Table 2. Lewis acidity constants at 45°C from vapor pressure measurements of polar organic solvents in toluene and methylcyclohexane solutions.

Polar solvent	K_x
2,3-Butanedione	1.2 ± 0.3
Dimethylcarbonate	1.7 ± .2
Acetone	2.3 ± .2
Methoxyacetone	2.5 ± .2
Nitroethane	5.5 ± .4

coefficients (γ) of the polar solute at infinite dilution in the two hydrocarbons,

$$K_x = \frac{\gamma_1^\infty}{\gamma_1^{\infty\prime}} - 1 \qquad (6)$$

One method for determining the ratio $\gamma_1^\infty/\gamma_1^{\infty\prime}$ is through the measurement of distribution coefficients. Since saturated and unsaturated hydrocarbons are normally miscible, it is necessary to use a third solvent immiscible with the hydrocarbons, such as water, and to measure the distribution of the polar material between water and each hydrocarbon independently. After extrapolating these distribution coefficients (S) to infinite dilution of the polar species the effect of the water phase may be eliminated, and the desired ratio of activity coefficients in hydrocarbons may be obtained. That is, if

$$S_1^\infty = \frac{\gamma_1^\infty \text{ in saturated hydrocarbon}}{\gamma_1^\infty \text{ in water}} \qquad (7)$$

and

$$S_1^{\infty\prime} = \frac{\gamma_1^{\infty\prime} \text{ in unsaturated hydrocarbon}}{\gamma_1^\infty \text{ in water}}, \qquad (8)$$

then

$$\frac{S_1^\infty}{S_1^{\infty\prime}} = \frac{\gamma_1^\infty \text{ in saturated hydrocarbon}}{\gamma_1^{\infty\prime} \text{ in unsaturated hydrocarbon}}, \qquad (9)$$

which is the desired ratio. Lewis acidity constants for twelve polar solvents have been obtained in this way from the ratios of their activity coefficients in *n*-hexane and *p*-xylene (*4*) (Table 1).

Activity coefficients of polar solvents in hydrocarbon solutions have also been obtained from isothermal total vapor pressure measurements at 45°C by the data-reduction method of Barker (*5*). From the activity coefficients at infinite dilution, five Lewis acidity constants were calculated from Eq. 6; the results are given in Table 2. In this case comparison is made between the activity coefficients of the polar organic solvent in toluene and in methylcyclohexane.

The interesting feature of our measurements is that the volatility of a polar organic solvent is always lower when dissolved in an unsaturated hydrocarbon than when dissolved under the same conditions in a saturated hydrocarbon of approximately equal size. Although this has been known for many years, it has not been emphasized that this fact may be ascribed quantitatively to the acidic nature of the polar solvent.

The hypothesis that polar organic solvents form complexes with unsaturated hydrocarbons is also supported by our calorimetric data. We find that the heat of mixing of a polar solvent with an unsaturated hydrocarbon is always more exothermic than the heat of mixing with a saturated hydrocarbon of similar size. For example, at 45°C the heat of mixing of an equimolar mixture of acetone and cyclohexane is 410 cal/mole whereas that for an equimolar mixture of acetone and benzene is only 38 cal/mole (*6*); the lower heat for the benzene solution is due to the exothermic formation of a complex between the aromatic and the polar solvent. Further, since lower temperatures favor complex stability, we would expect that the heat of mixing for solutions of aromatics and polar solvents should decrease with falling temperature. We find that this is indeed the case. In Table 3 we report some calorimetric measurements which show the effect of temperature on the heat of mixing for three solutions of polar solvents and toluene (*7*).

The data of Schäfer (*8*) on mixtures of acetone with straight-chain normal paraffins also show increased exothermicity with decreasing temperature from 20° to −30°C. However, these heats of mixing are an order of magnitude larger than those reported in our work and, as Schäfer indicates, the positive temperature coefficients of the heats of mixing in his experiments are a result of the acetone-paraffin mixtures being near their critical solution temperatures. Schäfer confirms by Raman spectra that as the temperature is lowered acetone-*n*-paraffin systems become more and more incompletely mixed, which causes decreased endothermicity.

For mixtures of nitroethane, acetonitrile, and acetone with aromatics, such as toluene, the critical solution temperatures are much lower. Near room temperature the dispersion of the toluene molecules in solution should be nearly random. It appears probable that complex formation is the cause of reduced endothermicity in mixtures of polar solvents and aromatic hydrocarbons.

Table 3. Effect of temperature (T) on heats of mixing (h^M) in solutions which form complexes.

Mol fraction toluene	h^M (cal/mol) 45°C	h^M (cal/mol) 25°C	$\Delta h^M/\Delta T$ (cal/mol, °C)
	Acetone-toluene		
0.42	58.8	52.2	0.33
	Acetonitrile-toluene		
0.46	121.3	111.9*	0.38
	Nitroethane-toluene		
0.41	86.1	69.9	0.81

* At 20.5°C

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Precambrian Graphitic Compressions of Possible Biologic Origin from Canada

Abstract. *Further occurrences of elliptical graphitic bodies of possible biologic origin have been recovered from Proterozoic black shales of the Labrador Trough, Quebec. The bodies are plausibly organic because of constancy of form, manner of fossilization, and similarities to Michigan forms associated with extractable organic compounds.*

During the summer of 1964, graphitic compressions of possible biologic origin were collected from Proterozoic rocks of the Labrador Trough, Quebec, Canada (*1*). The strata from which the collections were made are

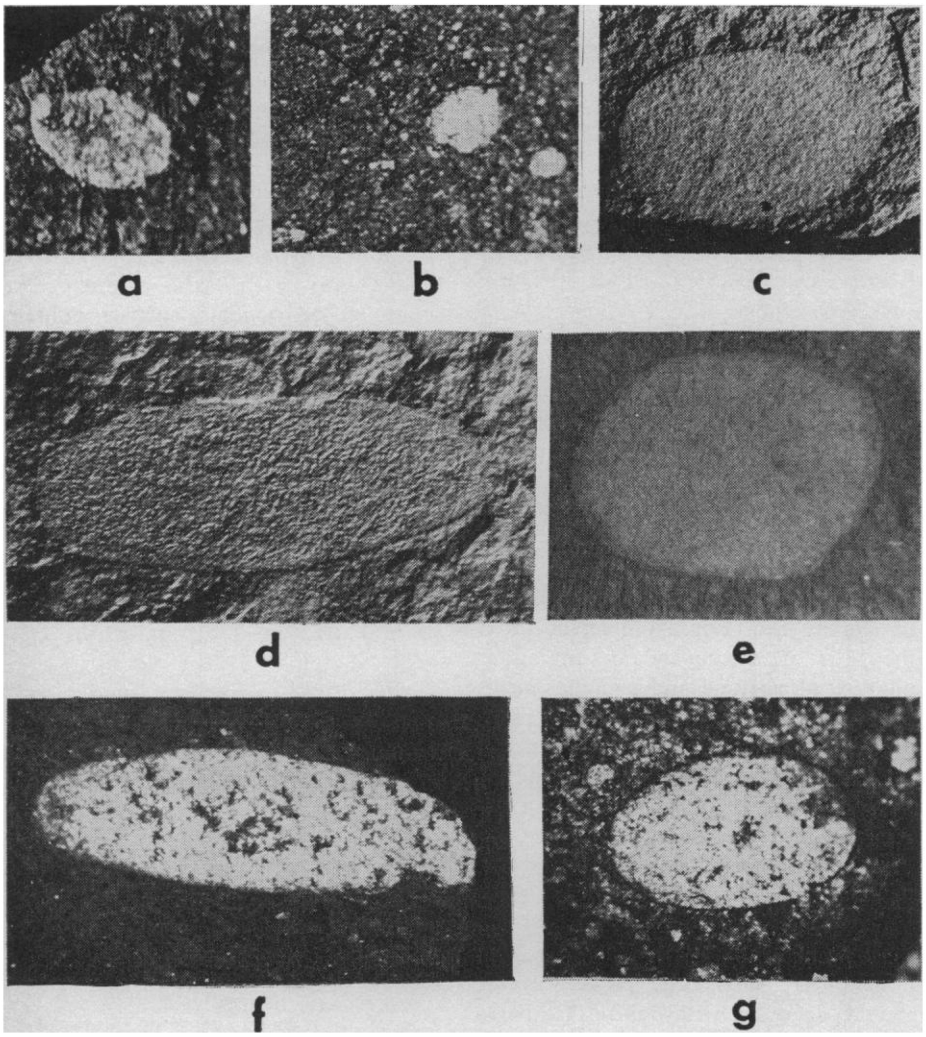

Fig. 1. Specimens *a* and *b* are High Falls; *c–e*, Schefferville; *f* and *g*, Michigamme Shale. *a*, Elliptical form, × 4; *b*, typical concentration of graphitic impressions; *c*, characteristic elliptical form, × 2; *d*, elongate form (axial ratio 3.2) showing characteristic surface texture and relief, × 4; *e*, irregular large form, × 1; *f*, elongate Michigamme form (axial ratio 3.3), × 4; *g*, Michigamme form, × 3.

relatively unmetamorphosed shales which appear to hold considerable promise for research on Proterozoic life. The black shales contain numerous small, compressed, elliptical, carbonized, and occasionally pyritized bodies. On careful disaggregation, flattened three-dimensional forms are found which may represent internal molds.

Small, graphitic bodies were initially discovered in carbonaceous, fissile shales exposed 0.8 km south of High Falls in a bluff on the east side of Swampy Bay River, 56°7′15″N, and 68°19′30″W. This locality is approximately 179 km northwest of Schefferville, Quebec. The shale yielding the graphitic bodies is approximately 1.2 m thick and occurs about 0.6 m above a thin bed of carbonaceous limestone. The limestone bed lies approximately 450 m above a massive stromatolitic limestone.

As many as eight to ten of the graphitic bodies can be observed within a square centimeter along the bedding planes (Fig. 1, *a* and *b*). The majority of the compressions are elliptical, although circular and irregular forms are also present. Major axes of larger forms range from 1.5 to 4.5 mm. Measurements along minor axes range from 1.0 to 3.5 mm. The average axial ratio (major axis/minor axis) obtained from measurements of ten specimens from High Falls was 1.67.

A second group of samples was collected at Schefferville, Quebec. Here, the graphitic bodies occur along the bedding planes of hard, brittle, carbonaceous shales of the Attikamagen Formation. The Schefferville specimens (Fig. 1, *c–e*) are larger and show better preservation than those collected at High Falls. An axial ratio of 2.09 was obtained from measurements of ten of the specimens from Schefferville. The surfaces of the Schefferville compressions exhibit a peculiar granular texture which may be a reflection of a similar texture in the cuticle-like surface of the imprinted body (Fig. 1*d*). The dimensions of the Schefferville forms indicated a range of 5.0 to 37.0 mm for the major axes, and 2.2 to 28.0 mm for the minor axes.

Graphitic forms almost identical to those described here were reported by Tyler, Barghoorn, and Barrett from the Huronian Michigamme Shales of the Iron River District of Michigan (*2*). The axial ratios obtained for the Michigamme material were similar to those obtained from the Schefferville specimens. In addition, the elliptical bodies occur on bedding planes in carbonaceous shales, and the method of preservation is almost identical with that noted at the Schefferville and High Falls localities. Tyler *et al.*, after exhaustive tests, concluded that their specimens represented compressed remains of organisms not dissimilar from primitive free-floating blue-green algae. Organic compounds extracted from the graphitic anthracites associated with the Michigamme shales provided additional evidence for the organic origin of the elliptical bodies. Barghoorn kindly loaned us specimens of the Michigamme Shale for comparison (Fig. 1, *f* and *g*). The elliptical structures are almost identical in rocks of both regions.

Similarities between the Michigamme shale specimens and those from Quebec, the constancy of shape of all the specimens, and their preservation by carbonization strongly indicate their biologic origin. These organisms apparently had wide geographic distribution during the Precambrian.

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References and Notes

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