm{B(OH)_4{}^-}} = \frac{^{11}A_{\mathrm{B(OH)_3}}}{(\alpha_B - \alpha_B \ ^{11}A_{\mathrm{B(OH)_3}} +^{11} A_{\mathrm{B(OH)_3}})} \tag{26}$$

The total ^{11}A of a pool can be expressed as a mixture of the two species.

$$^{11}A_T = \chi \ ^{11}A_{\mathrm{B(OH)_3}} + (1-\chi)^{11}A_{\mathrm{B(OH)_4{}^-}} \tag{27}$$

And the ^{11}A of each species can be expressed in terms of $^{11}A_T$, χ and the ^{11}A of the other species:

$$^{11}A_{\mathrm{B(OH)_3}} = \frac{^{11}A_T - (1-\chi)^{11}A_{\mathrm{B(OH)_4{}^-}}}{\chi} \tag{28}$$

$$^{11}A_{\mathrm{B(OH)_4{}^-}} = \frac{^{11}A_T - \chi \ ^{11}A_{\mathrm{B(OH)_3}}}{(1-\chi)} \tag{29}$$

Equations 24 and 27 can then be solved for the ^{11}A of each species as a function of $^{11}A_T$, α_B and χ.

$$^{11}A_{\mathrm{B(OH)_3}} = \frac{(\ ^{11}A_T\alpha_B - \ ^{11}A_T + \alpha_B\chi - \chi)}{2\chi\left(\alpha_B - 1\right)} - \frac{\sqrt{\ ^{11}A_T^2\alpha_B^2 - 2\ ^{11}A_T^2\alpha_B + \ ^{11}A_T^2 - 2\ ^{11}A_T\alpha_B^2\chi + 2\ ^{11}A_T\alpha_B + 2\ ^{11}A_T\chi - 2\ ^{11}A_T + \alpha_B^2\chi^2 - 2\alpha_B\chi^2 + 2\alpha_B\chi + \chi^2 - 2\chi + 1} + 1}{2\chi\left(\alpha_B - 1\right)} \tag{30}$$

$$^{11}A_{\mathrm{B(OH)_4{}^-}} = -\frac{(\ ^{11}A_T\alpha_B - \ ^{11}A_T - \alpha_B\chi + \chi)}{2\alpha_B\chi - 2\alpha_B - 2\chi + 2} + \frac{\sqrt{\ ^{11}A_T^2\alpha_B^2 - 2\ ^{11}A_T^2\alpha_B + \ ^{11}A_T^2 - 2\ ^{11}A_T\alpha_B^2\chi + 2\ ^{11}A_T\alpha_B + 2\ ^{11}A_T\chi - 2\ ^{11}A_T + \alpha_B^2\chi^2 - 2\alpha_B\chi^2 + 2\alpha_B\chi + \chi^2 - 2\chi + 1} - 1}{2\alpha_B\chi - 2\alpha_B - 2\chi + 2} \tag{31}$$

References

Richard E Zeebe and Dieter A Wolf-Gladrow. *CO2 in seawater*. equilibrium, kinetics, isotopes. Elsevier Science, 2001.