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Intercalation of natural flake graphites

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Natural flake graphites are characterized in terms of their ability to form intercalation compounds. Factors such as amounts and distribution of mineral matter, extents of intercalation by bisulphate and bromine, flake thickness and fissuring which control extents of intercalation are examined. Differences in stabilities of intercalates in the natural flake graphites are assessed. Techniques used to examine the flake graphites include image analysis to assess flake thickness and the degree of fissuring as well as bromine intercalation and desorption as an indication of crystal perfection in flake graphites. Amounts of mineral matter in the flakes and the amount and distribution of crystalline sulphur (not previously reported) in the intercalated flake graphites are studied using EDAX. The intercalated graphites were exfoliated at 1200° C and examined by SEM to assess their extent of expansion and the structure and extent of pinning within the graphite flakes. Results indicate that flake thickness is a primary factor influencing extents of intercalation in these materials, the optimum thickness for bromine intercalation being 25 μm. Bromine uptake could indicate the perfection of stacking within a graphite. Mineral impurity in the graphite flake is of importance as it influences flake thickness and cleavage properties.

1. Introduction

The well-orientated graphites (WOG) and natural graphites have the ability to form intercalated compounds [1–3]. The chemical potential for such reactions is electron transfer, from the graphite lamellae of carbon atoms as when bromine is intercalated, or into the graphitic lamellae when, for example, potassium is intercalated. Such studies are of interest to the chemist and physicist because of the relatively high electrical conductivities of the intercalates [2].

The well-orientated graphites (WOG) are expensive materials and are difficult to obtain. Synthetic polycrystalline graphites as used in arc-electrode manufacture are not sufficiently anisotropic and crystalline for worthwhile intercalation studies. The natural graphites, mined as single flakes a few millimetres in size are adequately crystalline for intercalation studies. However, despite similar visual appearances these natural flake graphites display significant differences in their intercalation ability.

This work characterizes this intercalation ability by studying the bisulphate and bromide intercalation compounds. To this end, this paper reports EDAX analyses of mineral matter in the flakes and of sulphur in the bisulphate intercalate, extents of bromine uptake [4] and extents of so-called bromide residue compound [5], flake dimensions and extent of fissuring within flakes as well as a scanning electron microscopy examination of the mode of exfoliation of bisulphate intercalation compound.

2. Materials used

Natural flake graphites were obtained from five sources: China, Brazil, Madagascar, Russia and Sri Lanka.

3. Experimental techniques

Bisulphate intercalated graphites were prepared by intercalation with a mixture of H_2SO_4/HNO_3 according to standard methods [3].

Exfoliated graphite was prepared from the bisulphate intercalate by dropping into a furnace held at $\sim$ 1200° C.

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3.1. SEM and energy dispersive analysis of X-rays (EDAX) study

A comparative measure of the elements (above silicon) present on cleaved surfaces of flake graphites was made on the natural flake graphites. Each of the flake graphites was first cleaved using sellotape. The flakes were examined using a JSM35 scanning electron microscope with the EDAX facility.

A semi-quantitative measurement of the amounts of sulphur and other elements of significant content was made on the bisulphate intercalated graphites. Each of the intercalated graphites was first cleaved using sellotape to expose the cleaved surface. The distribution of sulphur over the basal planes was recorded. The distribution of sulphur over the prismatic edge of the flakes of the bisulphate intercalated graphites was also monitored. The flakes were mounted in epoxy resin and the blocks cut so that the prismatic edge of the flakes was exposed.

The surfaces were prepared for SEM by polishing with progressively finer grades of diamond lapping compounds. "Hypres Diamond Lapping Compounds" (4 μm particle size), were used to remove scratches to obtain a polish (3 μm particle size), and to upgrade the polish (1 μm particle size). The graphites were polished on a rotating Selvyt cloth kept taut and wet with Hypres fluid. Diamond compounds were used rather than alumina powder so that residual alumina would not be detected preferentially in the study of mineral matter associated with the sulphur.

3.2. Bromine intercalation

The intercalation of bromine into the natural flake graphites was carried out in a vacuum apparatus. The apparatus consisted of a manifold to which two sample tubes, a bromine reservoir, a gas inlet system and a pumping system were attached. Silicone grease was used to seal the ground glass joints.

The rates of bromine uptake were measured using a McBain spring system. This operates by measuring the change in weight of the sample on adsorption of the vapour as an extension of a silica spring.

The weighed graphite sample (~ 0.1 g) was contained in a bucket suspended on the silica spring. The graphite was outgassed at 373 K until no further weight loss occurred. Liquid nitrogen was placed around the bromine reservoir and the bromine condensed into the evacuated reservoir. The liquid nitrogen was then removed from around the bromine reservoir and bromine vapour allowed to intercalate into the graphite flakes. Intercalation continued for 24 h to reach equilibrium at a vapour pressure of bromine of 22.3 kPa at 298 K. Amounts of adsorption were monitored throughout. Sri Lankan graphite, cleaved using sellotape to give flakes of reduced thickness, was also studied.

Liquid nitrogen was now placed around the bromine reservoir. Extents of desorption were monitored until a new equilibrium position was established with the bromide residual compound [5]. The amount of bromide residue was measured by the extension of the silica spring and confirmed by reweighing the residue compounds on a microbalance. Bromide residue compounds result from the trapping of bromide within the flake graphites.

3.3. Image analysis

The natural and intercalated flake graphites were mounted in resin blocks, cut and ground at right angles to the basal plane orientation to obtain the prismatic edge presentation of the flakes. The blocks were polished using a paste of 5/20 alumina powder (to remove most of the scratches), 3/50 alumina powder (to obtain a polish) and finally a gamma alumina powder to up-grade the polish. The resin block was rubbed on a rotating Selvyt cloth, kept taut and wet. Finally, the resin blocks were washed and cleaned in an ultrasonic bath to remove any residual powder.

The polished surfaces were analysed using a Vickers M17 microscope linked to a semi-automatic image analysis system. Flake outlines were displayed on a TV monitor via a TV camera mounted on the microscope. The outlines of the flakes (prismatic edge presentation) were traced using a graphics tablet and the traced outlines stored as digitized data. These data allowed measurements of flake thickness (in prismatic edge) and the calculation of percentage area of fissures within the prismatic edge presentations of natural and intercalated graphite [6]. The average number of fissures per flake can be obtained so providing a value for average width of fissures. About 300 flakes from each sample were used in the statistical image analysis.

3.4. SEM analyses of exfoliated graphites

The exfoliated graphites, prepared from the bisul-

TABLE I EDAX analysis of mineral matter on cleaved surfaces of natural flake graphites

Natural flake graphite	Relative peak intensity EDAX analysis				
	Al	Si	S	K	Fe
China (C)	12	45	9	–	–
Brazil (B)	5	34	–	10	–
Madagascar (M)	26	45	24	–	2
Russia (R)	16	40	–	8	2
Sri Lanka (SL)	22	32	–	10	–

phate intercalates, were mounted on aluminium stubs and gold-coated to examine their morphology using the JSM35 scanning electron microscope.

3.5. Thermogravimetric analyses of bisulphate intercalated flake graphites

The thermal decomposition profiles of the bisulphate intercalated graphites were monitored using the Stanton Redcroft Thermal Analyser. 5 mg intercalated graphite were placed in a crucible and transferred to the balance in the furnace. The graphites were heated to 800° C at a rate of 5° C min^{-1} under nitrogen and the weight loss as a function of temperature was recorded.

4. Results

4.1. SEM and energy dispersive analysis of X-rays (EDAX) study

Table I shows the intensity of the peaks for each of the non-carbon materials detected in the flake graphites.

Figs. 1 to 6 are SEM micrographs of the cleaved surfaces of the bisulphate intercalated flake graphites from China, Brazil and Russia.

4.2. Bromine intercalation

Table II gives the total bromide uptake (after 27 h) as percentage weight increases for all the natural flake graphites. The extents of bromine uptake in 24 h are shown in Fig. 7. Fig. 8 shows the desorption of bromine from the intercalated flake graphites. Table II gives the final wt% bromide residue compound following desorption under vacuum for 12 h.

TABLE II Total bromine uptake by natural flake graphites after 24 h in bromine vapour

Natural flake graphite	Total bromine uptake (wt%)	Final bromine residue (wt%)
China	83	1
Brazil	74	15
Madagascar	76	11
Russia	70	15
Sri Lanka	51	10
Sri Lanka (cleaved)	80	–

4.3. Image analyses

Table III gives the average flake thickness for the natural flake graphites, the percentage of this average thickness taken up by fissures, the average number of fissures per flake and the average fissure width. Table IV gives the percentage of flakes in defined thickness ranges of the natural flake graphites. Table V gives the percentage of area of projection of *natural* flakes taken up by fissures in the prismatic edge, and the variation of this percentage with flake thickness.

The average flake thickness for the bisulphate intercalated flake graphites together with the percentage of fissures within that thickness and the increase in thickness developed during intercalation by sulphuric acid, are given in Table VI.

Table VII gives the percentage of intercalated flakes in defined thickness ranges. Table VIII, like Table V, gives the percentage of the *intercalated* flake thickness (in different thicknesses) taken up by fissures, in prismatic area of projection.

4.4. SEM analyses of exfoliated graphites

Figs. 9 to 12 are SEM micrographs of the Chinese and Sri Lankan exfoliated graphites.

TABLE III Average flake thickness of natural flake graphites

Natural flake graphite	Average flake thickness (μm)	Area of flake thickness as fissures (%)	Average no. of fissures per flake	Average fissure width (μm)
China	24	14	0.82	7.3
Brazil	35	28	1.58	5.7
Madagascar	44	19	1.42	10.8
Russia	24	17	0.85	5.16
Sri Lanka	75	0	0	0

TABLE IV Percentage of flakes in each thickness range (natural flakes)

Natural flake graphite	Range of flake thickness (μm)												
	0–7	8–15	16–23	24–31	32–39	40–47	48–55	56–63	64–71	72–79	80–87	88–95	> 95
China	10	28	23	17	8	6	4	3	–	–	1	–	–
Brazil	3	10	23	18	15	8	8	4	4	2	2	2	1
Madagascar	3	9	17	17	16	14	10	4	3	2	1	3	1
Russia	15	31	20	11	11	7	2	1	1	1	–	–	–
Sri Lanka	–	4	6	5	7	10	7	4	8	13	3	6	27

TABLE V Percentage of area of projection of prismatic edge of natural flakes taken up by fissures – variation with flake thickness

Natural flake graphite	Percentage of area of projection taken up by fissures for flake thickness (μm):						
	0–15	16–31	32–47	48–63	64–79	80–95	> 95
China	0	6	47	64	19	0	0
Brazil	29	25	30	29	0	0	0
Madagascar	0	11	18	17	35	40	60
Russia	11	17	38	0	0	0	0
Sri Lanka	0	0	0	0	0	0	0

4.5. Thermogravimetric analyses of the bisulphate intercalated flake graphites

Thermogravimetric analyses of the bisulphate intercalated flake graphites (Fig. 13) show the relationship of weight loss to temperature.

5. Discussion

5.1. Energy dispersive analyses of X-rays (EDAX) study

The results of the EDAX study indicate that most of the mineral matter appears to be present in the form of aluminium silicates, probably as clay minerals (Table I). The sulphur in the bisulphate intercalated graphites is often in juxtaposition with silicon but not intimately associated with it. When the mineral matter is in the form of clay minerals, the natural flake has a tendency to cleave preferentially along the plane associated with the clay minerals. Therefore, the presence of mineral matter may influence flake thickness.

Figs. 1 and 2 are micrographs of cleaved surfaces of the Chinese intercalated flake graphite with Fig. 1, position A showing an area of graphite with sulphur particles. Fig. 2, positions B and C shows particles and clusters of sulphur. The sulphur is formed as crystalline needles and is evenly distributed over the surface of the flakes. No other element was detected with these sulphur crystals.

TABLE VI Average flake thickness of intercalated flake graphites (HSO_4^-)

Intercalated flake graphite	Average flake thickness (μm)	Average % fissures
China	77 (220)*	9
Brazil	103 (195)*	24
Madagascar	64 (45)*	21
Russia	59 (145)*	20
Sri Lanka	106 (40)*	–

*% increase in thickness after intercalation.

Fig. 3, position D, shows small particles ($\sim 5\,\mu$m) of sulphur on the basal planes of the Brazilian graphite, and the prismatic edges with accumulation of sulphur particles of the intercalate are shown at E in Fig. 4. Position F shows the sulphur particles to be more dispersed over the surfaces of the basal planes (cf. Fig. 2). EDAX analysis indicated that the particles were only of sulphur. The Madagascan graphite had similar properties.

Figs. 5 and 6 are SEM micrographs of the cleaved surface of the Russian intercalated flake graphite. EDAX analyses of this intercalate indicated that the sulphur was sparsely distributed over the basal planes, position G. Higher concentrations of sulphur occur along the fracture lines of the basal planes, H, Fig. 6. Sulphur in the Sri Lankan graphite was too low in content to be studied.

5.2. Bromine intercalation

The Chinese flake graphite had the highest and the Sri Lankan the lowest extents of bromine uptake (Table II). Boehm *et al.* [4] found that extents of bromine uptake are lower the less perfect is the graphite. This would suggest that the Chinese intercalated flakes have the more perfect stacking order with the Madagascan, Brazilian and Russian intermediate and the Sri Lankan as the least perfect.

However, when the Sri Lankan flake graphite was cleaved into thinner flakes using sellotape, and these intercalated with bromine, it then exhibited the second highest amounts of bromine uptake. This is because intercalation of bromine is controlled by flake thickness and cleavage of the flakes reduces the extent of imperfection within the flakes.

After 24 h, the Chinese and cleaved Sri Lankan flake graphite took up bromine to extents of 83 and 80 wt %, respectively (Table II). The bromine

TABLE VII Percentage of flakes in each thickness range (intercalated flakes)

Intercalated flake graphite	Percentage of flakes for flake thickness (μm) of:												
	0–7	8–15	16–23	24–31	32–39	40–47	48–55	56–63	64–71	72–79	80–87	88–95	> 95
China	–	–	1	5	10	8	2	12	8	8	12	9	25
Brazil	–	–	–	1	3	3	1	3	13	10	10	8	48
Madagascar	–	–	6	9	9	9	13	12	8	7	7	5	15
Russia	–	–	3	10	12	15	11	14	13	6	5	3	8
Sri Lanka	–	–	–	–	2	5	4	9	7	9	6	8	50

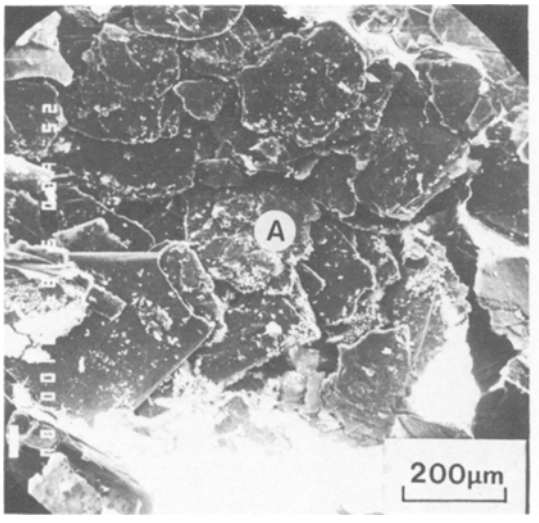

Figure 1 SEM micrograph of cleaved surface of intercalated flake graphite from China showing crystals of sulphur, positions A, C and particles, position B.

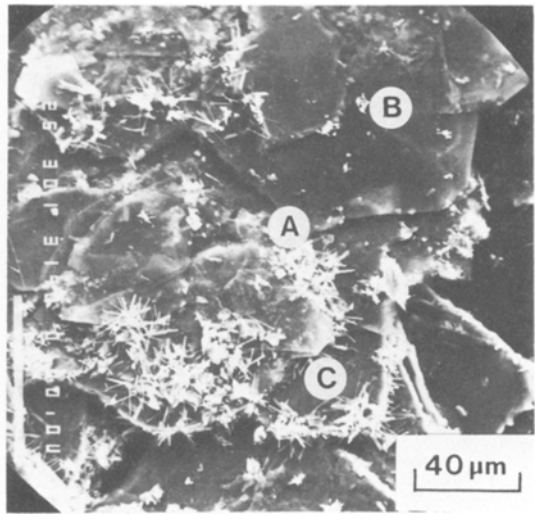

Figure 2 SEM micrograph of cleaved surface of intercalated flake graphite from China showing crystals of sulphur, positions A, C and particles, position B.

intercalation compound, C_8Br, has 45 wt% of bromine, i.e. 83 wt% increase of original graphite material [1]. The Madagascan and Brazilian flake graphites have similar amounts of bromine. Their bromine uptake after 24 h was 76.7 and 74.5 (wt%), respectively, indicating similar degrees of stacking order. The Russian flake graphite took up 70 wt% bromine after 24 h and the Sri Lankan flake graphite the lowest amount of bromine uptake, ~ 50 wt%, indicating the lowest order of stacking. The desorption of the bromine from the original flakes (Fig. 8) occurred rapidly for the first 2 h, after which a plateau developed. The Chinese flake graphite gave the lowest value of bromide (1%) in the residue compound.

5.3. Image analysis

The image analysis (Table III) shows that the Chinese and Russian flake graphites have the lowest average thickness of 24 μm and also the lowest percentage of fissure area (14% and 17%, respectively). The average number of fissures per flake for the Chinese and Russian flakes are similar, 0.82 and 0.85, respectively. The average fissure width of the Chinese flakes was larger (7.3 μm) than the Russian flakes (5.2 μm).

The Brazilian and Madagascan flakes had average thicknesses of 35 and 44 μm and contained 28% and 19% fissures, respectively. The average number of fissures per flake is higher than the Chinese and Russian, being 1.58 and 1.42, respectively. The average fissure width of the Brazilian flakes is lower (5.7 μm) than the Madagascan flakes (10.8 μm), indicating the Brazilian flakes contain many thin fissures.

For the natural flake graphites, the presence of wide (> 7 μm) fissuring is advantageous in flakes > 48 μm thick because they facilitate an average flake thickness of 24 μm by splitting along the fissures.

Table IV shows the percentages of flakes in each thickness range of the natural flake graphites.

TABLE VIII Percentage of area of projection of prismatic edge of intercalated flakes taken up by fissures – variation with flake thickness

Intercalated flake graphite	Percentage of area of projection taken up by fissures for flake thickness (μm) of:						
	0–15	16–31	32–47	48–63	64–79	80–95	> 95
China	0	4	12	30	15	15	25
Brazil	0	0	0	16	22	27	34
Madagascar	13	25	17	27	20	0	27
Russia	0	15	15	26	20	29	30
Sri Lanka	0	0	0	0	0	0	0

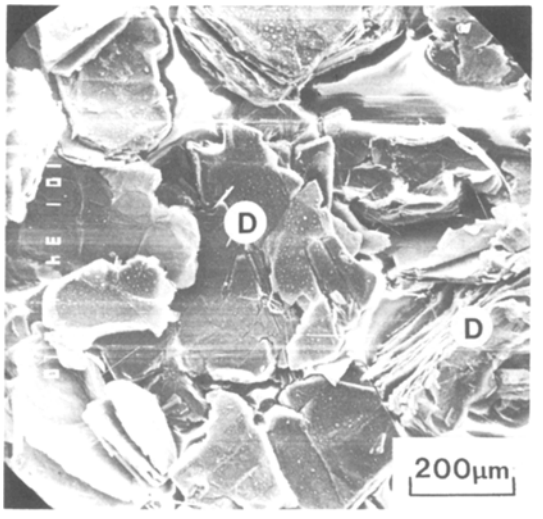

Figure 3 SEM micrographs of cleaved surface of intercalated flake graphite from Brazil showing isolated particles of sulphur, D, F, and accumulations at prismatic edges, E.

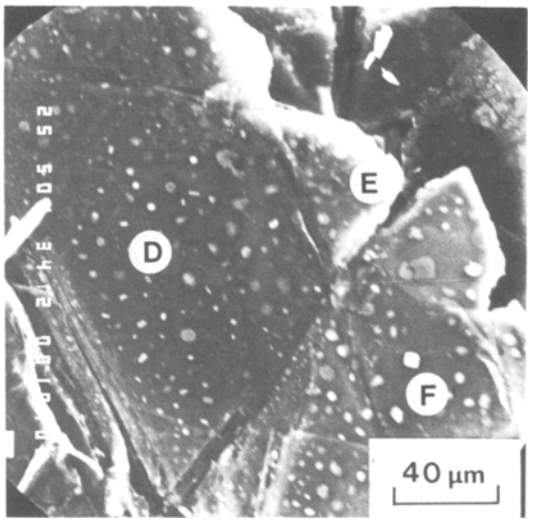

Figure 4 SEM micrographs of cleaved surface of intercalated flake graphite from Brazil showing isolated particles of sulphur, D, F, and accumulations at prismatic edges, E.

The Chinese and Russian flakes had a considerably higher proportion of flakes less than 32 μm (~ 70% to 80%) and few flakes > 71 μm thick. Flake graphites from Sri Lanka, Madagascar and Brazil showed a significantly lower proportion of flakes less than 23 μm thick than Chinese and Russian flake graphites. The Sri Lankan flake graphite had 27% of flakes greater than 95 μm thickness.

Table V shows the variation of percentage of fissure area with flake thickness in natural flake graphites. The Chinese flake graphite contains fissures 7.3 μm wide mainly in flakes 48 to 63 μm thick and no fissures in flakes less than 15 μm thick. The Brazilian flake graphite has a high proportion of fissures 5.7 μm wide in flakes less than 31 μm thick. It is thought that fissures in flakes less than 31 μm are undesirable as they facilitate splitting of flakes on intercalation. Fissures are desirable in the natural flake graphites greater than 31 μm to promote a mean flake thickness of ~ 25 μm. The Madagascan flake graphite has 60% of fissures in flakes greater than 95 μm.

The increase in thickness after bisulphate inter-

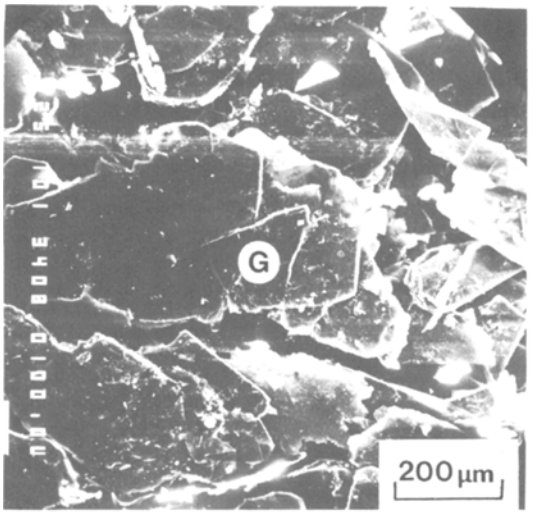

Figure 5 SEM micrographs of cleaved surface of intercalated flake graphite from Russia showing isolated particles of sulphur, G, and accumulations at H.

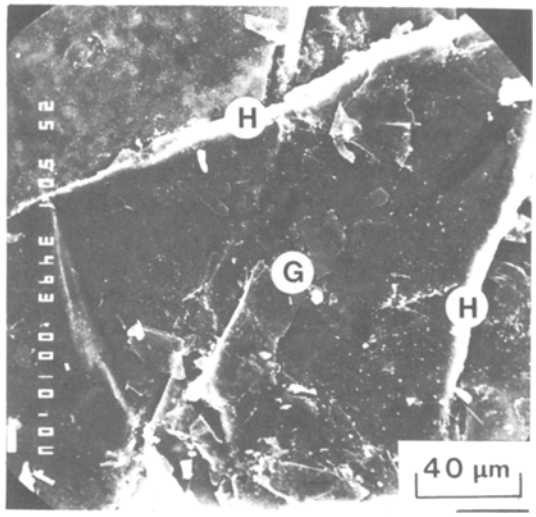

Figure 6 SEM micrographs of cleaved surface of intercalated flake graphite from Russia showing isolated particles of sulphur, G, and accumulations at H.

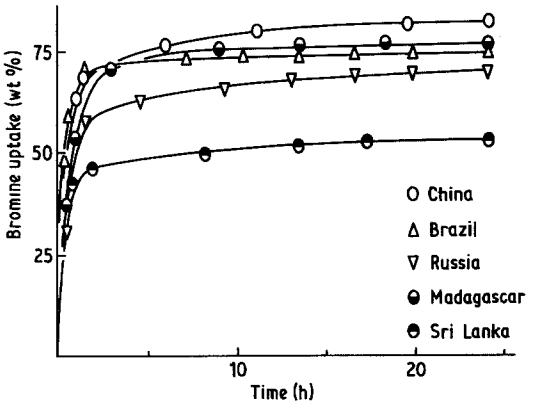

Figure 7 Variation of extents of bromine intercalation with time at 298 K for the natural flake graphites.

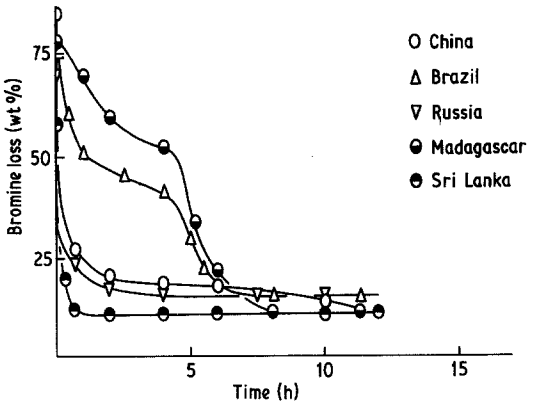

Figure 8 Variation of extents of bromine desorption with time at 298 K in vacuum, for the natural flake graphites.

calation (Table VI), shows that the Chinese intercalated graphite has the highest increase in thickness of ~220%. The Brazilian and Russian intercalated flakes showed intermediate increases of 195% and 145%, respectively. The Madagascan and Sri Lankan graphites showed the lowest percentage increase in thickness after intercalation of 45% and 40%, respectively.

The percentages for flake thickness (Table VII) of the intercalated flake graphites indicated a general shift in flake thickness towards thicker flakes ($>100\,\mu m$) compared with the natural flake graphites.

The Chinese and Brazilian bisulphate intercalated flake graphites had a high percentage of flakes $>95\,\mu m$ thickness, indicating a high extent of bisulphate intercalation. The distributions of Sri Lankan intercalated flake graphite showed no significant change from that of the natural flakes indicating no intercalation had occurred.

Table VIII shows the percentage of thickness area taken up by fissures for intercalated flake graphites. The Chinese intercalated graphite showed the least amount of fissuring and contained few fissures in flakes less than $31\,\mu m$ thick. However, the Madagascan and Russian intercalated graphites contained fissures in flakes less than $31\,\mu m$ thick (up to 25%). The Madagascan intercalated flake graphite had a lower percentage of fissures in flakes greater than $95\,\mu m$ (27%) than occurred in the natural flakes (60%). This indicates that the natural flakes may have split into thinner flakes on intercalation along the planes of weakness (fissures) and formed 2 to 3 intercalated flakes from what was originally one flake.

5.4. SEM analysis of exfoliated graphites

Scanning electron microscopy provides detailed information about the structure of the exfoliated graphites. Figs. 9 and 10 are SEM micrographs of

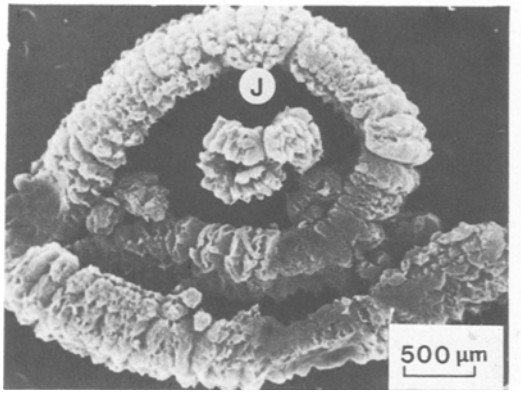

Figure 9 SEM micrographs of exfoliated Chinese graphite, showing uniform expansion, J, and disruption to the structure, K.

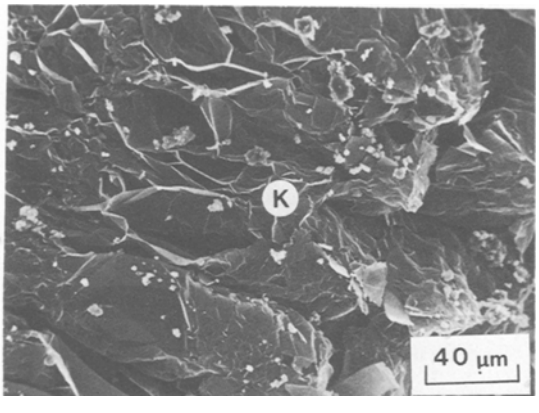

Figure 10 SEM micrographs of exfoliated Chinese graphite, showing uniform expansion, J, and disruption to the structure, K.

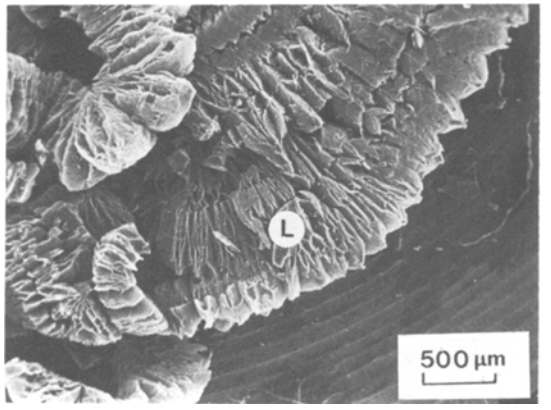

Figure 11 SEM micrograph of exfoliated Sri Lankan graphite showing structural pinning at L and M.

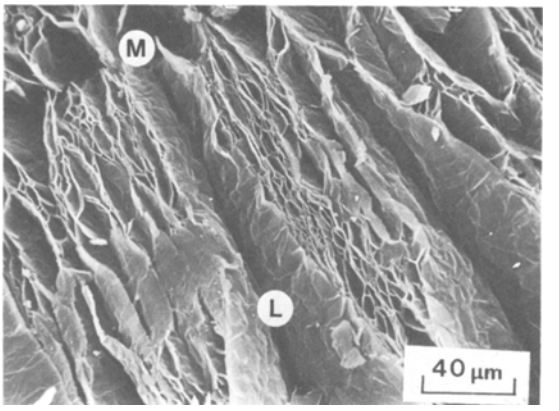

Figure 12 SEM micrograph of exfoliated Sri Lankan graphite showing structural pinning at L and M.

the Chinese exfoliated graphite. The process of expansion was uniform throughout the graphite, J, Fig. 9. From the disordered array of sheets of graphite, K, Fig. 10, shows that the exfoliation was disruptive to structure of the intercalated flake. The Chinese exfoliated graphite was the most heavily disrupted of the graphites studied.

Figs. 11 and 12 are SEM micrographs of the Sri Lankan exfoliated graphite showing that limited expansion had occurred which was restricted because of structural pinning which prevented exfoliation, e.g. L, M, Fig. 12.

5.5. Thermogravimetric analyses of the bisulphate intercalated flake graphites

The thermogravimetric analyses of the bisulphate intercalated graphites (Fig. 13) show that the Chinese intercalated flake graphite had the highest percentage weight loss of ~ 25%. The Sri Lankan intercalated graphite showed the lowest percentage weight loss of 4% indicating that very little intercalation had occurred. This is in good agreement with the SEM analyses of the exfoliated graphites which indicated that the Chinese exfoliated graphite showed the greatest amount of disruption caused by exfoliation, with the Sri Lankan graphite showing restricted expansion.

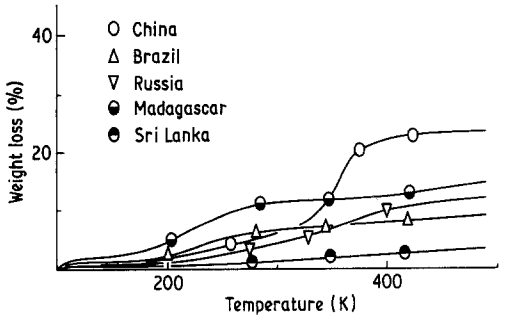

Figure 13 Thermogravimetric analyses of bisulphate intercalated flake graphite showing weight loss as a function of temperature.

6. Conclusions

1. EDAX analyses of the distribution of mineral matter present on cleaved surfaces indicate that mineral matter was not intimately related to the distribution of sulphur from bisulphate intercalate. The presence of crystalline sulphur in bisulphate intercalates is not previously reported. Mineral matter may control the flake thickness, with flakes preferentially splitting where clay minerals are associated with fissures in the flakes.

2. Bromine intercalation is a useful technique to indicate the perfection of natural flake graphites. The uptake of bromine increases the greater the graphite perfection. The Chinese graphite had the highest uptake of bromine and lowest value for the residue compound.

3. Optical microscopy linked to an image analysis system enabled measurement of flake thicknesses, this being a primary factor influencing bromine intercalation. Natural flakes suitable for such studies were found to have a mean thickness of 24 μm. They had few individual flakes greater than 48 μm thick and the majority of flakes were between 16 and 40 μm thick.

4. The extent of fissuring in natural flake graphites influences extents of bromine intercalation. Fissures in natural flake graphites are advantageous for intercalation in flakes greater than 31 μm by providing an effective flake thickness of ~ 25 μm.

References

1. A. R. UBBELOHDE and F. A. LEWIS, "Graphite and its Crystal Compounds" (Oxford University Press, London, 1960) p. 121.
2. A. R. UBBELOHDE, *Chem. Ind.* 15 August, no. 16 (1983) 636.
3. M. C. ROBERT, M. OBERLIN and J. MERING, "Chemistry and Physics of Carbon", Vol. 10, edited by P. L. Walker Jr (Marcel Dekker, New York, 1979) p. 141.
4. H. P. BOEHM and I. PFLUGMACHER, Extended Abstracts, 10th Biennial Conference on Carbon, Bethlehem, Pennsylvania, 27 June–2 July 1971 (American Carbon Society) p. 259.
5. G. A. SAUNDERS, A. R. UBBELOHDE and D. A. YOUNG, *Proc. Roy. Soc.* A-271 (1963) 499.
6. J. G. HOOLEY, *Carbon* **10** (1972) 155.

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