Precision and accuracy of the determination of the ionic product of hydroxy-apatite

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Keywords: hydroxy-apatite, solubility, phosphate

Abstract

The formation of hydroxy-apatite may be a major determinant of the concentration of dissolved ortho-phosphate in many natural hard fresh waters. Tests of this hypothesis require knowledge of the precision and accuracy of the calculated ionic product $[Ca^{2+}]^5 [PO_4^{3-}]^3 [OH^-]$. In routine analyses the largest contribution to overall error is probably that of pH: precision and bias better than 0.02 units are desirable. There is also a large uncertainty present in the possible bias of the third ionisation 'constant' of ortho-phosphoric acid.

Methods

The values of four variables are measured for a water sample: $[Ca^{2+}]$, pH, [total dissolved ortho-phosphate] = [o-P], and temperature. The concentration (assumed sufficiently close to the activity) of H^+ is calculated from $[H^+] = 10^{-pH}$, and $[OH^-]$ from $[OH^-] = K_W / [H^+]$, where K_W is the ionisation 'constant' of water. The concentration of dissolved ortho-phosphate is calculated from $[PO_4^{3-}] = [o\text{-}P] / \{1 + [H^+] / K_{3P} + [H^+]^2 / (K_{2P} K_{3P})\}$, where K_{2P} and K_{3P} are the second and third ionisation 'constants' of ortho-phosphoric acid. The ionisation 'constants' K_W, K_{2P}, and K_{3P} are all temperature-dependent, and K_W particularly so. The dependence of each may be represented by $K = \alpha + \beta T + \gamma / T$ where α, β, and γ define the vertical shift, slope, and curvature of the relation. Let $[Ca^{2+}]$, $[H^+]$, $[PO_4^{3-}]$ and temperature be represented by C, H, P, and T, and the ionic product of hydroxy-apatite by I. Then $I = C^5 P^3 K_W / \{H[1 + H / K_{3P} + H^2 / (K_{2P} K_{3P})]\}$, where the K's are functions of T. Let the imprecision in the four main variables be represented by their standard errors s_C, s_H, s_P, and s_T. There is also imprecision in the values of the α, β, and γ parameters of the temperature-dependent descriptions of K_W, K_{2P}, and K_{3P}. (These are parameters when estimated but become variables when used to calculate I.) The values of these nine parameters were estimated by fitting the equations for the K's minimising $[\Sigma(K - \hat{K})^2] / n \bar{K}^2$, using a simplex method (Nelder & Mead, 1965). The standard errors were estimated by a parabolic error analysis after establishing that in the region of the minimum the surface was approximately quadratic. The values of K_W and K_{2P} at different temperatures were taken from Perrin (1982), the value of K_{3P} from Ghosh *et al.* (1980). The values of K_W and K_{2P} have been measured many times and by a variety of methods, and there is close agreement among most sets of measurements. For example, pK_{2P} at 25 °C and zero ionic strength is 7.204 with standard error of 0.005 for 7 wholly independent estimates. But the variation of K_{3P} with temperature has rarely been reported. The most detailed work (Ghosh *et al.*, 1980) shows 20% increase in K_{3P} between 10 and 30 °C compared with 20% over the same temperature range for K_{1P} and K_{2P}. Less detailed measurements are given by Perrin (1982) quoting Mesmer & Baes (1974). These values show a ten-fold increase in K_{3P} between 0 and 25 °C. But it is clear from the original (Mesmer & Baes, 1974) that the values quoted in Perrin (1982) are not

Hydrobiologia 126, 31–34 (1985).

pK_{3P} and pK_{2P} but are $\log_{10} Q_1$ and $\log_{10} Q_2$, where Q_1 applies to $H_3PO_4 + OH^- \rightleftharpoons H_2PO_4^- + H_2O$ i.e. Q_1 is related inversely through K_W to K_{1P}. This leaves only one other set of data where the temperature dependence was measured: Bjerrum & Unmack (1929) made measurements at 18, 25 and 37 °C. Their pK_{3P} values are consistently higher by 0.25–0.48 than those of Ghosh *et al.* (1980). The values of K_{3P} are thus markedly fewer and more inconsistent than those of K_{2P} and K_W. The consequences of bias in the assumed values of K_{3P} are considered later.

The contributions of the thirteen components to s_I (the overall imprecision in I) may be assessed approximately by making use of the fact that for $Z = f(U, V, W, \ldots)$ and for s_U/U, s_V/V, s_W/W etc. < 0.05, then

$$s_Z^2 \simeq \left(\frac{\partial Z}{\partial U} s_U\right)^2 + \left(\frac{\partial Z}{\partial V} s_V\right)^2 + \left(\frac{\partial Z}{\partial W} s_W\right)^2 + \ldots$$

The component standard errors are weighted by the corresponding partial differentials, and the weighted components of variance are summed. This weighting amounts to recognizing that a small error in a variable along which the function value is changing rapidly – a line of steep slope – will produce a relatively large error in the function value. Details of the partial differentials are shown in the Appendix.

This analysis also assumes that the errors are independent, and this is not strictly true of the α, β, and γ for a particular K. But it should nevertheless be possible to get some idea of the size of errors which might be expected.

Results

For a fairly calcareous water, such as that in the Rhine or Rhone, with $[Ca^{2+}] = 40$ mg l^{-1}, pH = 8, $[PO_4^{3-}] = 0.1$ mg l^{-1}, and T = 10 °C, then the largest partial differentials are for β and α for K_W: on a relative scale these slopes are 98 and 1. All the other eleven slopes are $\ll 1$ (Table 1). But the standard errors in the α's, β's, and γ's are all very small. When the proportional error (s_Z/Z) in the four main variables C, H, P, and T is about 5% then the contribution to overall error from the K's is negligible. In the specific case in Table 1, for 5% proportional error in C and P, 0.02 units in pH, and 0.5 °C in T, then the contribution from C, H, P, and T are 46, 30, 17, and 4%. The K's contribute < 3% collectively to overall error, and the overall proportional error is 37%.

The 0.02 unit standard error in pH (about 5% of the mean) is probably optimistic for routine measurements. If it is actually 0.1 units the overall proportional error increases from 37 to 97%, and the contribution from H is now 90% of the total.

Next we examine a very calcareous water with $[Ca^{2+}] = 80$ mg l^{-1}, pH = 7, and P and T as in the first case. The standard errors are as before; 5% for C and P, 0.02 units for H, and 0.5 °C for T. The overall proportional error is a little larger (41%), but H now contributes substantially more (43%) of the total, even though the standard error in pH is only 0.02 units.

As might be expected from its very small partial differential, temperature has only a modest effect on the ionic product and on the overall error. Given the same values as in Table 1, except that T = 0 and T = 25 °C then $I = 1.6 \times 10^{-50}$ and $I = 2.8 \times 10^{-49}$. The overall proportional error is 37 and 36%. The relative contribution to error from the other twelve components is scarcely altered.

Discussion

This analysis has revealed the importance of precise measurement of pH for the calculation of meaningful values of the ionic product of hydroxyapatite. The analysis has explicitly concerned precision – that part of error attributable to random variation. But the real interest lies in accuracy. This can be defined in several ways. A useful one is that accuracy^2 = bias^2 + precision^2, where precision is assessed by the standard error. Accuracy can then be considered as the length of the hypotenuse of a right triangle, the other two sides of which are the bias and standard error. The same accuracy may be achieved with a small standard error and a large bias as with a large standard error and a small bias. If accuracy is defined in this way then much the same analysis can be used as for precision alone, except that in place of the standard error we now have the accuracy (which compounds standard error and bias). Much the same conclusions are reached: the overall accuracy will be acceptable only if the accu-

Table 1. Contributions to standard error of the ionic product for hydroxy-apatite in a solution, which resembles a fairly calcareous natural river water, and contains Ca^{2+} (40 mg l^{-1}), ortho-phosphate (0.1 mg l^{-1}), has pH = 8 and temperature 10 °C. The values of K_W, K_{2P} and K_{3P} at this temperature are 2.6×10^{-15}, 5.5×10^{-8} and 9.3×10^{-13} mol l^{-1}. The ionic product is 4.2×10^{-51} and the standard error in this value, using the component standard errors shown below, is 1.6×10^{-51}; the proportional error is thus 37%.

Component	Value	Units	Standard error	Relative partial differential*
Ca	1.0×10^{-3}	mol l^{-1}	5×10^{-5} (5%)	1.4×10^{-13}
o-P	3.2×10^{-6}	mol l^{-1}	1.6×10^{-5} (5%)	2.6×10^{-11}
H	1.0×10^{-8}	mol l^{-1}	4.5×10^{-10} (0.02 units)	-1.3×10^{-8}
$^{+}T' = T + 80$	90	+	0.5 °C	4.4×10^{-17}
$^{+}\alpha$	-3.01×10^{-13}	mol l^{-1}	1.1×10^{-17}	0.011
β K_W	1.84×10^{-15}	mol l^{-1} °C^{-1}	6.0×10^{-19}	0.98
γ	1.24×10^{-11}	mol l^{-1} °C	5.6×10^{-15}	0.00012
α	6.40×10^{-9}		2.1×10^{-10}	2.4×10^{-10}
β K_{2P}	5.45×10^{-10}		1.9×10^{-12}	2.1×10^{-8}
γ	-3.01×10^{-8}	as for K_W	3.6×10^{-8}	2.6×10^{-12}
α	1.10×10^{-13}		6.5×10^{-15}	9.1×10^{-5}
β K_{3P}	9.54×10^{-15}		6.5×10^{-17}	0.0082
γ	-3.62×10^{-12}		1.3×10^{-12}	1.0×10^{-6}

* Component partial differential / Σ| partial differentials|

\+ In the relation $K = \alpha + \beta T' + \gamma / T'$, where $T' = T + 80$ (°C). This avoids attempts at division by zero, and improves the precision of estimation of the γ parameters. Valid for the range 0–30 °C.

racy of pH measurement is better than 0.02 units. If bias and precision are equal then both should be at most $0.02/\sqrt{2} = 0.014$ units. The accuracy analysis differs from that of precision alone, however, in that the published values of K_{3P} may be discordant, so there may be substantial bias in those used, increasing with temperature difference from 10 °C. The sort of effects to be expected were investigated by increasing the inaccuracy (equivalent to standard error in the earlier analyses) in the slope determining parameter (β for K_{3P}) first to the same value as the slope (1.0×10^{-14} mol l^{-1} °C^{-1}), and then to ten times the slope (1.0×10^{-13}). This last value reflects the possible bias if K_{3P} is actually strongly temperature-dependent. The other values were those in Table 1. The ionic product is not affected, of course. The overall proportional inaccuracy becomes 47 and 290%, and the contribution of β for K_{3P} is 38 and 98% of the total.

If K_{3P} *is* strongly temperature dependent and a different temperature is used, then the value of the ionic product is much affected too. At 25 °C the more temperature-dependent set of values of K_{3P} gives a thousand-fold smaller value of I than that given by the less temperature-dependent set of values. This corresponds to pI three units larger. This is a substantial difference, and much larger than the *standard error* in measured values in the Rhine and Rhone (Golterman & Meyer, 1985).

It is unfortunate that *demonstrably* unbiased measurements of K_{3P} – i.e. a minimum of two independent sets of measurements, made by totally different methods and preferably by different workers, and which have little difference between them – do not exist at present. Until they do the accuracy of determination of the ionic product of hydroxy-apatite remains in doubt. Once this uncertainty is removed then accuracy is dominated in routine measurements by imprecision and bias in the measurement of pH.

Appendix

The equation for the ionic product of hydroxy-apatite, I, may be written

$$I = C^5 P^3 K_W / \{H^{1/3} + H^{4/3} / K_{3P} + H^{7/3} / (K_{2P} K_{3P})\}^3$$

For convenience, let

$$X = H^{4/3} / K_{3P} \qquad Y = H^{7/3} / (K_{2P}\, K_{3P})$$
$$Q = H^{1/3} + X + Y \qquad R = C^5\, P^3\, K_W$$
$$U = K_W / Q^3 \qquad K_W = \alpha_W + \beta_W\, T + \gamma_W / T$$
$$V = C^5\, P^3 / Q^3 \qquad K_2 = \alpha_2 + \beta_2\, T + \gamma_2 / T$$
$$W = 3\, R / Q^4 \qquad K_3 = \alpha_3 + \beta_3\, T + \gamma_3 / T$$

The partial differentials (used as weights) are then

$$\partial I / \partial C = 5\, C^4\, P^3\, U \qquad \partial I / \partial P = 3\, C^5\, P^2\, U$$
$$\partial I / \partial H = -W \{1 / 3\, H^{2/3} + 4\, H^{1/3} / 3\, K_{3P} + 7\, H^{4/3} / 3\, K_{2P}\, K_{3P}\}$$
$$\partial I / \partial T = V\,(\beta_W - \gamma_W / T^2) + W\, \{[X(\beta_3 - \gamma_3) / T^2\,] / K_{3P} + Y / (K_{2P}\, K_{3P})$$
$$[2\, \beta_2\, \beta_3\, T + \alpha_2\, \beta_3 + \beta_2\, \alpha_3 - (\alpha_2\, \gamma_3 + \gamma_2\, \alpha_3) / T^3 - 2\, \gamma_2\, \gamma_3 / T^3]\}$$

$$\partial I / \partial \alpha_W = V \qquad \partial I / \partial \beta_W = V\, T \qquad \partial I / \partial \gamma_W = V / T$$
$$\partial I / \partial \alpha_2 = A = W\, Y / K_{2P} \qquad \partial I / \partial \beta_2 = A\, T \qquad \partial I / \partial \gamma_2 = A / T$$
$$\partial I / \partial \alpha_3 = B = W\, (X + Y) / K_{3P} \qquad \partial I / \partial \beta_3 = B\, T \qquad \partial I / \partial \gamma_3 = B / T$$

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