Implications of uncertainties in equilibrium constants and analytical measurements

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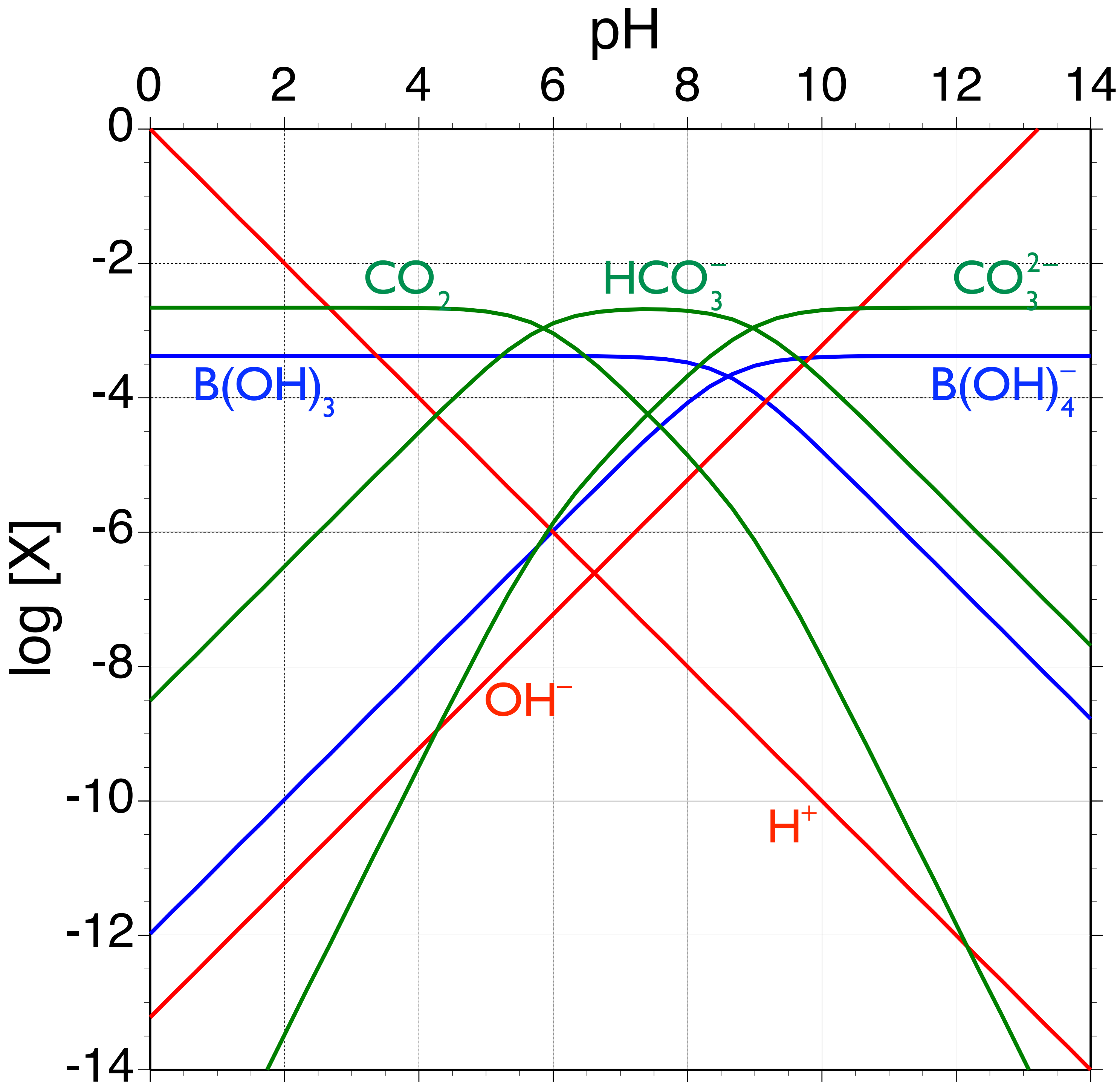
Logarithmic diagram for sea water



7 species (H_2O implicit in concentration)

4 equilibrium constants K_1, K_2, K_B, K_W are $f(T, p, S)$

total borate B_T is $f(S)$

need 2 more pieces of information

Analytical parameters of the CO_2 system

1. Total dissolved inorganic carbon

$$C_T = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

2. Hydrogen ion concentration (pH)

$$pH = -\lg [H^+]$$

3. Partial pressure of CO_2
(in solubility equilibrium with water sample)

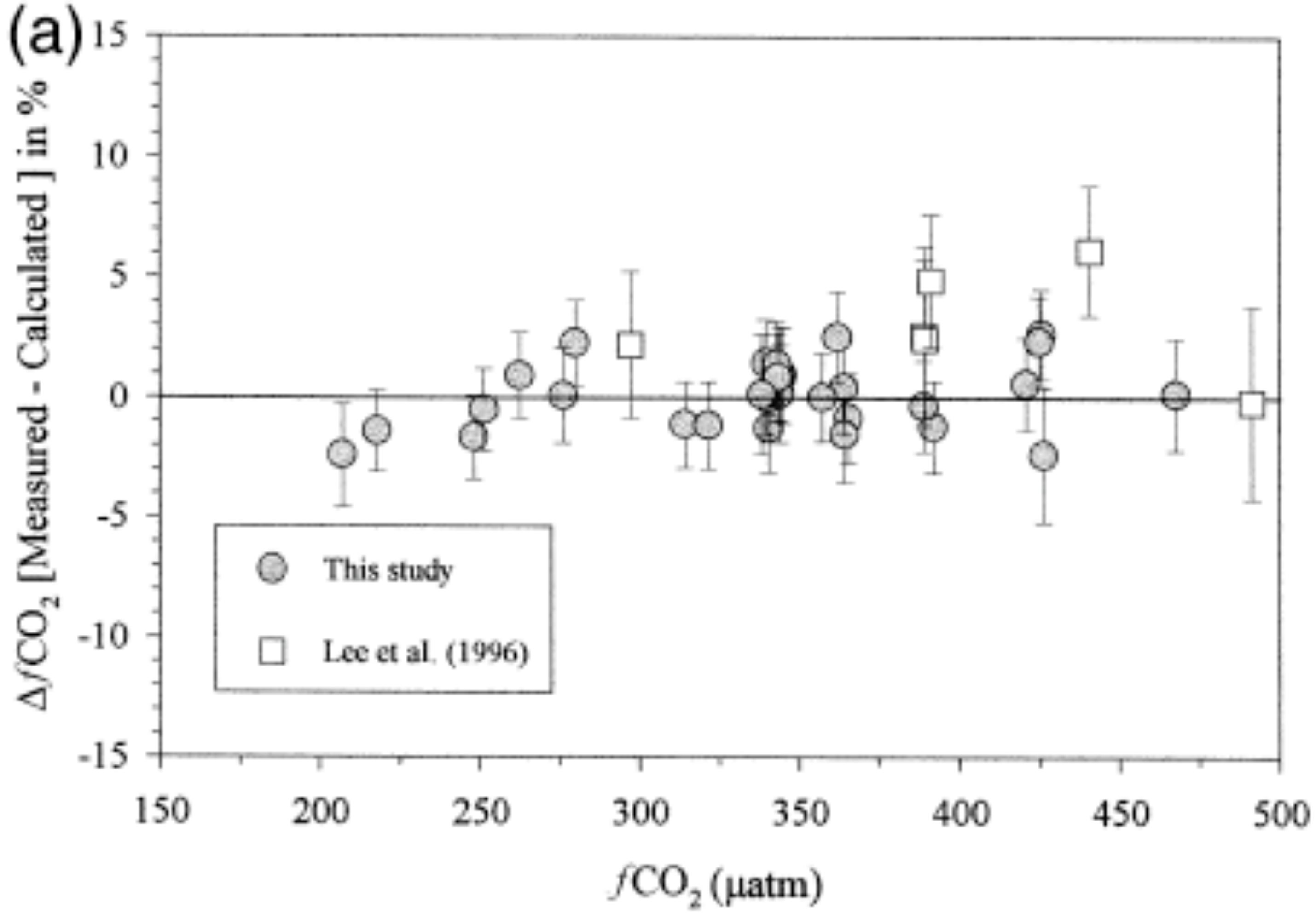
$$p(CO_2) = [CO_2] / K_0$$

4. Total alkalinity

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

Mathematically, all choices should be equivalent: in practice that is not the case. Every one of these terms is an experimental quantity with an associated uncertainty. These uncertainties propagate through the calculations resulting in uncertainties that can be associated with the various calculated values.

There are, of course, uncertainties in the measured CO_2 parameters. However, there are also uncertainties in the various equilibrium constants, and in the total concentrations of other acid-base systems such as boron.



(a) Δ*f*(CO_2) for samples under 500 µatm. The data of Lee et al. (1996) are shown with the result of this study for comparison.

Lueker *et al.* (2000)

Error propagation

combined standard uncertainty

$$u_c(y(x_1, x_2, \ldots, x_n)) = \sqrt{\sum_{i=1,n} \left(\frac{\partial y}{\partial x_i} \right)^2 u(x_i)^2}$$

(usually obtained numerically)

uncertainty in parameter x_i

Marine Chemistry, 6(1978) 77—85

THE EFFECT OF ANALYTICAL ERROR ON THE EVALUATION OF THE COMPONENTS OF THE AQUATIC CARBON-DIOXIDE SYSTEM

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(Received March 11, 1977; revision accepted August 23, 1977)

wrote error propagation expression in terms of *relative uncertainties*

$$\frac{u_c(y(x_1, x_2, \ldots, x_n))}{y} = \sqrt{\sum_{i=1,n} \left(\frac{\partial y}{y} \Big/ \frac{\partial x_i}{x_i} \right)^2 \left(\frac{u(x_i)}{x_i} \right)^2}$$

Table 2. Calculated sensitivities

II b (pH and C_T)

Derived parameters	Measured parameters					Combined resultant errors (%)	
	H	C_T	K_0	K_1	K_2	(*i*)	(*ii*)
H_2CO_3*	1.1	1.0		−0.98	−0.12	2.6	3.5
HCO_3^-	0.11	1.0		0.00	−0.12	0.6	0.8
CO_3^{2-}	−0.88	1.0		0.00	0.88	2.1	4.6
A_c	−0.10	1.0		0.00	0.09	0.6	0.7
P_{CO_2}	1.1	1.0	−0.99	−0.98	−0.12	2.6	3.5

Dickson & Riley (1978)

Estimated uncertainties†

Parameter	State-of-the-art laboratory	State-of-the-art at-sea (suitable RMs)	Other techniques (suitable RMs)	Techniques not using RMs
Total alkalinity	1.2 μmol kg^{-1}	2–3 μmol kg^{-1}	4–10 μmol kg^{-1}	?
Total carbon	1.0 μmol kg^{-1}	2–3 μmol kg^{-1}	4–10 μmol kg^{-1}	?
pH	0.003	~0.005	0.01–0.02	?
$p(CO_2)$	1.0 μatm	~2 μatm	5–10 μatm	?

† Based on surface oceanic CO_2 levels

Pair of parameters	Relative uncertainty	Reference Methods	State-of-the-art (using RMs)*	Other techniques (using RMs)
pH / A_T	$u_c([CO_2^*])/[CO_2^*]$	2.6%	2.9%	6.1–8.7%
	$u_c([CO_3^{2-}])/[CO_3^{2-}]$	3.6%	3.7%	5.1–6.5%
pH / C_T	$u_c([CO_2^*])/[CO_2^*]$	2.4%	2.6%	5.6–8.0%
	$u_c([CO_3^{2-}])/[CO_3^{2-}]$	4.1%	4.2%	5.7–7.3%
A_T / C_T	$u_c([CO_2^*])/[CO_2^*]$	4.9%	5.4%	5.8–9.3%
	$u_c([CO_3^{2-}])/[CO_3^{2-}]$	0.6%	1.7%	2.2–5.5%
pH / $p(CO_2)$	$u_c([CO_2^*])/[CO_2^*]$	0.6%	0.8%	1.5–2.9%
	$u_c([CO_3^{2-}])/[CO_3^{2-}]$	5.3%	5.7%	10.6–15.0%
A_T / $p(CO_2)$	$u_c([CO_2^*])/[CO_2^*]$	0.6%	0.8%	1.5–2.9%
	$u_c([CO_3^{2-}])/[CO_3^{2-}]$	3.3%	3.3%	3.4–3.8%
C_T / $p(CO_2)$	$u_c([CO_2^*])/[CO_2^*]$	0.6%	0.8%	1.5–2.9%
	$u_c([CO_3^{2-}])/[CO_3^{2-}]$	4.0%	4.1%	4.2–4.9%

too many sig. figs!

includes uncertainties in the constants

There is a need for:

1. A community discussion of appropriate target uncertainties for [CO_2] or [CO_3^{2-}] for ocean acidification experiments.
2. A more rigorous evaluation of the overall uncertainties of the various methods.
3. A program (like CO2SYS or seacarb) that can not only perform the calculation, but can also propagate the errors appropriately.

It will then be simpler to judge *fitness for purpose* of particular analytical methods, and to optimize the resources needed to do the CO_2 measurements required for high-quality ocean acidification studies.

Provocative opinion?

. . . , it is not – as yet – straightforward to make accurate measurements of sea water CO_2 parameters. Most of the methods require trained analysts, and in many cases equipment is not easily available. At this time, it is probably desirable for individuals studying ocean acidification to plan to work closely with a scientist with a good understanding of sea water acid-base chemistry and with access to a working laboratory that can perform the necessary measurements. Alternately, it may be practical to send samples to a central laboratory for analysis provided that such a laboratory has an appropriate quality assurance program in place, and can provide the results in a timely fashion.

need a clearer understanding of costs /benefits


WARNING
CO2