and fusion of material must have occurred during shatter cone formation (*4*), especially in the shale horizon where the argillaceous material apparently facilitated melting. This explanation agrees with the observation of Friedman *et al.* (*5*) who suggested that "impurities" in quartzose sandstones facilitated glass formation during frictional sliding. The destruction of the spherules by later shearing movements or compaction was apparently prevented by the fact that the shatter cone event was accompanied by considerable dilation across the individual surfaces. The resultant open spaces have remained sufficiently open during the subsequent history of the rocks for the spheres to be preserved. This argument is consistent with shatter cone formation during the passage of a shock wave and subsequent decompression.

The occurrence of the spherules in the Vredefort collar rocks indicates that an event of cataclysmic violence occurred during the formation of the Vredefort structure. At first sight, this event correlates with the meteorite impact origin proposed by Daly (*6*) and Dietz (*7*). However, there is a body of evidence that the Vredefort region incorporated a singular igneous and metamorphic center before the shatter cone event (*8*), and the possibility of an internal origin for the structure should not be discounted.

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Sodium Liquid Ion Exchanger Microelectrode Used to Measure Large Extracellular Sodium Transients

Abstract. *A new liquid membrane microelectrode has been developed that is easily fabricated and can measure fast sodium transients in the presence of potassium interference. It responds to a sudden change in sodium activity within 1 second. The electrode has been used to provide the first direct evidence of large sodium transients in the extracellular space of the brain of the catfish.*

Ion-selective electrodes are being widely used in many areas of biological investigation (*1*). Liquid ion exchanger microelectrodes are very useful in these applications because of their ease of fabrication (*2*). At present, however, microelectrodes capable of measuring Na^+ must be made from Na^+-sensitive glass (*3*). Such glass electrodes suffer from several drawbacks. Although they have tip diameters of about 1 μm, they commonly have reactive lengths of 10 μm or more and are difficult to fabricate. Most importantly, when subjected to a sudden change in K^+ activity, a Na^+-sensitive glass electrode displays an emf (electromotive force) transient which decays to an equilibrium value in 30 seconds and represents a diminished (1:1) $Na^+:K^+$ selectivity (*4*). Furthermore, in the presence of K^+, the response time to a sudden change in Na^+ activity may be increased by a factor of 100 (*4*). Clearly, Na^+ changes on the order of seconds cannot be recorded with a Na^+-sensitive glass electrode that requires minutes to respond.

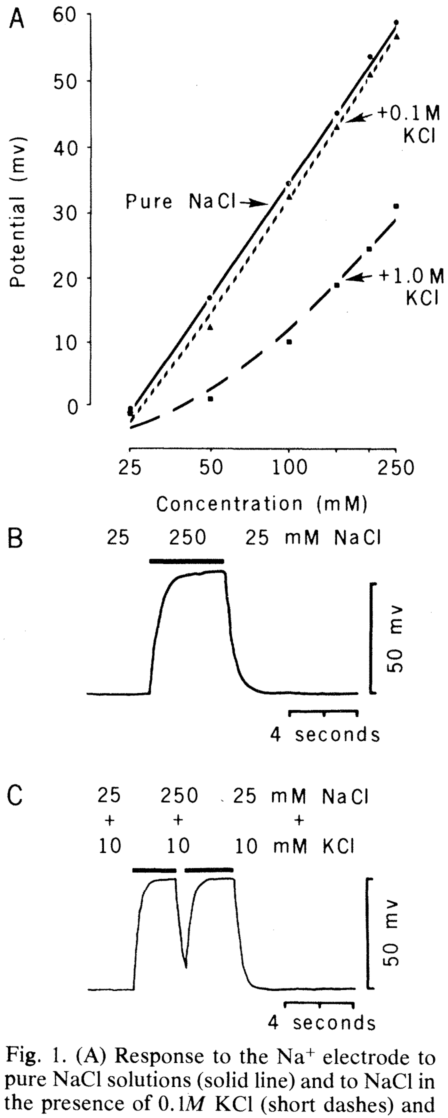

Fig. 1. (A) Response to the Na^+ electrode to pure NaCl solutions (solid line) and to NaCl in the presence of 0.1*M* KCl (short dashes) and 1.0*M* KCl (long dashes). (B) Response of the electrode to a step change (25 to 250 m*M*) in NaCl. (C) Response of the electrode to a step change (25 to 250 m*M*) in NaCl in the presence of 10 m*M* KCl.

We alleviated all of these difficulties by fabricating a Na^+-selective liquid ion exchanger microelectrode. This electrode incorporates as the ion exchanger a 10 percent (weight to weight) solution of monensin in nitrobenzene. Monensin is a biologically active compound produced by *Streptomyces cinnamonensis* (*5*) that preferentially binds Na^+ (*6*) and has been proposed for use in macroelectrodes (*7*). Monensin is commercially available as the sodium salt (*8*) and can be readily converted to the free acid as used here (*9*).

The electrode is made by introducing the exchanger into presiliconized micropipettes (*10, 11*). The electrode is filled with 150 m*M* NaCl and positioned with a reference micropipette filled with 150 m*M* $NaC_2H_3O_2$ and 2 m*M* $CaCl_2$ (*12*). Diffusion from the reference pipette does not influence the ion electrode. Electrodes with tips 1 to 2 μm in diameter are glued using rapid-setting epoxy with a tip spacing of less than 10 μm and connected via Ag-AgCl wires to buffer amplifiers having a gain of unity and an ultralow capacity (*13*). The reference signal is electronically subtracted from the ion electrode signal to yield the pure Na^+ signal (*11*). The electrode can be used immediately and still displays slopes greater than 50 mv per decade change in Na^+ after 24 hours.

The emf of a typical electrode as a function of Na^+ concentration is shown by the solid line in Fig. 1A. A linear regression line with a slope of 58.9 mv per decade change in Na^+ was obtained at 25°C for the range 25 to 250 m*M*. The effect of including 0.1*M* or 1.0*M* KCl in the NaCl solutions is shown by the dashed lines (*14*).

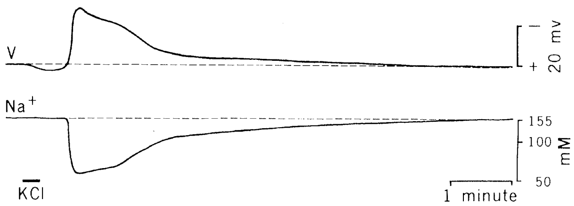

Fig. 2. Simultaneous recording of slow potentials and the Na$^+$ signal during spreading depression. The upper trace (*V*) shows the slow potential during spreading depression elicited by KCl microinjection (KCl). The lower trace shows the $[Na^+]_0$ decrease recorded on a logarithmic scale.

We determined selectivity constants by comparing the response of the electrode to step changes (25 to 250 m*M*) in Na$^+$ activity with constant concentrations (0.1*M* and 1.0*M*) of background interference. These measurements indicate that the electrode has a selectivity ratio against K$^+$ of 15 : 1 at 0.1*M* and 13 : 1 at 1.0*M* and selectivity ratios at 1.0*M* interference of 143 : 1 for Ca^{2+}, 154 : 1 for NH$_4^+$, 14 : 1 for H$^+$, and 7 : 1 for Mg^{2+}.

The electrode responds to a sudden change in Na$^+$ activity within 1 second (Fig. 1B) (*15*). No anomalous behavior was found in the response of the electrode to K$^+$. The time constant of the electrode is unchanged when it experiences a change in Na$^+$ activity in the presence of K$^+$ (Fig. 1, B and C). The resistance of the Na$^+$ electrode was not systematically measured, although it always showed more noise than both K$^+$ and Cl$^-$ liquid ion exchanger microelectrodes which have resistances of 10^9 to 10^{10} ohms. The electrode was not sensitive to protons from *p*H 5 to 9. Thus this electrode has a superior response and Na$^+$: K$^+$ selectivity as compared to a recently reported liquid membrane Na$^+$-selective macroelectrode (*16*).

To demonstrate the utility of the electrode in biological systems, we recorded changes in extracellular sodium ($[Na^+]_0$) during spreading depression (*11, 17*) in the catfish cerebellum. Large (75 to 100 m*M*) decreases in extracellular chloride ($[Cl^-]_0$) associated with large (40 to 60 m*M*) increases in extracellular potassium ($[K^+]_0$) have been recorded during spreading depression (*11*). This finding suggests that a large shift in $[Na^+]_0$ should be associated with this change in $[K^+]_0$ and $[Cl^-]_0$.

Using the same experimental paradigm as described in (*11*), we recorded a resting $[Na^+]_0$ level of 149 m*M*, which fell to around 57 m*M* during spreading depression (Fig. 2). This shift of 92 m*M* in $[Na^+]_0$ can account for the majority of the shifts in $[K^+]_0$ and $[Cl^-]_0$; furthermore, it supports recent data on changes in cerebral impedance measured during spreading depression (*18*).

This large shift in $[Na^+]_0$ casts doubt on the tendency to regard the extracellular space of the brain as a homogeneous ionic milieu. In addition, such a change may have a profound influence on synaptic function and neural transmitter transport and metabolism. This Na$^+$-sensitive electrode provides the first direct evidence of a large Na$^+$ shift in the extracellular space during spreading depression.

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$$V = A \log([a_i] + K_{ij}[b_j]) + \text{constant}$$

is appropriate for the Na$^+$ electrode.
15. Time constants were measured as the 95 percent response time of an electrode to an activity change created by pressure injection from a second microelectrode placed less than 10 μm away.
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Stereochemical Requirements for Intercalation of Platinum Complexes into Double-Stranded DNA's

Abstract. *The complexes 1,10-phenanthrolineethylenediamineplatinum(II) and 2,2′-bipyridineethylenediamineplatinum(II) have a planar, aromatic ligand system that facilitates intercalation, as shown by their ability to unwind closed circular duplex DNA. Nonbonded steric interactions can rotate the pyridine ligands out of the coordination plane in bis(pyridine)ethylenediamineplatinum(II), thus preventing intercalation. Fiber x-ray diffraction patterns of the two metallointercalators indicate that the binding is governed by the neighbor exclusion principle.*

The complex 2-hydroxyethanethiolato-2,2′,2″-terpyridineplatinum(II) {[(terpy)-Pt(HET)]$^+$} has been shown to bind to double-stranded DNA's by intercalating between adjacent base pairs and unwinding the double helix (*1*). The behavior of this metallointercalation reagent is similar in many respects to that of classical organic intercalators such as ethidium bromide (*2*). The electron-dense platinum atom in [(terpy)Pt(HET)]$^+$, moreover, gives rise to intense, near-meridional reflections at 10.2 Å in x-ray diffraction patterns of highly oriented DNA fibers containing this reagent (*3*). The existence of these reflections supports the neighbor exclusion binding model (*4*), in which the intercalators occupy every other site between base pairs in the DNA duplex at saturation.

The study reported here expands the class of known metallointercalation reagents to include 2,2′-bipyridineethylenediamineplatinum(II) {[(bipy)Pt(en)]$^{2+}$} and 1,10-phenanthrolineethylenediamineplatinum(II) {[(*o*-phen)Pt(en)]$^{2+}$}, complexes that are doubly charged and contain only one chelate ring (*5*). In these two complexes, as in [(terpy)Pt(HET)]$^+$, the aromatic ligands lie strictly in the coordination plane of the metal atom. The closely related complex bis(pyridine)-