sufficiently high P-wave levels for detection purposes to permit atrioventricular synchronous pacing.

The method of "duplexing" the function of the implantable receiver may be applied to various other biologic events as well as to implanted mechanical apparatus capable of generating electrical signals within the body.

C. E. Anagnostopoulos
W. G. Holcomb
W. W. L. Glenn

333 Cedar Street,
New Haven, Connecticut 06504

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Calcium and Bromide Contents of Natural Waters

Abstract. *The linear relation observed in a log Ca^{++} versus log Br^- plot for subsurface Cl^- waters is attributed to ultrafiltration by shale of sea water and fresh water that have passed through sedimentary rocks since their formation. Reactions between these solutions and sedimentary minerals, particularly dolomitization, must have contributed additional Ca^{++} to solution.*

The Ca^{++} and Br^- contents of subsurface Cl^- waters in marine sedimentary basins are proportional over a wide range of concentration. The values plotted in Fig. 1 are for waters from saline springs and from oil wells, except for waters from the surface sources mentioned. Most of the subsurface data are from Illinois, Michigan, California, Alabama, Mississippi, Alberta, and the Irkutsk area of the U.S.S.R.

Determination of Br^-, especially at the lower end of the concentration range of Fig. 1, is still a difficult analysis; some scatter should be expected in Fig. 1 because of the different analysts and techniques involved. In particular, the very low Br^- concentrations must be viewed with caution, even though they were determined by a highly sensitive catalytic method (*1*) that is more reliable than conventional techniques. However, excellent linear relations are shown by some groups of samples from single areas, such as the six from Michigan and the seven from the Dead Sea area, through which the straight line of Fig. 1 has been drawn. The equation of the line is

$$\log Ca^{++}\ [g/10^6\ g\ (solution)] = 1.263 + 1.406 \log Br^-\ [g/10^6\ g\ (solution)]$$

In other words, there is one Br^- ion to every 36 Ca^{++} ions at the lowest salinity represented in Fig. 1 and 1 : 53 at the highest.

The proportionality shown in Fig. 1 is not repeated in graphs involving Na^+ or Cl^-. Thus, if Na^+ is plotted against Br^-, most of the points concentrate in the log interval of highest Na^+ concentration and show a high degree of scatter, particularly for the Michigan samples. In a graph of Ca^{++} versus Cl^-, scatter in the interval between 10^3 and 10^4 g Ca^{++} per 10^6 g of solution is greater than in Fig. 1, and there is a marked break toward reduced slope above 10^4 g Ca^{++} per 10^6 g of solution because Cl^- concentration becomes nearly constant.

The highly concentrated Cl^- waters found at depth in sedimentary basins contain Ca^{++} as a principal cation, sometimes exceeding even Na^+ in abundance. It has recently been argued that this accumulation of Ca^{++} results from the operation of shale ultrafilters that retain Ca^{++} and Cl^- but pass Na^+ balanced by HCO_3^- equivalent in amount to (HCO_3^- + SO_4^{--} in the original surface waters (*2, 3*). A variant of this mechanism, in which ion transport through the ultrafilters takes place by means of neutral complexes, appears to be favored by the conclusion (*4*) that considerable amounts of the SO_4^{--}, HCO_3^-, and CO_2^{--} in sea water are complexed, but essentially none of the Cl^- is.

Because even the most-concentrated subsurface brine is far from saturation in calcium chloride, all the Ca^{++} and Br^- contained in fresh water and sea water, that have passed through the system since deposition of sediment, could have been retained in solution behind ultrafilters. Part of the Ca^{++} now in solution has probably been derived from the dolomitization reaction

$$2\,CaCO_3 + Mg^{++} \rightleftharpoons CaMg(CO_3)_2 + Ca^{++}$$

No doubt some Mg^{++} has gone into regrading and diagenetic formation of chlorite and other silicates, but presumably little Ca is returned to solution (*2*) because exchange positions of these silicates, originally formed in marine environments, should be Na-saturated.

One plausible explanation of the increase in $Ca^{++}:Br^-$ ratio along the line in Fig. 1 is that the dolomitization reaction proceeds more nearly to completion in more concentrated brines; such brines typically occur at greater

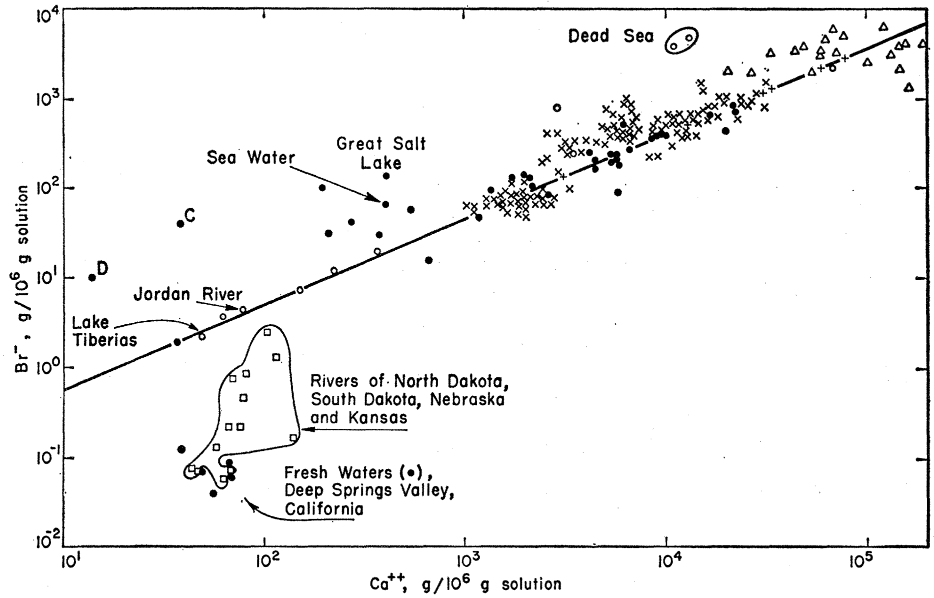

Fig. 1. The Ca^{++} and Br^- contents of a group of natural waters. Samples shown by plus signs (Michigan), open circles (Dead Sea region), and dots (Alberta; various U.S. localities) are tabulated in table 6 and appendix II of (*2*); by triangles (Irkutsk region), in table 2 of (*5*); and by crosses (Alabama and Mississippi), in (*8, 9*). All samples not otherwise identified in the figure are subsurface brines, sampled from either oil wells or points at which the brines reach the surface as saline springs.

depth and higher temperature than less-concentrated ones, although there are exceptions to this simple progression. Valyashko and Vlasova (*5*) invoked dolomitization and exchange reactions as important means of increasing Ca^{++} in solution in brines of the Irkutsk area.

The points for sea water, and for fresh water as represented by samples from major Great Plains rivers and from waters in contact with ancient marine sediments in the Deep Springs Valley, California, lie on opposite sides of the line in Fig. 1. This distribution is required if the plotted brine compositions are to be obtained by concentration from mixtures of both kinds of water. One should note that Bentor (*6*) believes that saline springs make the major contribution to the Dead Sea system. The waters that define the lower end of the line in Fig. 1, including the Jordan River and Lake Tiberias samples, may thus have been formed largely by the processes responsible for oil-field brines.

Water compositions plotted on a Ca^{++} versus Br^- diagram will, to a good approximation, shift either vertically or horizontally during the solution and precipitation of geologically important phases. If $CaCO_3$, $CaSO_4$, or $CaSO_4 \cdot 2H_2O$ precipitates because of mixing with HCO_3^-–bearing or SO_4^{--}–bearing surface waters, the shift will be to the left—that is, toward the part of the diagram above the line. The Br^- content of these phases is slight.

Likewise, relatively dilute waters, in which HCO_3^- is a significant proportion of total anions and in which P_{CO_2} is markedly greater than that of the atmosphere, are likely to precipitate $CaCO_3$ on reaching the surface because of loss of CO_2. An example of the latter process is afforded by Alberta samples *C* and *D*, from which $CaCO_3$ was precipitating on their arrival in the laboratory; no attempt was made to dissolve the precipitate and calculate back to an *in situ* brine composition because it appeared that considerable precipitation may have taken place even before sampling. The plotted values for *C* and *D* are therefore those for ions still in solution at the time of analysis.

As to other possible reactions that may affect the geometry of Fig. 1, dolomitization and solution of $CaCO_3$, $CaSO_4$, or $CaSO_4 \cdot 2H_2O$ will move water compositions to the right. If NaCl precipitates in a surface body of water because of evaporation, the plotted composition in Fig. 1 will move downward because of loss of Br^-. The converse is, of course, true, and in either case the size of the shift will depend upon not only the amount of NaCl involved but also its particular Br^- content—that is, upon the solution composition and the value of the Br^- partition coefficient at precipitation (*7*). Phases containing significant amounts of both Ca^{++} and Br^- are unimportant geologically, so that diagonal shifts need not be considered.

The points plotted in Fig. 1, excluding those for freshwater samples, occupy a field extending upward from a rather well-defined lower edge. Two possible explanations of the relative absence of points in the lower portion of the figure are: (i) Higher degrees of evaporation of natural waters are progressively less frequent, that is, $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ precipitate much more often than does NaCl; (ii) even if some NaCl precipitates, the downward shift that results may be less than the effective upward shift (shift to the left across the line) occasioned by a preceding Ca-phase precipitation in the same evaporation cycle.

The most concentrated of the Michigan brines are saturated with respect to halite, so that further increase in salinity must be achieved by increasing the proportion of cations of the more-soluble chlorides, Ca^{++} and Mg^{++}, relative to Na^+ and K^+. Details of the process differ somewhat for the two mechanisms of increase in Ca^{++} that we have discussed. Additional Ca^{++} arriving in later increments of water should be accompanied by sufficient Br^- to maintain the general slope of Fig. 1, and the additional Ca^{++} could be retained and the salinity at saturation could be increased by loss of Na^+ through ultrafilters.

On the other hand, Ca^{++} returned to solution, in exchange for Mg^{++} lost in the formation of sedimentary minerals, would be accompanied by an insignificant amount of Br^-, and the waters resulting from such a process should plot along an essentially horizontal line in Fig. 1. The horizontal aspect of the cluster of points for Irkutsk-area samples, and of the two subgroups of Alabama-Mississippi samples, could have resulted from dolomitization occurring within individual hydrologic units. Dolomitization would significantly increase the value of salinity at saturation with respect to halite because of the difference between the solubilities of calcium chloride and magnesium chloride, although the increase would not be nearly so great as with the exchange of Ca^{++} for $2Na^+$.

The similarity in Fig. 1 of the slopes for sets of points from various geographical areas suggests a common process or processes in operation, such as those we have discussed. The fact that the sets form a single line suggests a common starting composition, most probably that of the oceanic reservoir.

The further usefulness of the $Ca^{++} : Br^-$ ratio in interpreting water histories in marine sedimentary basins will clearly depend upon other input solutions having a limited range of $Ca^{++} : Br^-$ ratios. It is difficult to estimate the ratio for the solutions saturated in $CaSO_4$ or $CaSO_4 + NaCl$ that must result from the conversion of $CaSO_4 \cdot 2H_2O$ (gypsum) to $CaSO_4$ (anhydrite) at depth, but it is probably very high. The range of the ratio among various fresh waters is not yet known, but it is likely to show considerable variation in waters from crystalline terranes. The anionic dominance of SO_4^{--} in typical Great Plains river waters (*9*), coupled with the sharp rise in Br^- among such samples as are plotted in Fig. 1, suggests the derivation of SO_4^{--} from S^{--} and the association of both Br^- and S^{--} with the organic matter of shales.

RAYMOND J. ANDERSON
DONALD L. GRAF*
BLAIR F. JONES
The Dow Chemical Company, Midland, Michigan, Illinois State Geological Survey, Urbana, and *U.S. Geological Survey, Washington, D.C.*

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* Present address: Department of Geology and Geophysics, University of Minnesota, Minneapolis.

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