

## THE COMPOSITION OF *PYRITOSPHAERA* *BARBARIA* LOVE 1957

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ABSTRACT. A bulk sample of *Pyritosphaera barbaria* Love 1957 is shown by microchemical analysis, following other indications, to be dominantly organic in composition.

*Pyritosphaera barbaria* was isolated (Love 1957) by removal of the pyrite by nitric acid from pyrite microspheres of the Pumpherston Shell Bed and adjacent strata of the Scottish Lower Carboniferous Lower Oil Shale Group. The residual bodies, which average about  $8\ \mu$  in size and are of much the same diameter as the spheres from which they come, are spherical and microgranular in appearance. They were regarded as being organic on the basis of their pale brown colour, translucency, isotropic character, and chemical inertness except to further oxidation or combustion. Further they were regarded as the remains of micro-organisms on the basis of the regularity of their form, coupled with their great abundance in an environment in which such material might be expected to flourish. The suggestion that they might have had an active significance in the formation of the sulphide is not of immediate concern here. Similar forms were obtained by Love (1962*a, b*) from pyrite spheres of Upper Palaeozoic and Mesozoic rocks and much detail of the manner of occurrence was noted. Somewhat similar forms were recorded by Love and Murray from pyrite spheres from Recent sediments.

Direct analysis of the material of *P. barbaria* of Carboniferous age has been made difficult both by problems in adequately concentrating the pyrite spheres from the rock and, of greater importance, in obtaining samples in which the pyrite spheres, and thus the *P. barbaria* bodies, were free from other organic material which often encloses them. A sample recently examined, however, conformed with the latter requirement as far as detailed microscopic examination of the pyrite and of the residues could show, and yielded a good separation of pyrite spheres. It came from Namurian marine shale of R<sub>1</sub> age, from River Noe, Derbyshire, England.

The pyrite was dissolved with brominated concentrated nitric acid acting for one hour at room temperature and the residue consisted dominantly of *P. barbaria*. Preliminary examination of a portion by emission spectrograph between copper electrodes indicated at least 35 per cent. of carbon by the method developed by Dennen (1957), whose observation that a substantial upward correction may be necessary is amply borne out. Electron probe micro-analysis of the spherical bodies in another part of the sample indicated (to a 1 per cent. limit) the absence of iron (which might be expected as insoluble ferric oxide), and of sulphur, silica, calcium, and other metallic elements. Carbon cannot be detected by this method. On a third portion normal microchemical analysis indicated 56 per cent. carbon. Based on bulk analysis of Carboniferous 'kerogen' (Down 1939) this might represent as much as 80 per cent. organic matter but perhaps as low as 70 per cent. if the oxidizing acid had removed any organic material, as indeed is indicated by the C:H ratio being 15.7:1 for the oxidized sample compared with that of 11.3:1 for the

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unoxidized material quoted below. The balancing weight of the sample, proportionately less by volume, was observed to consist of heavy minerals while the *P. barbaria* material was observed to be only a little heavier than water. Infra-red spectroscopy showed the presence of undoubted organic compounds, since C-H bonds, carbonyl groups, and possibly N-H groupings were recognized.

Part of a parallel original unoxidized sample of pyrite spheres was shown by micro-chemical analysis to consist of approximately 85 per cent. pyrite (40.9 per cent. Fe, 45.1 per cent. S) and 3.4 per cent. carbon by weight. The latter perhaps represents 4.25 per cent. of organic material by weight. Heavy minerals and some insoluble residue from the use of hydrofluoric acid were seen to be present (giving 11.2 per cent. ash) but no visible organic matter. A ratio of organic matter to pyrite in the spheres of 1:20 by weight is therefore given.

This demonstration of the organic composition of *P. barbaria* puts the argument that these are remains of micro-organisms occurring *in situ* in the pyrite on a surer basis but is not in itself proof. The data will be of value for comparison with other sediments but this work is not complete and will be discussed elsewhere (Love, *in the press*).

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#### REFERENCES

- DENNEN, W. H. 1957. Spectrographic determination of carbon in sedimentary rocks by using direct-current arc excitation. *Spectrochim. Acta*, **9**, 89-97.
- DOWN, A. L. 1939. The analysis of the Kerogen of Oil Shales. *J. Inst. Petrol.* **25**, 230-7.
- LOVE, L. G. 1957. Micro-organisms and the presence of syngenetic pyrite. *Quart. J. geol. Soc. Lond.* **113**, 429-40.
- 1962a. Biogenic primary sulfide of the Kupferschiefer and Marl Slate. *Econ. Geol.* **57**, 350-66.
- 1962b. Further studies on micro-organisms and the presence of syngenetic pyrite. *Palaontology*, **5**, 449-59, pl. 63, 64.
- Pyrite spheres in sediments. *The biogeochemical cycle of sulfur isotopes: Symposium*, ed. M. L. Jensen, Yale University. *In the press*.
- and MURRAY, J. W. 1963. Biogenic pyrite in Recent sediments of Christchurch Harbour, England. *Amer. J. Sci.* *In the press*.

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