

involved, and they may even have been important in the formation of the parallel longitudinal grooves on the landslide surface and the narrow flow-like lobes at its western edge. Air as the primary lubricant, however, accounts more simply for the pronounced terminal increase in friction suggested by some of the other features of the landslide. Leakage of air from beneath the flanks of the leading edge, for example, being unopposed by the forward motion of the landslide, would very quickly permit the margin to settle to the glacier surface and stop, forming the lateral ridges, which would channel the sliding debris and hinder further leakage. Similarly, the slower but inevitable loss of air at the leading edge would ultimately allow it to hit the surface, causing the debris behind to pile up. Initially this would occur at overwidened longitudinal grooves, forming the debris buttresses, which would split the sliding mass into multiple minor lobes; but eventually it would occur over the whole leading edge, forming the distal rim. Finally, the progressive thinning of the air layer at the rear of the landslide, as ever more air is dragged forward by the sliding debris, would cause widespread zones of impact to form and propagate forward, producing the swarms of successive transverse tension fissures. Thus, although direct evidence is lacking, the circumstantial evidence strongly supports the hypothesis of air-layer lubrication for the Sherman landslide.

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8. Supported by the American Geographical Society. I thank W. O. Field, American Geo-

graphical Society, for the necessary administrative arrangements and for photographs and other information; S. J. Tuthill, Muskingum College, Ohio, for use of base camp and helicopter (National Science Foundation grant GP 4424); and G. Plafker and A. Post, U.S. Geological Survey, for aerial photographs, topographic map, and general information. Publication No. 534, Institute of Geophysics and Planetary Physics, University of California, Los Angeles 90024.

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Calcium in Sea Water by Electrode Measurement

Abstract. *Ionized calcium in standard International Association of Physical Oceanography sea water (chlorinity, 19.373 parts per thousand) was measured with a recently developed, highly selective, calcium electrode. We found that 84 percent of the calcium in sea water exists as Ca⁺⁺, in fair agreement with the 91 percent calculated for the chemical model of sea water of Garrels and Thompson. If one used the activity coefficient for calcium ion of Garrels and Thompson, 0.28, calcium-ion activity in this sea water would be 0.00249. Another activity coefficient for calcium ion in sea water, 0.24, derived from Berner's measured total-activity coefficient and our measurement of the fraction of ionized calcium, yields a slightly lower activity, 0.00214.*

A recently developed calcium electrode (*I*) was used to measure the percentage of ionized calcium in standard International Association of Physical Oceanography sea water of 19.373-ppt chlorinity. The electrode-potential measurements were made against a saturated KCl-calomel reference electrode by use of an expanded-scale voltmeter and a strip-chart recorder. Temperature was controlled at 25° ± 0.1°C, and the solutions were stirred magnetically.

The electrode is highly selective for calcium ion, and, if it is calibrated in solutions similar to the unknown, the effects of other cations or of moderate variations in pH may be neglected. The response to calcium is linear

in the presence of a constant amount of other cations; that is, a plot of electrode potentials versus the log of calcium-ion activity is rectilinear over a range of calcium-ion concentration bracketing that of sea water. Of course, for preparations of such plots, assumptions must be introduced about single-ion activity coefficients. In the preliminary studies of the electrode behavior, the responses to calcium were measured in various aqueous solutions: NaCl, MgCl₂, NaCl + MgCl₂, and finally NaCl + MgCl₂ + KCl—each in its approximate sea-water concentration. The slope of the electrode response to calcium in solutions containing MgCl₂ was consistently steeper than would be predicted by a Nernst electrode equation such as:

$$E = E^0_{Ca} + 2.303(RT/2F) \log (Ca^{++})$$

in which *E* is the observed potential, *E*⁰_{Ca} is an empirical constant, *R*, *T*, and *F* are as usually defined and (Ca⁺⁺) indicates a calculated calcium-ion activity. Moreover, unpredictable variations in the *E*⁰_{Ca} term were observed, it being about 10 mv more positive in the NaCl than in the MgCl₂ solutions, and intermediate in the NaCl + MgCl₂ or the NaCl + MgCl₂ + KCl solutions. Because the slope measurements were made in solutions having nearly the same ionic strength, we could not rectify the data by changing the assumed single-ion activity coefficients. We finally concluded that changes in liquid-junction potential might explain the changes in *E*⁰_{Ca}, and that it would be best to proceed empirically by calibrating the electrode in solutions having nearly the same ionic strength and sodium-, magnesium-, and potassium-ion content as the standard sea water.

With respect to anions, however, the problem is different. Sulfate, carbonate, and bicarbonate ions in sea water complex part of the cations, but there is no known complexing of these cations by chloride ions (2). In order to avoid introduction of any assumptions about magnitude of the effects of those anions on calcium ion, we made our calibrating solutions with

Table 1. Composition of calibrating solutions and of sea water of 19.373-ppt chlorinity, and electrode-potential measurements of the solutions.

Solution	Ion (<i>M</i>)				<i>E</i> (mv)		
	Na	K	Mg	Ca	1	2	3
No. 1	0.459	0.0097	0.0496	0.00516	-55.0	-55.0	-55.5
No. 2	.459	.0097	.0496	.01032	-43.9	-44.0	-44.3
Sea water	.469	.0097	.0534	.0102	-47.2	-47.0	-47.0

chloride as the only anion. The solution compositions, and the cationic composition of sea water from reported data (3), as well as the electrode-potential measurements, appear in Table 1. The electrode measurements were repeated several times; reproducibility was within 0.3 mv.

We have attempted to make the calibrating solutions so like the sea water that we can assume that calcium ion has the same activity coefficient in the several solutions. Then, using an empirical electrode equation written in terms of concentrations rather than activities, we determine from the data in Table 1 the ionized calcium in this sea water to be $0.0086 \pm 0.0002M$.

The total calcium in sea water of this chlorinity being 0.0102M, we compute that about 84 percent of the calcium in sea water is ionized and that about 16 percent is presumably complexed with sulfate, carbonate, and bicarbonate. This result is in fair agreement with Garrels and Thompson's (2) value of 91 percent ionized calcium. Their chemical model for sea water made use of individual-ion activity coefficients and thermodynamic dissociation constants for a number of quantitatively important ion pairs or complex ions. They used an activity coefficient for calcium ion of 0.28, calculated from mean salt activity-coefficient data for KCl and $CaCl_2$ by use of data from Latimer (4) and Harned and Owen (5).

For purposes of comparison with the results of Garrels and Thompson, we may compute the activity of calcium ion in this sea water, using their activity coefficient and our measurement of the percentage of ionized calcium. Because calcium is 0.0106M in sea water of 19.373-ppt chlorinity, the activity of calcium is

$$(0.0106)(0.84)(0.28) = 0.00249$$

a value slightly lower than Garrels and Thompson's calculation—0.00264 for sea water of 19.00-ppt chlorinity.

Another activity coefficient for calcium ion in sea water has been reported by Berner (6), who measured the pH of sea water in equilibrium with calcite or aragonite at known pressures of carbon dioxide. His experiments yielded a total-activity coefficient, relating the activity of calcium ion to the total concentration of calcium in the sea water. For standard artificial sea water of 19.00-ppt chlorinity Berner determined the total-activity coefficient for calcium at 0.203 ± 0.010 .

Because the products of total concentration and total-activity coefficient and of ionic-activity coefficient and ionic concentration equal the same activity, our measurement of concentration of ionized calcium may be combined with Berner's total-activity coefficient and with the known total concentration to evaluate the ionic-activity coefficient of calcium in sea water. The small difference in chlorinities is neglected, and the ionic-activity coefficient is found to be 0.24 ± 0.02 —somewhat lower than the value used by Garrels and Thompson, but within the range of results from mean-salt data, depending on whose mean salt activity-coefficient data are used (7). With this smaller activity coefficient, the activity of calcium in this sea water is

$$(0.0106)(0.84)(0.24) = 0.00214 \pm 0.00023$$

We conclude, as did Berner, that these results, together with the recently reported (8) electrode measurement of magnesium in sea water, affirm the essential validity of the sea-water model of Garrels and Thompson. Their assumptions that individual-ion activity coefficients are, to a first approximation, dependent only on ionic strength, and that major deviations may be attributed to ion-pair or complex-ion formation, are useful as long as too much ac-

curacy is not expected. As more ion-specific electrodes become available one should be able to establish the distribution of the chemical species in sea water with somewhat greater precision.

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7. Using other data compiled by Harned and Owen (5, pp. 731, 735) and the method of computation used by Garrels and Thompson, and obtaining by graphical extrapolation the mean-salt data at an ionic strength of 0.7, we find

$$\gamma_{Ca^{++}} = (\gamma \pm CaCl_2)^3 / (\gamma \pm KCl)^2 = (0.460)^3 / (0.626)^2 = 0.248$$

Moreover, activity coefficients obtained in this way for calcium change very little, if at all, in this region of ionic strength.

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Lower Cretaceous Rocks (Neocomian-Albian) Dredged from Blake Escarpment

Abstract. *Algal calcarenites, Neocomian to Aptian in age, dredged from 3000- to 5000-meter depth on Blake Escarpment, are the oldest rocks yet obtained from deep-sea outcrops. Five thousand meters of post-Aptian subsidence of the Blake Plateau is thus established. Aptian-Albian calcilutites obtained from depths of less than 3000 meters mark the establishment of an offshore environment.*

The semiconsolidated Upper Cretaceous and Tertiary coastal-plain sediments that underlie Blake Plateau have been cored where they outcrop on the upper part of Blake Escarpment (1, 2, 3). Below 2500 m the escarpment is precipitous, and the high seismic velocity (5.1 km/sec) of the material implies a well-consolidated rock that could not be sampled by normal techniques for deep-sea coring (4).

Dredging was first attempted from Blake Escarpment in March 1966 (5). Of ten dredge lowerings near 29°N in depths of 2300 to 4800 m, three hauls (No. 3, 4, and 7) were productive (Fig. 1). From three more low-

erings in the area of Blake Nose (Fig. 1), a fourth successful haul (No. 12) was taken in 4800-m depth from near the base of the steep north face of this feature.

All rocks recovered are carbonates resembling the formations of the coastal-plain sequence of Florida and the Gulf Coast. That each dredge haul recovered in-place rocks is suggested by the relatively large size of the fresh angular fragments; by the broken surfaces (Fig. 2); by the uniform lithology of the contents of any one haul; and by the strong pulls on the cable, measured by the accumulator (5500 to 6000 kg) (6). Bottom-photographs of