cus, (ii) the romeriid-pelycosaur assemblage, (iii) the Limnoscelidae, and (iv) the Diadectomorpha (*14*) (Fig. 3). Despite the presence of an otic notch in the Port Hood specimen, the proportions of its skull table and the configuration of the atlas and axis vertebrae show closest resemblance to the Limnoscelidae. *Romeriscus* differs from the later (and larger) members of this family in lacking swollen neural arches. Expanded arches, however, are a functional adaptation to be expected in large forms and could easily have evolved from the condition seen in *Romeriscus*. The configuration of the otic region in *Limnoscelis* suggests that the notch had only recently been closed and might well have been open in early Pennsylvanian predecessors.

In having nonswollen neural arches and paired postparietals, *Romeriscus* is more similar to other early captorhinomorphs than are the later limnoscelids. Despite these similarities, it is unlikely that *Romeriscus* itself could have been ancestral to the other captorhinomorph families, the Romeriidae and the Captorhinidae. At least one morphological peculiarity of the limnoscelids, the considerable expansion of the rib heads, is already evident in *Romeriscus*, which indicates some specialization away from the presumably primitive pattern that is retained in the other captorhinomorph families.

By Westphalian B time, not only romeriid captorhinomorphs but also pelycosaurs had evolved. These two groups show close affinities and in all probability the features in which they are advanced over limnoscelids had been achieved by an immediate common ancestor that was already distinct from *Romeriscus*. We must therefore assume that limnoscelids and more advanced captorhinomorphs had a yet earlier common ancestor. Such an ancestral form, of late Mississippian or earliest Pennsylvanian age, may have been similar to *Romeriscus* in its general morphology.

The precise relationship of this postulated reptile-ancestor to the amphibians is still not clear. Retention of an otic notch by *Romeriscus* points to an ancestry among the anthracosaurian labyrinthodonts. There are, however, no anthracosaurs—either contemporary with *Romeriscus* or from earlier beds—that appear to be at all close to the ancestry of reptiles. The seymouriamorphs are usually considered as relicts of such a group, but the Permian genera (none are definitely known from the Carboniferous) are too specialized and too late in time to contribute much to our understanding of reptile-ancestors that must have existed in the Mississippian.

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21 April 1967

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High-Pressure Dissociation of Carbonic and Boric Acids in Seawater

Abstract. *The apparent dissociation constants of carbonic and boric acids were determined for pressures up to 654 atmospheres in seawater of 34.8 per mille salinity at 22°C. Our values for the ratios of the apparent dissociation constants at 654 atmospheres to the constants at 1 atmosphere are 1.84 1.48, and 1.94 for* K'_1, K'_2, *and* K'_B, *respectively. At this pressure the commonly accepted values of Buch and Gripenberg for these ratios are 2.03 and 1.30 for* K'_1 *and* K'_2, *respectively.*

The apparent dissociation constants of carbonic and boric acids at high pressures are needed to determine the effect of pressure on the *p*H and on the distribution of carbonate species in seawater.

Lyman (*1*) defined these constants as $K'_1 = a_H(HCO_3^-)/(H_2CO_3)$, $K'_2 = a_H(CO_3^=)/(HCO_3^-)$, and $K'_B = a_H(H_2BO_3^-)/(H_3BO_3)$, where the parentheses represent molal concentrations, and (H_2CO_3) is the sum of the concentrations of carbon dioxide and carbonic acid.

Brander (*2*) determined the first dissociation constant of carbonic acid and the dissociation constant of acetic acid as a function of pressure in distilled water at 20°C. To calculate the effect of pressure on the *p*H and on the distribution of carbonate species in seawater, Buch and Gripenberg (*3*) applied Brander's (*2*) pressure coefficient for carbonic acid to K'_1, and his coefficient for acetic acid to K'_2. Pytkowicz (*4*) suggested the need to verify these pressure coefficients, because they depend on ion-pair formation and on partial molal volumes, both of which vary with the pressure, temperature, and composition of the medium. Further, in their calculation of the effect of pressure on *p*H, Buch and Gripenberg (*3*) did not consider the effect of boric acid. Disteche and Disteche (*5*) recently reported values for the pressure coefficients of the apparent dissociation constants of carbonic acid in seawater at 1000 atm and 22°C.

Our determination of the effect of pressure on K'_1, K'_2, and K'_B was based on *p*H measurements at high pressures. The following cell, which is essentially that of Disteche (*6*), was used to measure *p*H:

$$\text{Ag; AgCl, SW}_e \parallel \text{Glass} \parallel \text{SW}_i\text{, AgCl; Ag} \qquad (1)$$

The seawater in the external compartment, SW_e, had a salinity of 34.8 per mille and was prepared by the formula of Lyman and Fleming (*7*), with the following exceptions: KCl was substituted for KBr; boric acid was omitted in the determination of the effect of pressure on K'_1 and K'_2; and in the boric acid experiments the total boron was increased to 3 mmole/liter, $NaHCO_3$ was omitted, and 1.25 mmole of Na_2CO_3 per liter was added. The

Table 1. Comparison of our pressure coefficients and those of Buch and Gripenberg (*3*).

P	K'_1		K'_2		K'_B
(atm)	This work	B & G	This work	B & G	This work
1	1.00	1.00	1.00	1.00	1.00
221	1.24 ±0.02	1.27	1.14 ±0.01	1.09	1.25 ±0.01
437	1.52 ±0.03	1.60	1.30 ±0.02	1.19	1.55 ±0.01
654	1.84 ±0.04	2.03	1.48 ±0.02	1.30	1.94 ±0.01

reference seawater, SW_i, was similar to that outside except that it was made 0.1*N* in HCl by replacing an equivalent amount of NaCl with HCl.

The electrode assembly is shown in Fig. 1. Before each pressure run the *p*H of the seawater sample was measured with a Beckman combination glass electrode (No. 39142). The high-pressure electrode was then inserted into the sample, and the electrode assembly placed in a pressure vessel similar to that described by ZoBell and Oppenheimer (*8*). Pressure was transmitted to the cell through the rubber stoppers. Temperature was maintained at 22.00° ± 0.05°C. The electrode output was measured by a potentiometric circuit consisting of a Leeds and Northrup type K-3 potentiometer with a Cary model 31 vibrating-reed electrometer used as a null detector.

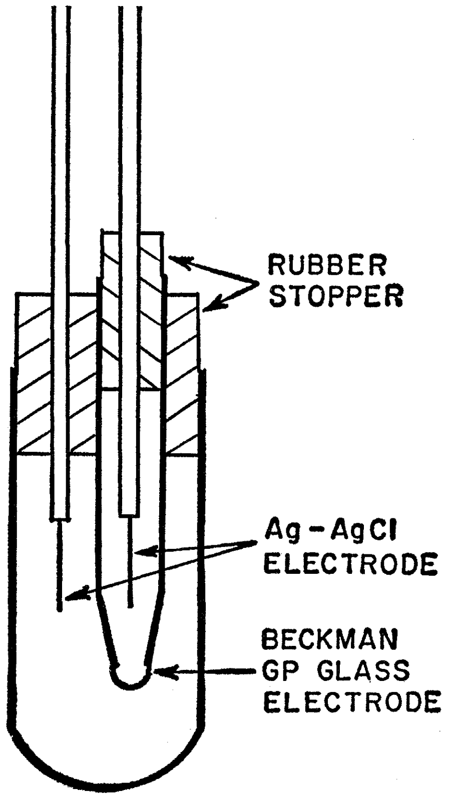

Fig. 1. The high-pressure *p*H cell.

The electromotive force of cell 1 at any pressure is

$$E = S \cdot \log(a_H a_{Cl})_i - S \cdot \log(a_H a_{Cl})_e + E_{asym} \quad (2)$$

where E_{asym} is the asymmetry potential and *S* is the slope of the glass electrode response, theoretically equal to 2.3 RT/F.

The change $E_P - E_1$ in the electromotive force of cell 1 with pressure is

$$E_P - E_1 = S \cdot \log[(a_{H_P}/a_{H_1})_i \times (a_{H_1}/a_{H_P})_e] + S \cdot \log[(a_{Cl_P}/a_{Cl_1})_i \times (a_{Cl_1}/a_{Cl_P})_e] + \Delta E_{asym} \quad (3)$$

where the subscripts *i* and *e* refer to the compartments inside and outside the glass electrode. The difference in asymmetry potential with pressure, ΔE_{asym}, is obtained from the electromotive force dependence with pressure when both compartments are filled with reference solution.

Disteche (*6*) has shown that the slope of the glass electrode response is independent of pressure. Therefore, the value of *S* determined at atmospheric pressure can be used at any pressure.

If the environment of chloride ion is similar inside and outside the glass electrode, Eq. 3 may be simplified because $(a_{Cl_P}/a_{Cl_1})_i = (a_{Cl_P}/a_{Cl_1})_e$. According to Harned and Owen (*9*) the mean ionic activity coefficient of HCl varies by less than 1.5 percent over a range of 650 atm of pressure. Thus, $(a_{H_P}/a_{H_1})_i$ is almost 1. With these assumptions, Eq. 3 may be written,

$$pH_P = pH_1 + (1/S)(E_P - E_1 - \Delta E_{asym}) \quad (4)$$

Equation 4 was used to calculate the *p*H at pressure pH_P from the *p*H measured at 1 atm. Part of the pressure effect on the electromotive force was due to the dissociation of HSO_{4-} in the reference compartment. We corrected for this effect by adding to Eq. 3 the electromotive force obtained with a sulfate-free reference solution (0.71*M* NaCl + 0.01*M* HCl) in the inner compartment and the original reference solution in the external compartment. This correction was linear with pressure and amounted to −0.72 mv at 654 atm.

Table 2. Comparison of the effect of increase in pressure on *p*H calculated in this report and by Buch and Gripenberg (*3*).

Values of	Δ *p*H/Δ 100 atm at surface *p*H:		
	7.4	7.8	8.2
B & G	−0.038	−0.024	−0.018
This work	−0.037	−0.034	−0.032

The apparent dissociation constants, $(K'_1)_P$ and $(K'_2)_P$, at pressure *P*, were determined in borate-free seawater by use of the following equation first derived by Buch and Gripenberg (*3*):

$$(a_{H_P})^2 - (A - 1)(K'_1)_P(a_{H_P}) - (2A - 1)(K'_1)_P(K'_2)_P = 0 \quad (5)$$

A is the ratio of the total inorganic carbon [$T(CO_2) = (H_2CO_3) + (HCO_3^-) + (CO_3^=)$] to the carbonate alkalinity [$CA = (HCO_3^-) + 2(CO_3^=)$]. Buch and Gripenberg (*3*) showed that for a system containing only carbonic acid, *A* is constant with pressure.

In our calculations *A* was obtained from Eq. 5 at 1 atm. For each seawater sample pH_1 was measured, $(K'_1)_1$ and $(K'_2)_1$ were known from Lyman's (*1*) work, and *A* could be calculated.

Determinations of *p*H at pressure were made on pairs of seawater samples that had different carbonate alkalinities and, therefore, different values of a_H and *A*. When substituted into Eq. 5 these values provided two simultaneous equations that could be solved for the two unknowns $(K'_1)_P$ and $(K'_2)_P$.

The apparent dissociation constant of boric acid (K'_B) was calculated from the equation

$$T(CO_2)/T(B) = \{[TA/T(B)] - [(K'_B)/(K'_B + a_H)]\} \times [(a_H^2 + a_H K'_1 + K'_1 K'_2)/(a_H K'_1 + 2K'_1 K'_2)] \quad (6)$$

where T(B) is equal to $(H_3B_3O) + (H_2BO_3^-)$ and TA is equal to $(HCO_3^-) + 2(CO_3^=) + (H_2BO_3^-) + (OH^- - H^+)$. Since $T(CO_2)$, T(B), and TA are unaffected by pressure, the ratios $T(CO_2)/T(B)$ and TA/T(B) are constant with pressure. For each sample, $T(CO_2)/T(B)$ was calculated at atmospheric pressure with measured values of T(B), TA, and a_H, and Lyman's (*1*) values of K'_1, K'_2, and K'_B. The *p*H at pressure was then measured, and $(K'_B)_P$ was calculated with the previously obtained values of $(K'_1)_P$ and $(K'_2)_P$.

Our results are given in Table 1 in the form of pressure coefficients, that is, the ratio of the apparent constant at pressure *P*, $(K')_P$, to the constant at atmospheric pressure, $(K')_1$. Each value is the average of three determinations and is given with the average deviation from the mean. Our results indicate that Buch and Gripenberg's (*3*) values for the pressure coefficient of K'_2 are too small, and that the dissociation of boric acid must be considered when studying the effect of pressure on the *p*H of seawater (*10*).

In Table 2 we have computed the effect of pressure on *p*H for a seawater with T(B) = 0.437 m*M* per kilogram of H_2O and TA = 2.57 meq per kilogram of H_2O. The *p*H decrease is linear with pressure and does not vary significantly with the variations in TA that occur in the ocean.

The main differences between our *p*H shifts and those calculated by Buch and Gripenberg (*3*) are due to the dissociation of boric acid under pressure, and to the fact that the effect of pressure on K'_2 is larger than Buch and Gripenberg estimated.

It is possible to use our measurements of the pressure coefficients at 22°C, in conjunction with Lyman's (*1*) values of the apparent dissociation constants at 1 atm and 2°C, to process oceanic data. However, we are presently measuring the pressure coefficients of carbonic and boric acids in seawater at low temperatures, and we feel that it would be best not to apply a pressure correction to deep-sea *p*H data until the temperature effect is known.

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11. A. Disteche offered valuable advice throughout this research. This work was supported by NSF grant GA-301.

13 April 1967; revised 22 May 1967

Tektites That Were Partially Plastic after Completion of Surface Sculpturing

Abstract. *Among the 50,000 tektites collected over an 8-year period as part of a representative collection of the indochinities in an area near Dalat, South Vietnam, several individual ones have been found that show evidence of having been internally plastic after surface sculpturing was essentially completed. Two drops, which were bent after having formed a thin exterior skin or crust, exhibit surface breaks and stretching of their plastic interiors within the breaks. The lack of deep sculpturing in this interior stretched area, coupled with twisting within the break on one of them, indicates that the surface features on these tektites were formed in the atmosphere and not by etching by soil acids, as had been widely believed.*

The external features of tektites from southeast Asia have generally been considered to be the result of deep etching by soil acids. Evidence found in the surface features of several indochinites from an area near Dalat, South Vietnam, now indicates that this concept may be in error and that the general surface features are the result of aerial ablation. This evidence was discovered during the examination of field collections, totaling 50,000 specimens, made during an 8-year period beginning in 1958.

In inspecting the first 40,000 specimens, many shapes were found that indicated stretching: elongate drops, rods and straps that appeared to represent portions of the tails of drops that had been elongated to perhaps 6 inches (15 cm) or more, dumbbells, and discoidal shapes that showed whirlpool or swirling effects that had resulted from spinning. A large percentage of the elongate specimens also showed twisting and bending. Sixty-six percent of all specimens showed breakage, and an even larger percentage showed spalling. However, it was only during examination of the next 10,000 specimens that the full significance of these forms began to be realized.

As long ago as 1900, Suess (*1*) concluded that the surface sculpturing of tektites was due to aerial ablation and was "not due to some sort of corrosion process," because corrosion causes a matte appearance that is lacking on the surfaces of most tektites and that fails to account for the grooves and cupules found on tektite surfaces. Most students of the subject disagreed with this hypothesis, insisting that the present surfaces of tektites, particularly those of indochinites, were the result of deep etching by acids in soil.

Serious difficulties for the theory of attack by ground chemicals come from a study of the broken indochinites. Many indochinites have flattish surfaces that cut sharply across the rounded surfaces that seem to be part of the original shape, and these flattish surfaces are logically interpreted as breakage surfaces. The degree of pitting and sculpturing is much less on the broken surfaces than it is on the rounder original surfaces. In terms of the theory of attack by ground acids, this clearly implied that breakage had taken place after more than half the life of the tektites on the ground and that it had occurred simultaneously throughout the area strewn with indochinites. It was suggested (*2*) that this breakage might have resulted from an enormous tidal wave.

Doubts about these solutions to the problem were enhanced by the discovery of a number of onion-shaped tektites (Fig. 1) that look as though they had encountered either the surface of the ground or else the denser layers of the atmosphere while still in a molten condition.

The really decisive evidence was furnished, however, by two tektites (Fig. 2) that seem to have suffered sharp bending while the interior was still plastic. The exteriors of these had actually broken. Close inspection showed that breakage had occurred after cooling from the outside had produced a thin skin or crust over a plastic interior. The broken skin of the tektites had pulled apart, much as the skin of a cut finger would, while the plastic interior stretched but did not break. Thus, we conclude that although more than two-thirds of the indochinites were broken after more or less complete cooling had taken place, not all of them were cold rigid bodies at this point.

The internal plasticity of these tektites this late in flight is explained by the conclusion that tektites did not arrive at the earth's atmosphere as a