On the Physical and Geometrical Properties of Graphite.

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E D. CLARKE was the first mineralogist by whom crystallised graphite was observed and examined. As early as 1821,* he described some graphite crystals from the mines at Borrowdale, in Cumberland. Clarke designated graphite by the name of " carburet of iron " or " plumbago," and stated its form to be that of an oblique four sided prism, the obtuse angle of which was found by measurement with the contact goniometer (" the common goniometer ") to be 118°.

Since then crystallised graphite has been examined by several mineralogists. Haidinger† and Kenngott‡ have pronounced the system of axes to be hexagonal, but Nordenskiöld,§ who has made the most complete research, is of Clarke's opinion, that the system of crystallisation is monoclinic. The determinations of Nordenskiöld have been most generally accepted, and quoted in most manuals. In the present paper the twins of

* Annals of Philosophy, New Series, vol. ii. p. 417.

† Handbuch der bestimmenden Mineralogie, p. 513, 1845.

‡ Sitzungsber. d. math. naturw. Classe der Wiener-Akad. vol. xiii. p. 469, 1854.

§ Pogg. Ann. vol. xcvi. p. 110, 1855.

graphite, its gliding-faces " *Gleitfläche*," its percussion-figures, the nature of its etching-figures, and its relative conduction of heat in different directions will be described. The numerical values of the angle measurements made by me have been left out of this brief paper, as they have not led to any unequivocal result ; with regard to several other points, the reader is referred to my more detailed account in " Ofversigt af Kongl. Svenska vetenskaps akademiens förhandlingar," p. 29, 1884. The material that I have made use of consists of natural crystals from Ceylon, and from Pargas in Finland, and artificial graphite from some furnaces in Wermland.

Angle Measurements.

In computing the angle measurements carried out on six crystals, the most importance is attached to those angles which are situate in the plane of the cleavage surface, *i.e.* the so-called horizontal angles. If the system of crystallisation be hexagonal, the values 60° and 120° must be met with among these angles. The computations showed that the angles in question always deviated somewhat from the above values, and that the variations amounted to above 2° towards each side.

In order to check these results, direct measurements were executed of those plane angles which are formed on the basal plane by the striæ running in three directions, and forming triangles on the cleavage surface. Those angles were measured under a microscope provided with a capillary cross and movable stage.

The measurements could be performed with great accuracy, and the degree of accuracy was checked by means of measuring the three angles of the same triangle. It appeared from measurements executed on five crystals, that the angles varied quite irregularly from 61°40′ to 57°16′. If the largest, mean, and smallest angles of the same triangle are denoted respectively by α, β, and γ, we find the values of α to vary from 61°40′ to 60°6′ ; those of β from 61°24′ to 59°18′ ; and those of γ from 59°53′ to 57°16′. Sometimes *two* angles of the same triangle are above 60°, and the third below ; sometimes only *one* angle is larger and both the others smaller than 60°.

The variation in each of the angles α, β, and γ, is considerably greater than can be explained by errors of measurement, for while the errors of the sum $\alpha + \beta + \gamma$ do not exceed 0°16′, the variations in α are 1°34′, in β 2°6′, and in γ 2°37′.

From these facts it seems quite evident that the angles between the three crystallographic directions represented by the systems of striæ are not constant, but subject to considerable variations. It is thus easy to

understand why other angles also manifest an equal want of constancy. This variableness of the plane angles as well as of solid angles agrees with the results of previous investigations of graphite. For neither can the measurements obtained by different authors, as Kenngott, Haidinger, and Nordenskiöld, be brought into accordance with one another, nor even the angles measured by Nordenskiöld on different crystals be reduced to the same system of axes.*

The three angles of the basal plane varying irregularly from 60°, the crystallographic development evidently presents no obstacle to the mineral being regarded as hexagonal. But in order to arrive at a surer determination of the system of crystallisation, the physical properties of the mineral must be inquired into, and after having described its twins we shall pass over to that part of the subject.

Twins.

Although the striæ of the basal plane have been mentioned by all authors who have occupied themselves with this mineral, no one has investigated their nature. I have found them to consist of ridge-like elevations. These ridges are enclosed either by three planes, two of which form the sides of the ridge, and the third, parallel to the basal plane of the principal crystal, truncates the edge of the ridge; or else by only two planes that intersect at the edge of the ridge.

On cleaving the crystal scales, the ridges are found not to lie above the basal plane, but each ridge goes down into the crystal itself (figs. 1 and 2).

FIG. 1.   FIG. 2.

The cleavages of the ridge are parallel to its sides, and form obtuse angles with the corresponding cleavages of the crystal scale.

It is easy to measure the re-entering angle A between the sides of the ridge and the basal plane.

The mean value of a great number of measurements of crystals from Pargas and Ceylon is—

$$A = 159°32'$$

The plane bisecting this angle is a plane of symmetry with regard to both the elements of the crystal, and accordingly a twinning-plane. Its inclination B to the basal plane is—

$$B = \frac{360° - A}{2} = 100°14'$$

* Pogg. Ann. vol. xcvi. p. 110, 1855.

Being a twinning-plane this plane must be a real or potential crystal surface ; it is, in fact, a real crystal plane occurring in crystals both from Pargas and Ceylon.

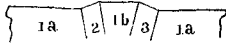On examining the ridges more closely, they are in general found to be constructed of three differently arranged crystal elements, two of these forming the sides of the ridge, and the third its edge (fig. 4). Other ridges consist of only two elements (fig. 3). The middle element 1 *b*, imbedded between the lateral elements, is situated parallel to the crystal 1*a*, and ought accordingly to be regarded as forming part of this. It is evident that the elements 1 *b* and 2 have the same position with regard to each other as 1 *a* and 2, and that in both cases the same plane, the pyramid plane *P*, is a twinning-face. Of course, there is the same twinning law also between the elements 1 *b* and 3, and 1 *a* and 3. On the contrary, the twinning law between the elements 2 and 3, which are symmetrically situated with regard to a vertical plane, is a different one. This plane, which is thus also a composition face, is a pyramid surface ½ *P*, the vertical axis of which is half as long as that of the other composition face.

Fig. 4.

Fig. 3.

Thus the ridges are constructed of two differently arranged crystal elements, without counting the principal scale itself. Within every ridge twinning has taken place according to two different laws.

It is not without interest to consider how these twins are to be regarded, according as the graphite is supposed to crystallise in the hexagonal, rhombic, monoclinic, or triclinic system. While the three directions of the ridges are equal, if we suppose the system of crystallisation to be hexagonal, it is seen by a simple deduction that with the other systems two or even all the three directions become unequal in value. With those systems of crystallisation which are less symmetrical the twins accordingly become more complicated. If the crystal form is supposed to be hexagonal, the crystal-complex is constructed according to two twinning laws ; if it is supposed to be rhombic, according to four ; if it is supposed to be monoclinic, according to six or nine different laws, according as the cleavage is supposed to be parallel or at right angles to the plane of symmetry ; and lastly, if the crystal form is supposed to be triclinic, nine different twinning laws must also exist.

Gliding-faces and Artificial Twins.

In many minerals with very distinct cleavages in one or more directions,

i.e. with very different degrees of cohesion in different directions, there occur gliding-faces. Such are known to exist in mica, calcite, soda-nitre, cyanite, galena, gypsum, stibnite, bismuthite, and orpiment. The graphite, which has such a distinct cleavage, is also found, in analogy with the above-mentioned minerals, to possess this kind of structural faces. The existence of gliding-faces is proved by bending crystal scales cautiously, as ridge-like striæ then appear strictly analogous to the natural ridges produced by twinning.

Thus, by means of the gliding-faces, it becomes possible to produce artificial twin crystals of graphite, just as artificial crystal twins of calcite may be produced, which have $-\frac{1}{2}R$ for their twinning-face.

We have designated P and $\frac{1}{2}P$, the faces occurring in the ridges, as twinning-faces, and it has been shown that the same symbols are those of the gliding-faces.

On bending a crystal scale the ridges are formed on the concave side and spring out in three directions, which, as we have seen before, make angles of about 60° with one another. The stronger the bending is, the higher and more numerous they become. It is clear that the line $a\ b\ c\ d\ e$ is equal in length to the line $a'\ b'\ c'\ d'\ e'$ (fig. 5). If the crystal scale is bent back so as to become plane, or so as to make that surface convex which was before concave, the ridges partly maintain themselves, and new ones arise on the other side that was concave before,

Fig. 5.

but is now plane or convex. This proves that there is a degree of stability in the new state of equilibrium of the molecules comparable to the stability of the molecules in their normal state. Thus by repeatedly bending the crystal scale in both directions ridge-like elevations are produced on both sides of it (fig. 6).
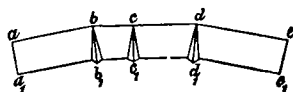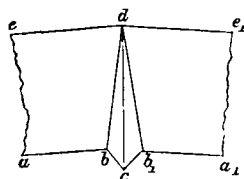

Fig. 6.

If such a scale is pressed between paper, the ridges recede and vanish completely, a gliding or turning of the molecules taking place in the opposite direction, so that they resume their normal position. If the scale is bent, the ridges come forth again in the same places as before.

Percussion-figures.

The percussion-figures exhibited by the graphite after suitably arranged experiments are closely connected with the gliding-faces and the twinning. Such figures are very easily produced on natural crystal scales

as well as on artificial graphite. According to the nature of the material the conditions of the experiments must be somewhat varied, for instance the firmness of the substratum, the sharpness of the point, &c.

If such a scale is chosen for the experiment as is free, as much as possible, from the ridge-like striæ, such striæ will generally be found after the experiment, radiating from the hole into which the point has penetrated. The percussion-figure consists of these striæ that run out in three directions, forming a percussion star with six or three rays (fig. 7). The percussion-figures produced are in general not very regular; the directi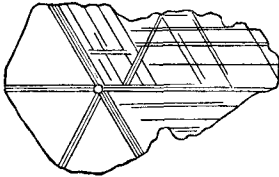ons of the ridges are certainly always constant, but the ridges are not equal in size. On the contrary, in the same star they present many variations with respect to the height, breadth, and length of the rays. In numerous experiments these variations have been found to be altogether irregular, so that there is no reason to suppose that the unequal ridges denote crystallographic directions of different values.

Fig. 7.

If the crystal scales are thin and firm, for instance in furnace graphite or Cingalese graphite, it is advantageous to employ a hard substratum, such as glass. One then gets small, fine, and regular stars, which are best seen in a microscope, magnified about 70 diameters. If the scales are thicker and softer, for instance in Pargas graphite, no percussion-figures are effected with a glass substratum, but only round holes. In this case softer substrata, wood or paste-board, are used with advantage; by that means percussion-figures are obtained that are large, coarse, and irregular, and best to be seen with the naked eye or with a lens.

The percussion-figures of graphite are of quite a different nature for instance to those of the micas. In the last named mineral a rupture takes place, so that the connection between the molecules in certain directions is broken. In graphite no rupture is ever to be perceived, but only a dislocation. The percussion-figures of this mineral may be altogether referred to the gliding-faces mentioned above. While the percussion-figure of the micas shows in what direction the cohesion is at its minimum with regard to a certain kind of action, the corresponding figure in graphite shows in what direction the resistance against gliding is at its minimum with regard to the same kind of action.

Cohesion.

The cohesiveness of graphite and the cleavages dependent thereon

differ very much in different varieties.   In furnace-graphite the cleavage parallel to the basal plane is much less distinct than that in the natural varieties.

The statements in different manuals of mineralogy as to the other cleavages do not at all accord with one another.   Tschermak and Naumann-Zirkel mention prismatic cleavages besides the basal.   Descloizeaux, on the contrary, records cleavages parallel to Kenngott's fundamental rhombohedron, while Dana does not mention any other cleavage than the basal one.

An examination of Cingalese graphite has proved it to possess no other cleavage than the basal one ; on crystal scales being torn asunder by forces parallel to the basal plane, the rupture takes place either quite irregularly or else along gliding-faces and twinning-planes.   Pargas graphite agrees with it in this respect.

Combustion and Etching Figures.

The etching-figures of graphite have a very great interest, because they supply us with a better guidance than any other properties of the mineral in determining the system of crystallisation.

In order to produce etching-figures in graphite, the mineral may either be heated in a current of dry oxygen or treated with a mixture of potassium-chromate and sulphuric-acid.   By both methods the same sort of etching-figures are obtained.

Graphite is burnt with difficulty ; even in a finely disintegrated state it burns with more difficulty than diamond.   It being necessary to employ whole crystal scales in order to obtain combustion-figures, the resistance to combination is still more considerable, and one is obliged to use strong heating and much oxygen.   It is on furnace-graphite that combustion-figures are most easily produced.

By suitably arranged experiments, small but sharp and distinct etching-figures with marked symmetry are obtained.   If the temperature is too high, or the heating is continued too long, the etching-figures become large, their limits uneven, and their shape approaches more and more that of a circle.   A crystal scale that has been exposed to such action is lacerated and torn at its edges and perforated in many places by holes 0·1—0·3 mm. in diameter, which are generally round, but sometimes show a tendency to the hexagonal form.

In a great number of experiments the most beautiful combustion-figures were obtained on artificial graphite that was etched in a current of oxygen during one minute.

On being examined with a microscope the combustion-figures were found to occur rather sparsely, and to be small but sharp and distinct. They were extremely regular hexagons 0·003—0·105 mm. in diameter. If the same sort of graphite was etched during $2\frac{1}{2}$ minutes in a current of oxygen, it was covered with numerous combustion-figures, partly larger and expanded, partly smaller and deeper. Their form was generally round, or irreg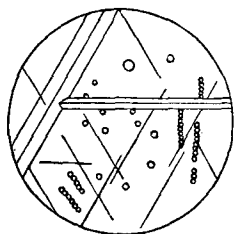ular with notched edges. In some places the figures joined into parallel rows, that were at right angles to one of the directions of the striæ. In other places the preparation was perforated; the holes were hexagonal. There were also found on the same preparation very fine etching-figures, visible only when highly magnified; these formed extremely regular hexagons 0·012—0·015 mm. in diameter, with only slightly rounded corners. The sides of the hexagons coincide with the three directions of the striæ (fig. 8).

FIG. 8.

The same result was obtained on the natural graphite from Pargas and Ceylon.

If the etching is effected by means of a mixture of potassium-chromate and sulphuric-acid the figures always become hexagonal, unless the attack is so violent that they become round or quite irregular.

The nature of the combustion-figures and etching-figures of graphite affords a strong reason to regard the mineral as hexagonal, because, as far as we know at present, the symmetrical properties of the etching-figures are very intimately allied with the system of crystallisation.

It is interesting to compare graphite in this respect with a group of minerals that is closely related to it in external and even some physical properties, viz. the micas. They agree with graphite in the distinct basal cleavage and the pseudo-hexagonal habit shown by their crystals, but, inasmuch as they belong with certainty to the monoclinic system, they differ from it by giving on the basal cleavage etching-figures the symmetry of which is in general *not* hexagonal.

Conduction of Heat.

In order to ascertain the system of crystallisation in another way, the melting-curve of the basal plane was examined.

Senarmont's method, as it has been modified by V. von Lang, was employed, as well as that indicated by Röntgen. The former method seems to be more convenient for graphite, as it allows one to make the

diameter of the curve larger.   The curve was regular and sharp until it reached a size of about 4·5 mm.; larger curves showed great irregularities, on account of the wax being liable to melt at the same time over the whole crystal after the curve had attained that size.

The melting-figures obtained appeared to the naked eye as perfect circles.   In order to determine their form more accurately, their diameters were measured in three different directions parallel to the three directions of striæ, accordingly making angles approximately of 60° with one another. The measurements were made with a dividing instrument belonging to the Physical Institution of the University of Upsala ; with that instrument lengths might be read off as near as $\frac{1}{1000}$ mm.   It resulted from this examination that the melting-curve is a circle, if such casual irregularities are disregarded as are called forth by heterogeneity or unevenness of the wax layer.   This result, as well as several of the physical properties set forth above, denotes the hexagonal system of crystallisation.

Summary.

We here put together the results obtained by the above examination of the physical and geometrical properties of graphite.

1. The striæ or ridges occurring in graphite crystals from different localities arise from twinning, which takes place in every ridge according to several different laws.   If the mineral is supposed to crystallise hexagonally, two twinning laws suffice to explain the structure of the crystal-complex; whereas on the supposition of a less symmetrical system of crystallisation, this twinning becomes far more complicated.

2. The same sort of twin crystals as the natural ones may be artificially produced by bending crystal scales ; thus it is evident that those surfaces which are twin-planes are also gliding-faces.

3. The percussion-figures of graphite may be referred to the gliding-faces, and are of another kind than the percussion-figures of micas and many other minerals.

4. The solid angles of graphite as well as the plane angles on the cleavage, show so little constancy that the geometrical structure of the mineral cannot be employed to determine the system of crystallisation.

5. The combustion- and etching-figures are regular hexagons.

6. The melting-curve of the cleavage is a circle, as far as can be ascertained by means of the methods that have been used.

7. *The nature of the twinning, together with the etching-figures and the melting-curve, make it probable that graphite crystallises in the hexagonal system.   This is not contradicted by its geometrical properties, which are too inconstant to form the ground of any decision on this point.*