from Jupiter have been observed by J. W. Warwick and G. A. Dulk [*Science* **145**, 380 (1964)].

6. The effect of the sampling frequency on the apparent frequency of a sine wave is discussed by R. B. Blackman and J. W. Tukey [*The Measurement of Power Spectra* (Dover, New York, 1968), p. 31].
7. F. F. Gardner and J. B. Whiteoak, *Nature* **197**, 1162 (1963).
8. Our value for the integrated electron density, 28 parsec cm^{-3}, is in good agreement with the value of 26.8 parsec cm^{-3} reported by A. G. Lyne and B. J. Rickett [*Nature* **219**, 1339 (1968)].
9. The rotation measure for the path from Earth to Jupiter had a maximum value of 0.7 rad/m^2 according to our reduction of the observations of Warwick and Dulk (*5*). Thus, even if we allow for a fourfold increase with the solar cycle, the contribution of the ionosphere to our measurements is negligible.
10. F. G. Smith, *Nature* **220**, 891 (1968).
11. We are indebted to the staff of the National Radio Astronomy Observatory for the opportunity to make these observations. The National Radio Astronomy Observatory is operated by Associated Universities, Inc., under contract with the NSF. We thank the Computer Science Center of the University of Virginia for a grant for computer time. Supported by NSF grant GP 7803.

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Sedimentary Phosphate Method for Estimating Paleosalinities: Limited Applicability

Abstract. *The sedimentary phosphate method for estimating paleosalinities was tested on argillaceous sediments from different formations and environments. Results reveal that the method cannot be used generally.*

A new method (*1*) for estimating paleosalinities in argillaceous sediments, the sedimentary phosphate method, is based on the fact that sediments act as a phosphorus reservoir in natural systems, the mineral or chemical composition of the phosphorus compounds being different in different environments. The Al-phosphate variscite and the Fe-phosphate strengite reportedly prevail in soils and fine-grained freshwater sediments, whereas the Ca-phosphate apatite is the phosphate of marine muds (*1*).

In Recent sediments from the Rappahannock River estuary, a tributary of Chesapeake Bay, a systematic change of the Fe- and Ca-phosphate proportions with increasing salinity was observed (*1*). Here the calcium to iron + calcium molar ratio increases from about 0.20 at a salinity of 1.5 per mille to 1.00 at 36 per mille and can be used as a sensitive salinity indicator over the observed salinity range.

Nelson (*1*) applied the sedimentary phosphate method to Paleozoic shales and clays from Ohio and Pennsylvania, and concluded that "the results are consistent with previous stratigraphic and fossil evidence."

We tested the new method with argillaceous muds and mudstones of Recent, Pleistocene, Tertiary, Permian, and Carboniferous ages derived from different depositional basins ranging from freshwater to hypersaline (salt clays) environment (Table 1).

The results obtained by the sedimentary phosphate method in most cases do not agree with the salinities observed directly (Recent muds, varved sediments, and Pleistocene moraines) or derived from geological or paleontological evidence.

Sediments which are nonmarine (Recent lake deposits, varved sediments, moraines, Lower Permian siltstones, and some claystones of the Upper Carboniferous) were almost marine to fully marine by the sedimentary phosphate method.

The failure of the method may be due to: (i) The materials tested may not have been exposed to weathering. The bulk minerals of Lake Constance muds and of the suspended load of its main influent, the Rhine, are not derived from soils but directly from older (mostly marine!) sediments or igneous or metamorphic rocks (containing apatite!). The same is true for the glacial sediments and most of the siltstones of the Lower Permian, the latter having been formed in an arid climate. The mineral particles were transported into the depositional basins before soil formation had taken place and, after deposition, were covered so quickly by younger sediments that no

Table 1. Salinities and paleosalinities determined by the sedimentary phosphate method (SPM) versus those obtained by direct, geological, or paleontological evidence.

Number of samples	Nature of sediment*	Salinity	
		By SPM (‰)	Direct (‰)
	Recent		
2	Gulf of Naples; muds from pyroclastic material	35	35
3	North Sea, south of Helgoland; muds from glacial outwash	35	35
3	Lake Constance; muds, detritus from Alps via Rhine River	35	0
2	Rhine River; suspended load	35	0
2	Stockacher Aach; drainage from cultivated land	15–17	0
	Pleistocene		
3	Foreland of Alps; varved silty clays	30–35	0
2	Foreland of Alps; boulder clays	30–35	0
	Tertiary		
4	Upper Rhine Valley; mudstones, lacustrine (Neogene)	6–18	< 5
4	Upper Rhine Valley; mudstones, lacustrine "Obere Pechelbronner Schichten" (Oligocene)	30–33	< 5
3	Upper Rhine Valley; mudstones, brackish "Untere Pechelbronner Schichten" (Oligocene)	35	10–25
3	Upper Rhine Valley; mudstones, marine "Fischschiefer" (Oligocene)	30–35	30–35
	Upper Permian		
3	North Germany, Zechstein deposits; salt clays (evaporites)	35	> 35
	Lower Permian		
10	Saar-Nahe region, Continental Permian Basin; reddish clayey siltstones	35	0
	Upper Carboniferous		
10	Ruhr; dark claystones overlying coal seam Plasshofsbank †	35	0–35
2	Ruhr; dark claystones from brackish environment	28–35	10–25
5	Ruhr; dark claystones from marine environment	28–35	> 30

* Source and description. † Sampled at 1-cm intervals from top of coal seam. Environment changes from nonmarine (coal/claystone interface) to fully marine (10 cm above coal).

significant chemical changes could occur. The Ca-phosphate now found in these sediments is of detrital origin and does not indicate salinity in the depositional environment. (ii) A previously existing small amount of Ca-phosphate may have become enriched and indicate falsely a marine environment. The dark claystones under- and overlying coal measures of the Upper Carboniferous soon after deposition were reduced due to their high content of organic material. In a lacustrine environment Fe-phosphate, if present, will be transformed under reducing conditions in the presence of H_2S into FeS, and phosphate ions are liberated.

These two disadvantages of the new method are so frequently found in sedimentary rocks that this method cannot be used extensively.

GERMAN MÜLLER
Laboratorium für Sedimentforschung,
University of Heidelberg,
Berliner Strasse 79
69 Heidelberg, Germany

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1. B. W. Nelson, *Science* **158**, 917 (1967).
2. I thank Professor Falke and Drs. Rabitz and Fiebig for providing sample material.

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Coalescence of Two Immiscible Liquid Drops

Abstract. *When two immiscible liquid drops suspended in a third immiscible liquid are brought into contact, three equilibrium configurations which depend upon the spreading coefficients are possible. Experiments for a large number of systems, including three-phase emulsions, confirm the theory and indicate the mechanisms of reaching equilibrium.*

We have studied the interaction of two immiscible liquid drops brought into collision in a third immiscible liquid by shear motion or by mutual electrostatic attraction in an externally imposed electrical field or by a combination of the two effects. This report is an extension of earlier work on the coalescence of two identical liquid drops interacting under similar conditions (*1, 2*).

We have considered the equilibrium configurations to be expected when the two drops, designated as phases 1 and 3 with radii b_1 and b_3, respectively, come into intimate contact in the liquid medium (phase 2) so that, in addition to the existing 12 and 23 interfaces, the 13 interface can also form. We assume that the final equilibrium states are determined solely by the three interfacial tensions σ_{ij} $(i \neq j \neq k = 1, 2, 3)$; thus gravity, fluid motion, and forces between particles do not determine the position of equilibrium, even though, in practice, these other factors may be important in promoting its attainment.

After considering the three spreading coefficients $S_i = \sigma_{jk} - (\sigma_{ij} + \sigma_{ik})$ and adopting, without loss of generality, the convention of designating phase 1 as that phase for which σ_{12} is greater than σ_{23} so that S_1 is less than 0, we have shown that there are only three possible sets of values for S_i:

$$S_1 < 0 \quad S_2 < 0 \quad S_3 > 0 \tag{1}$$

$$S_1 < 0 \quad S_2 < 0 \quad S_3 < 0 \tag{2}$$

$$S_1 < 0 \quad S_2 > 0 \quad S_3 < 0 \tag{3}$$

These three conditions lead to three different equilibrium configurations which are independent of b_1 and b_3.

1) Complete engulfing: Phase 1 is entirely absorbed into phase 3 to form a spherical drop which has two spherical interfaces (23 and 13). The external radius of this compound drop, which we define as a 2-singlet, is

$$r_{23} = (b_1^3 + b_3^3)^{1/3}$$

2) Partial engulfing: The three interfacial tensions form a closed (Neumann) triangle with the 12, 13, and 23 interfaces in equilibrium along a 123 line bounding the three phases. The geometrical details of the resulting drop, which we call a 3-singlet, are determined from capillarity equations and the interfacial tensions and initial radii of the drops.

3) Nonengulfing: The 13 interface cannot form spontaneously, and the drops remain separated as a 2-doublet.

We have confirmed the predictions by experiments with over 20 different systems. In all of these systems one of the phases is water or an aqueous solution of a surface-active agent, and the three phases are of nearly equal density. The systems reflect a wide range of values of S_i (-40 to $+15$ dyne cm^{-1}), b_i (10 μm to 1 mm), and phase viscosities (0.01 to 50 poise). Most of the experiments were performed in a Couette apparatus consisting of two concentric cylinders capable of counterrotation. Pairs of liquid drops were brought into collision at velocity gradients up to 2 sec^{-1} in transversely applied electric fields up to 2 kv/cm. The apparatus included provision for viewing the drops through a microscope and taking photographs of the events (*3*).

The equilibrium configurations attained were in accord with conditions 1 to 3 except for several systems in which either S_2 or S_3 was nearly zero. Here the extent of engulfing was smaller than predicted, presumably because the driving force S_i was too small to achieve true equilibrium.

The measured geometry of the 3-singlets was in fairly good agreement with the theory (Fig. 1) for a system in which the size ratio $R_0 = b_1/b_3$ was varied over wide limits. We conclude that in this system, in which the smallest drop radius was 300 μm, the 3-phase line tension σ_{123} (*4*), which, in principle, can influence the drop geometry, was not appreciable.

Systems which correspond to conditions 2 and 3 and which were forcibly engulfed by the injection of a droplet of phase 1 into phase 3, deengulfed to form either a 3-singlet or a 2-doublet in accordance with the theory. In some cases the 3-singlets had one of the phases dispersed as a myriad of tiny lenses at the surface of the other phase.

The mechanism of engulfing, as observed by high-speed photography, can best be illustrated by the formation of a 2-singlet. When two drops are pressed together, the phase-2 film between them drains until a hole suddenly forms in

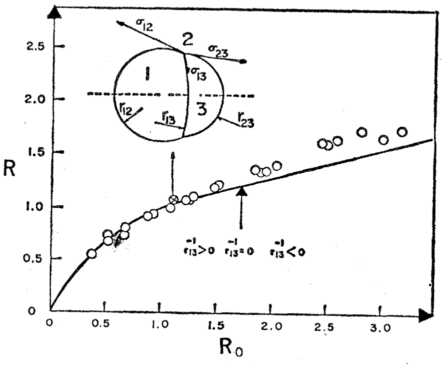

Fig. 1. Measured (points) and calculated (line) shapes of 3-singlets in the system H_2O + 10 percent (by volume) Tween 20 (phase 1), silicone oil (phase 2), and castor oil (phase 3). The arrow indicates the point at which the 13 interface changes its curvature from positive to negative. Inset is the configuration of the doublet drawn to scale for the system marked with a cross. Of the various geometrical parameters of the doublet, we have selected $R = r_{12}/r_{23}$. The quantity $R_0 = b_1/b_3$ is the ratio of the radii of the undeformed drops; R is the ratio of the final radii of curvature of the 12 and 23 interfaces.