Carbon Dioxide Partial Pressure in the Columbia River

Abstract. *Columbia River water is supersaturated with respect to atmospheric carbon dioxide by 200 to 870 parts per million. An equilibrium exists between the carbon dioxide partial pressure and* pH, *and Henry's law is obeyed in this natural water. The carbon dioxide pressure can be calculated by a determination of the* pH, *total carbon dioxide, and temperature.*

On 14 December 1968 the R.V. *Yaquina* of Oregon State University carried a recording infrared gas analyzer down the Willamette and Columbia rivers, from Portland to Astoria, Oregon (Fig. 1). The river water had high CO_2 pressure, 200 to 870 parts per million above that of the atmosphere. Concurrent determinations of *p*H, total CO_2, alkalinity, and temperature show that an equilibrium exists between the CO_2 pressure and *p*H. The Columbia River water obeys Henry's law.

We monitored the CO_2 pressure and other chemical parameters in the river water continuously at a depth of 2.5 m with an equilibrator system (*1*). Atmospheric CO_2 was measured intermittently; it was 341 ppm at Portland and 325 ppm at Astoria.

The Willamette River exhibited a CO_2 pressure of 1200 ppm and a *p*H of 7.12 measured at a river temperature of 7.40°C. Its alkalinity was 0.38 meq/liter, and the total CO_2 concentration was 0.38 mmole/liter. In the main stream of the Columbia River, the CO_2 pressure ranged from 541 to 981 ppm and the *p*H varied from 7.54 to 7.99 at river temperatures from 7.03° to 7.65°C. The alkalinity of the main stream of the Columbia River ranged from 0.70 to 1.09 meq/liter, and its total CO_2 concentration varied from 0.73 to 1.14 mmole/liter.

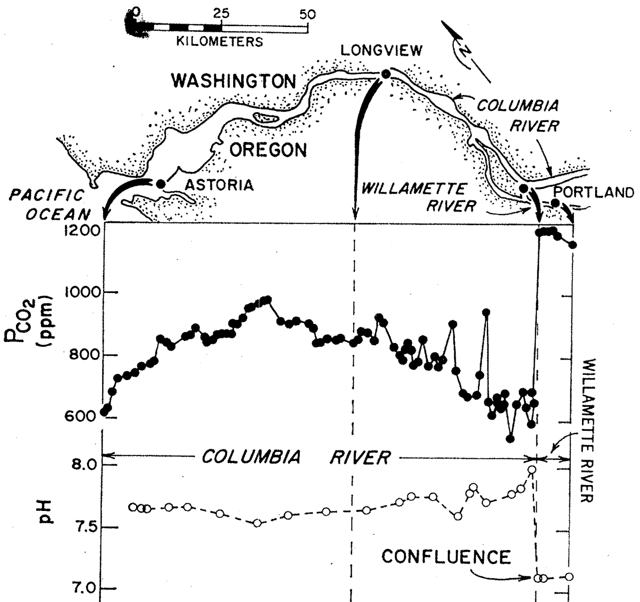
We can construct an equation relating the partial pressure and *p*H as follows:

$$P_{CO_2} = \frac{\gamma_1\gamma_2[H]^2\Sigma[CO_2]}{\alpha(\gamma_1\gamma_2[H]^2 + \gamma_2[H]K_1 + \gamma_1 K_1 K_2)} \qquad (1)$$

where P_{CO_2} is the CO_2 partial pressure, α is the solubility coefficient of CO_2 (*2*), [H] is the hydrogen ion activity as measured by a *p*H meter, and $\Sigma[CO_2]$ is the total CO_2 concentration defined as the sum of the stoichiometric concentrations of CO_2 (including H_2CO_3), and bicarbonate and carbonate ions. The terms γ_1 and γ_2 are the activity coefficients of bicarbonate and carbonate ions, respectively (*3*). The first and second thermodynamic dissociation constants of carbonic acid (*4*) are expressed as K_1 and K_2, respectively. We assume here that the activity coefficient of undissociated CO_2 is unity. Equation 1 is derived from Henry's law ($M_{CO_2} = \alpha P_{CO_2}$, where M is the molality), the equations for the first and second dissociations of carbonic acid, and the definition of the total concentration of CO_2 (*5*).

In order to obtain a representative relation between the CO_2 pressure and *p*H for the main stream, we used in Eq. 1 an average value for the total CO_2 concentration of 0.89 mmole/liter. The calculated relationship is shown by the upper curve in Fig. 2. Our field data are in agreement with the theoretical relation. When we use individual data for total CO_2, we obtain a relative precision of ± 5 percent for estimates of the CO_2 pressure by Eq. 1. Similarly, the theoretical relation between the CO_2 pressure and *p*H for the Willamette River is shown by the lower curve in Fig. 2. Our field data are in good agreement with the theory, which substantiates the applicability of Henry's law to the Columbia River water.

The *p*H value at which the river water is in equilibrium with an uncontaminated atmospheric CO_2 concentra-



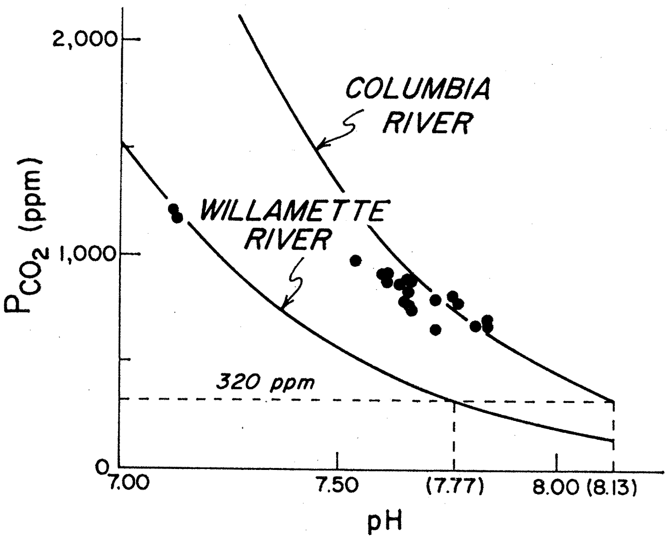


Fig. 1 (left). Partial pressure of CO_2 (filled circles) and *p*H distribution (open circles) in the Columbia River system, from Portland to Astoria, Oregon. R.V. *Yaquina* left Portland at 7:33 and arrived in Astoria at 14:10 P.S.T., 14 December 1968. There is a sudden change in the CO_2 pressure and *p*H at the confluence of the Willamette River and the main stream of the Columbia River. The two CO_2 pressure maxima just below the confluence represent the patches of tributary waters, which include the Willamette River, not yet mixed thoroughly with the main stream. Fig. 2 (right). Relation between CO_2 partial pressure and *p*H in the Columbia River and Willamette River. The theoretical relation, shown by the solid lines, is obtained by the use of a total CO_2 concentration of 0.89 and 0.38 mmole/liter for the Columbia River and the Willamette River, respectively, in Eq. 1. The equilibration *p*H with respect to the atmospheric CO_2 concentration of 320 ppm is 7.77 in the Willamette River and 8.13 in the Columbia River.

tion of 320 ppm (*6*) would be 7.77 in the Willamette River and 8.13 in the Columbia River (Fig. 2). Our observed *p*H values are over 0.3 unit less than the equilibrium *p*H.

The CO_2 pressure we monitored in the river is much higher than that in the atmosphere. This is contrary to the simple supposition that any flowing water would equilibrate rapidly with the atmosphere. Furthermore, any appreciable concentration of carbonic anhydrase in water also would facilitate rapid equilibration (*7*). The oversaturation we observed must be maintained by the combined net effect of the high concentration of CO_2 in source water such as soil water, biochemical oxidation *in situ*, and the rate of escape of CO_2 from the river to the atmosphere.

This study demonstrates that it is possible to calculate within a precision of ± 5 percent the CO_2 pressure in river water by measurements of *p*H, total CO_2, and temperature. Confining the method to these measurements involves less expensive equipment than the infrared analyzer and would be adequate for many purposes.

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References and Notes

1. C. D. Keeling, N. W. Rakestraw, L. S. Waterman, *J. Geophys. Res.* **70**, 6087 (1965). L. I. Gordon (thesis, Oregon State University, in preparation) describes the detailed analytical procedure for the measurement of CO_2 pressure. Since the CO_2 equilibrator system we used maintains the temperature *in situ*, no temperature correction is necessary for the determination of the CO_2 concentration. Other analytical techniques we used are given → P. K. Park, G. R. Webster, R. Yamamoto, *Limnol. Oceanogr.* **14**, 559 (1969).
2. H. S. Harned and R. Davis, Jr., *J. Amer. Chem. Soc.* **65**, 2030 (1943).
3. R. M. Garrels and C. L. Christ [*Solutions, Minerals, and Equilibria* (Harper & Row, New York, 1965)] describe in detail the way to obtain the activity coefficients for bicarbonate and carbonate ions by the use of the Debye-Hückel equation. Our estimation for the ionic strengths yielded 0.0015 for the main stream of the Columbia River and 0.0007 for the Willamette River. The activity coefficients we obtained were 0.96 and 0.85 for bicarbonate and carbonate ions, respectively, in the main stream, and 0.97 and 0.89 for bicarbonate and carbonate ions, respectively, in the Willamette River.
4. R. M. Garrels and C. L. Christ (*3*) tabulated K_1 and K_2 as a function of temperature. We used 3.16×10^{-7} for K_1 and 2.95×10^{-11} for K_2 in Eq. 1.

→ P. K. Park, *Limnol. Oceanogr.* **14**, 179 (1969).

6. J. C. Pales and C. D. Keeling [*J. Geophys. Res.* **70**, 6053 (1965)] reported that the 1963 average atmospheric CO_2 concentration at Mauna Loa Observatory in Hawaii was 315.8 ppm. They also showed that the rate of increase of atmospheric CO_2 during the period from 1959 to 1963 was 0.68 ppm/year. Therefore, the 1969 atmospheric CO_2 concentration is extrapolated to 320 ppm.
7. R. Berger and W. F. Libby, *Science* **164**, 1395 (1969).

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Graywacke Matrix Minerals: Hydrothermal Reactions with Columbia River Sediments

Abstract. *Experiments with sands chemically similar to graywackes produced "matrix" minerals at 250°C and a water pressure of 1 kilobar. Starting materials were moderately well sorted sands containing abundant volcanic rock fragments and no detectable clay minerals. The results support the concept that graywacke matrix may form diagenetically by hydration and recrystallization of unstable clasts. Matrix need not be a recrystallized detrial fine fraction. Texture, therefore, is not a reliable criterion for sandstone classification. For graywackes, chemical composition may be more significant.*

Whetten (*1*) demonstrated the similarity in mineral and chemical composition between sediments from the bed of the Columbia River and typical graywackes, in spite of the fact that Columbia River sediments are, in general, much better sorted for size than graywackes. He concluded that "sediments from the Columbia River could be used in an attempt to produce a graywacke in the laboratory" and thereby to test Cummins' hypothesis (*2*) that graywacke texture is postdepositional in origin, occurring when chemically unstable grains are hydrated and recrystallized to form matrix during weathering, deep burial, or low-grade metaphorism. Accordingly, we now report a series of hydrothermal experiments.

We used three typical samples of Columbia River sediments as starting materials to test the feasibility of forming graywacke matrix minerals in hydrous environments at elevated temperatures and pressures. The results of the experiments indicate that phyllosilicates and zeolites (matrix minerals) form readily under conditions equivalent to burial at 3 to 4 km and geothermal gradients of 60 to 80°C/km.

The original samples are moderately well sorted sands composed of quartz, labradorite, clinopyroxene, orthopyroxene, hornblende, biotite, muscovite, opaques, volcanic glass, and volcanic clasts of basaltic and andesitic compositions. Clay minerals are present only in small quantities; they are not detectable by x-ray diffraction unless they are concentrated from large volumes of sediment. Montmorillonite is the most abundant clay mineral in sediments from the section of the river where the samples were obtained (*3*). Chemical analyses of the samples and a comparison wtih typical eugeosynclinal graywackes of the Pacific rim are presented in Table 1.

The sediment samples were ground to −200 mesh in an alumina mortar. Charges were prepared by placing 0.100 g of ground sample plus 0.10 ml of fluid (either double-distilled water or an artificial seawater solution) in annealed silver tubes. The tubes were crimped flat to remove most of the air and were welded. The sealed tubes were heated externally in cold-seal stainless steel rod bombs by resistance furnaces. Both internal bomb pressure and external bomb temperature were monitored during the experiments; temperature variation was less than ± 12°C, and pressure variation was less than ± 300 pounds per square inch (approximately ± 20 bars). Charges were weighed before and after the experiments to check for possible gain or loss of material. Experiments were made at 1 kb $P_{\mathrm{H_2O}}$ and at temperatures of 150°, 250°, and 300°C. The experiments lasted from 21 to 60 days.

Reaction products were analyzed by comparison of x-ray diffraction patterns of approximately equal weights of heated and original samples mounted on ceramic tile by the suction technique (*4*). Clay mineral groups were identified by glycolation and heating tests. Clinoptilolite was distinguished from heulandite by Mumpton's method (*5*). The tentative identification of riebeckite was based on comparison of reaction products with three distinctive peaks [(110), (040), (310)] given in the American Society for Testing and Materials diffraction data. Curiously, the (110) peak disappeared when the sample was heated to 550°C in the open atmosphere during a test for clay minerals. Plagioclase compositions were determined by spacings of (131) and $(1\bar{3}1)$ diffractogram peaks (*6*). At least some of the glass in the original sample was retained in products of the experiment