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11. A three-port, round-bottom flask was used for the titrations. One port held the *p*H electrode, one held an aerator through which N_2 flowed, and the other was left open for the addition of titrant (NaOH). At all times a positive pressure of N_2 was maintained in the flask to exclude H_2CO_3 from the sample.
12. The precipitation samples from the Adirondack Mountains were collected and analyzed by C. Schofield, Natural Resources Department, Cornell University.
13. The values for the concentrations of Al^{3+}, Fe^{3+}, Mn^{2+}, H_4SiO_4, particulates, and NH_4^+ were selected from an Ithaca storm that had concentrations representing the yearly mean of composition for Ithaca precipitation. The rural precipitation samples (Hubbard Brook and Adirondack Mountains) had substantially lower concentrations.
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15. The chemical composition (concentrations given here are in microequivalents per liter), including *p*H, of this storm falls well within the range of that of storms in the Ithaca area (*1*, *2*). The inorganic composition is as follows: *p*H, 3.84; Ca^{2+}, 13.0; Mg^{2+}, 3.0; Na^+, 1.2; K^+, 0.26; NH_4^+, 29.4; NO_3^-, 45.2; SO_4^{2-}, 116.7; Cl^-, 19.2; PO_4^{3-}, 0.25; H_4SiO_4, 1.6; Al^{3+}, 3.8; Fe^{3+}, 0.72; and Mn^{2+}, 0.19. The following organic acids were present: formic, 0.4; acetic, 2.1; propionic, 1.0; butyric, 0.6; and glycolic, 1.6. These organic acids were determined by gas chromatography (*8*) and confirmed by mass spectrometry (*9*). Their total concentration in the sample is 5.7 μeq/liter. Their contribution to the *p*H of the sample is 2 μeq/liter, since they are only partially dissociated at this *p*H. The total concentration of cations is 196.1 μeq/liter. The total concentration of anions is 183.4 μeq/liter. The difference between the two is ~ 6 percent, which would be the equivalent of 0.03 *p*H unit. The contribution to the free acidity of NO_3^- and SO_4^{2-} is determined by a stoichiometric formation process in which a sea salt anionic component is subtracted from the total anions (*2*).
16. In our titration, H_2CO_3 was removed from the system by N_2 purging. If the H_2CO_3 had not been removed and the sample was then isolated from the atmosphere, only the H_2CO_3 initially in the sample (0.62 mg/liter) would be titrated, resulting in a contribution of 20 μeq/liter to the total acidity. If the system were at equilibrium with the atmosphere, there could have been a contribution of 5000 μeq/liter to the total acidity and no contribution to the free acidity in a titration from *p*H 4 to 9.
17. We thank D. Kuehl, Environmental Protection Agency National Water Quality Laboratory, Duluth, Minn., for his assistance in confirming the organic acids by mass spectrometry. We thank Drs. N. M. Johnson and J. J. Morgan for critical comments. This report is a contribution to the Hubbard Brook Ecosystem Study. Financial support was provided by the National Oceanic and Atmospheric Administration and by the National Science Foundation. The Hubbard Brook Experimental Forest is operated by the U.S. Department of Agriculture Forest Service, Upper Darby, Pa.

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Spherules on Shatter Cone Surfaces from the Vredefort Structure, South Africa

Abstract. *Spherical particles of silicate composition occur on the surface of some shatter cones from the collar rocks around the Vredefort structure, South Africa. They are best developed on shatter cones from a shale horizon but are also found on more arenaceous rocks and banded ironstones. They have not been found on shatter cones from the purer quartzites.*

Glassy and metallic spherules have been reported in lunar fines and impactite glasses from terrestrial craters by many workers and may be genetically related to meteor impact (*1*). I report here, to my knowledge for the first time, the presence of spherical and other structures on the surfaces of shatter cones. The shatter cones were collected from rocks of the Witwatersrand sediments which form the collar around the Vredefort structure and from Transvaal sediments in the rim syncline around the structure (*2*). The spheres are best developed on shatter cones in the Kimberley shales; they also occur in shatter cones from banded ironstones and argillaceous sandstones but appear to be absent or very poorly developed on quartzite specimens. They were discovered during a study of shatter cone surfaces with a scanning electron microscope (SEM).

The spheres range in diameter from 0.1 to 10 μm but are generally less than 5 μm. On the shale host rock they tend to be perfectly spherical (Fig. 1a) or to form parts of spheres. Cooling cracks can sometimes be seen on the surfaces (Fig. 1b), and small parasite spheres grow off them. The spheres tend to nestle in grooves or holes lower than the general surface where clusters of them can sometimes be seen (Fig. 1c), but they also occur on ridges (Fig. 1d). On shatter cones from other rock types the spheres have a more irregular lumpy form (Fig. 1e), which deteriorates to a rounded aggregate of particles in the purer quartzites (Fig. 1f). Doublets (Fig. 1g), hemispheres, and cup-shaped particles (Fig. 1h) are also found. When rotated into suitable orientations, the spheres are seen to be welded to the shatter cone surface (for example, Fig. 1e) and often have minute fragments adhering to them. Preliminary analyses of the spherules with an energy-dispersive x-ray analysis system attached to the SEM show that they have an elemental composition similar to that of the host rocks (*3*).

The presence of the spherules clearly indicates that extremely rapid melting

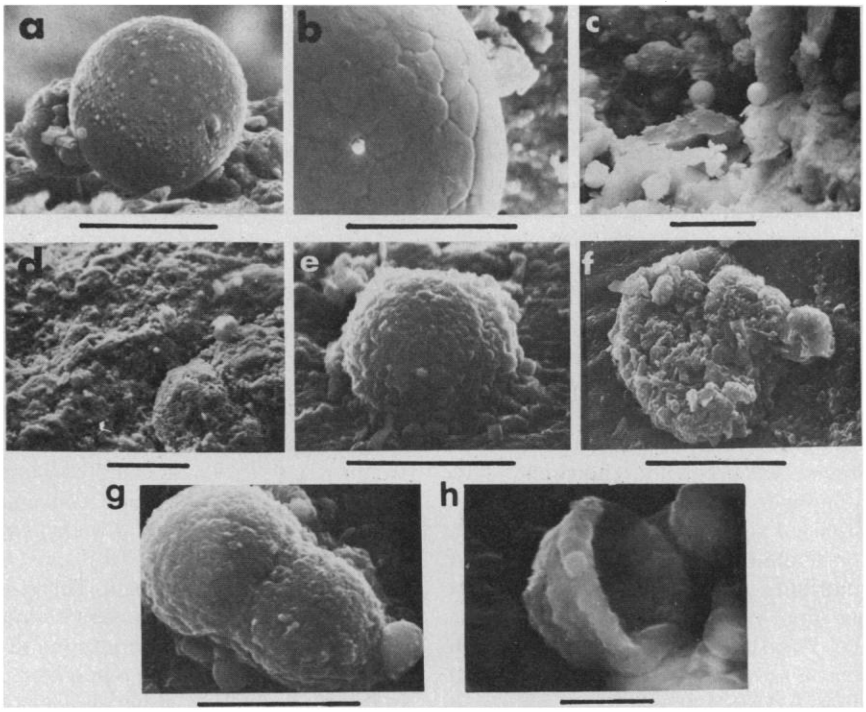

Fig. 1. Scanning electron micrographs of spherules and other structures on shatter cone surfaces: (a through c) on shale host rock, Kimberley-Elsburg Series; (d and h) on banded ironstone, Hospital Hill Series; (e and g) sandstone, Timeball Series, Transvaal system; (f) quartzite, Kimberley-Elsburg Series. Scale bars: for (a, b, e, g, and h), 2 μm; for (c and f), 5 μm; and for (d), 10 μm.

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.

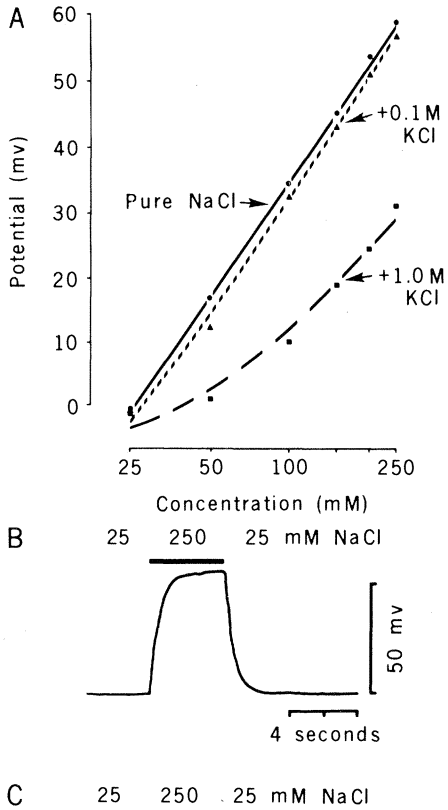

Fig. 1. (A) Response to the Na^+ electrode to pure NaCl solutions (solid line) and to NaCl in the presence of 0.1*M* KCl (short dashes) and 1.0*M* KCl (long dashes). (B) Response of the electrode to a step change (25 to 250 m*M*) in NaCl. (C) Response of the electrode to a step change (25 to 250 m*M*)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