

## MINERALOGICAL NOTES

## FORMATION OF LONSDALEITE FROM SINGLE-CRYSTAL GRAPHITE

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## ABSTRACT

Static pressure along  $c$  of single crystal hexagonal graphite (G) at room temperatures gives lonsdaleite (L), the rare wurtzite-like form of carbon, with L(10 $\bar{1}$ 0) parallel to the original G(0001), L[001] and L[100] being parallel respectively to G[120] and G[100]. This selective orientation is due not only to epitaxy, since L(0001) would fit equally well to G(0001), but also to the greater ease of transition of the sequence of G(0001) to L(10 $\bar{1}$ 0) planes as compared with the alternative transition (which does not occur) to L(0001) or even to diamond (111) planes.

Lonsdaleite is the rare wurtzite-like form of carbon. It is found in very small quantities, with diamond, from some meteorites (Fron del and Marvin, 1967; Hanneman, Strong, and Bundy, 1967) and in synthetic diamond prepared by shock-loading well-oriented graphite (Netherland Patent, 1965). It can be obtained almost pure by static pressure along  $c$  of good single-crystal graphite at room temperature, although it needs to be stabilized by heating to above 1000°C under high pressure (Bundy and Kasper, 1967). It is then found that the lonsdaleite formed has its (10 $\bar{1}$ 0) plane parallel to the original graphite (0001), unlike diamond which converts to graphite in such a way that, initially at least, D(111)<sub>diamond</sub> → G(0001)<sub>graphite</sub>. This L(10 $\bar{1}$ 0):G(0001) relationship was observed by Bundy and Kasper (1967) as the result of X-ray diffraction studies. They noted that these nets fit well together, although the spacings of L(10 $\bar{1}$ 0) and of G(0001) are quite different. It is implied that epitaxy governs the formation of lonsdaleite in that particular orientation, L[001] and L[100] being parallel to G[120] and G[100], respectively.

This, however, is not altogether the case. If one considers a single (111) diamond net, there is no difference between diamond (111) and lonsdaleite (0001) (Fig. 1). The difference lies in the *sequence* of the nets of puckered hexagons and hence in the structure and symmetry of the whole (Figs. 2 and 3).

In diamond all the puckered C<sub>6</sub> hexagons are of the chair type, in whatever direction (mean planes {111}) they occur. In lonsdaleite it is only

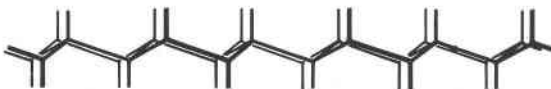


FIG. 1. Single net for diamond or lonsdaleite.

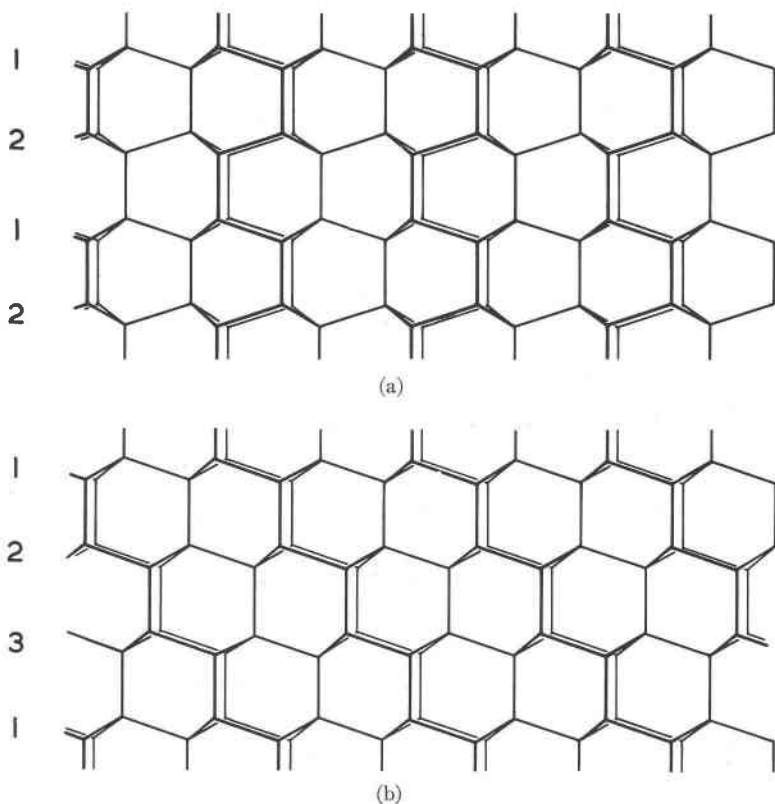


FIG. 2. Sequence of nets in (a) lonsdaleite and (b) diamond.

the  $C_6$  hexagons whose mean plane is  $(0001)$  that are of the chair type. Those whose mean plane is one of  $\{10\bar{1}0\}$  are of the boat type.

If the  $(0001)$  planes of lonsdaleite were straightened and separated the resultant arrangement (Fig. 4) would be of the hexagonal (low-pressure) BN type, which has its hexagons in line along the  $c$  direction (B and N alternating). To change this to the hexagonal graphite type would require a shift of about  $1.4 \text{ \AA}$  (the C-C distance) along a  $\langle 120 \rangle$  direction (that is, along the hexagon edge), in successive or alternate layers. It is significant that the high pressure ( $> 110 \text{ kbar}$ ) form of boron nitride is the wurtzite form (Bundy and Wentorf, 1963).

If, however, it is the  $(10\bar{1}0)$  planes of lonsdaleite that are straightened (from the boat form) and separated (Fig. 4) then the resultant structure could be transformed to ordinary hexagonal graphite by a shift of only  $0.7 \text{ \AA}$  (one-half the C-C distance) along any  $\langle 120 \rangle$  direction in successive

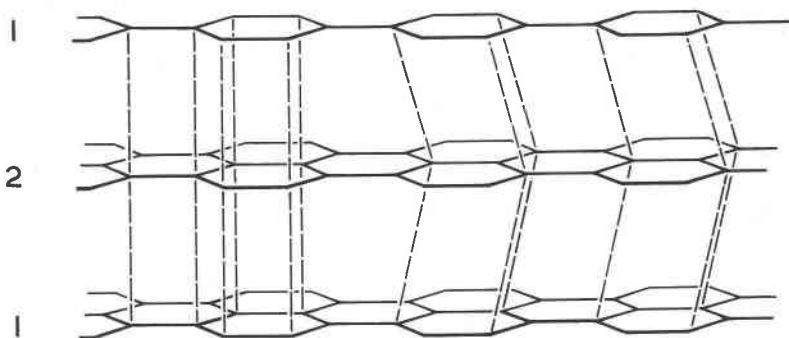


FIG. 3. Structure of lonsdaleite straightened on (0001) planes and separated, resembles structure of normal boron nitride.

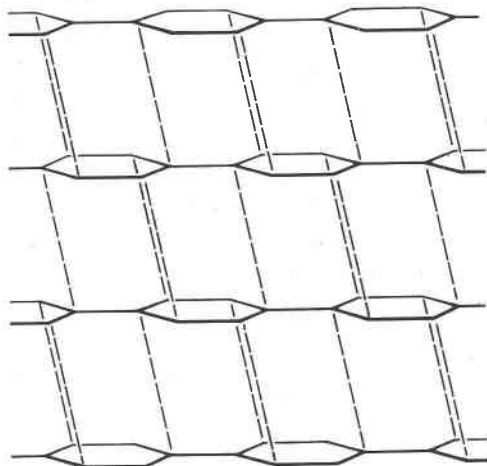


FIG. 4. Structure of lonsdaleite straightened on (10 $\bar{1}$ 0) planes and separated, to give hexagonal graphite structure, after gliding as shown.

or alternate layers. Conversely, if *single-crystal* graphite is compressed, it is lonsdaleite that would be expected (from the hexagonal graphite) with a (10 $\bar{1}$ 0) plane parallel to the graphite (0001).

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THE AMERICAN MINERALOGIST, VOL. 56, JANUARY-FEBRUARY, 1971

### ON THE ELECTROCHEMICAL ORIGIN OF NATURAL GRAPHITE

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#### ABSTRACT

The hypothesis is advanced that pyrrhotite, an accessory mineral, could electrochemically control the deposition of natural graphite from an aqueous solution of carbon dioxide. It could do this as a simple short-circuited voltaic cell under moderate solution temperatures and pressures.

#### DISCUSSION

The origin of natural graphite is a geochemical problem of some importance. In many occurrences, isotopic evidence (Craig, 1953) suggests an inorganic source of the carbon, namely carbon dioxide or carbonates. Because of the exceptional temperature stability of carbon dioxide, a reducing agent seems needed for the conversion to graphite.

It may be more than coincidence that one of the most electronegative and electroconductive minerals, pyrrhotite, is so frequently mentioned as an accessory mineral in graphite deposits. Rankama (1948) even has stated that in Finland "pyrite and pyrrhotite occur in carbon-bearing schists almost invariably, irrespective of their degree of metamorphism". As a simple short-circuited voltaic cell, the possibility exists for pyrrhotite to control the electrodeposition of graphite from an aqueous solution of carbon dioxide. Voltaic cells are not uncommon in nature. They account for the self-potential anomalies associated with sulfide ore bodies (Sato and Mooney, 1960).

The reduction of carbon dioxide to carbon monoxide, the first step in a reduction process, is thermodynamically less favored than the reduction of water to hydrogen. It is difficult, therefore, to electrochemically reduce carbon dioxide in an aqueous solution. High hydrogen-overvoltage elec-