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\overline{1}0) parallel to the original G(0001), L[00\overline{1}] 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\overline{1}0) planes as compared with the alternative transition (which does not occur) to L(0001) or even to diamond (11\overline{1}) planes.

Lonsdaleite is the rare wurtzite-like form of carbon. It is found in very small quantities, with diamond, from some meteorites (Frondel 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\overline{1}0) plane parallel to the original graphite (0001), unlike diamond which converts to graphite in such a way that, initially at least, D(11\overline{1}) → G(0001). This L(10\overline{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\overline{1}0) and of G(0001) are quite different. It is implied that epitaxy governs the formation of lonsdaleite in that particular orientation, L[00\overline{1}] and L[100] being parallel to G[120] and G[100], respectively.

This, however, is not altogether the case. If one considers a single (11\overline{1}) diamond net, there is no difference between diamond (11\overline{1}) 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\textsubscript{6} hexagons are of the chair type, in whatever direction (mean planes \{11\overline{1}\}) they occur. In lonsdaleite it is only

Fig. 1. Single net for diamond or lonsdaleite.
the C₆ hexagons whose mean plane is (0001) that are of the chair type. Those whose mean plane is one of \{1010\} 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 Å (the C-C distance) along a (120) direction (that is, along the hexagon edge), in successive or alternate layers. It is significant that the high pressure (>110 kbar) form of boron nitride is the wurtzite form (Bundy and Wentorf, 1963).

If, however, it is the (1010) 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 Å (one-half the C-C distance) along any (120) direction in successive
Irrc. 3. Structure of lonsdaleite straightened on (0001) planes and separated, resembles structure of normal boron nitride.

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

or alternate layers. Conversely, if single-crystal graphite is compressed, it is lonsdaleite that would be expected (from the hexagonal graphite) with a (1010) plane parallel to the graphite (0001).

Fig. 4. Structure of lonsdaleite straightened on (1010) planes and separated, to give hexagonal graphite structure, after gliding as shown.

References


ON THE ELECTROCHEMICAL ORIGIN OF NATURAL GRAPHITE

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摘要

提出了一个假设，即黄铁矿，一种辅助矿物，可以通过电化学方式控制自然界中石墨的沉积。它可以在中等溶液温度和压力下作为简单短路的电压电池作用。

讨论

自然石墨的起源是一个重要的 geochemical 问题。在许多情况下，同位素证据（Craig, 1953）表明碳的来源是无机的，即二氧化碳或碳酸盐。由于二氧化碳的温度稳定性特别高，因此需要还原剂将其转化为石墨。可能不是巧合的是，最电负和电导矿物之一，黄铁矿，被频繁地提到在石墨矿床的辅助矿物。Rankama (1949) 甚至声称在芬兰“黄铁矿和黄铁矿在含碳的片麻岩中几乎不可避免地出现，与它们的变质程度无关”。

作为简单短路的电压电池，黄铁矿有可能控制从二氧化碳的水溶液中沉积石墨。电压电池在自然界中并不罕见。它们可以解释硫化物矿体自极化异常（Sato and Mooney, 1960）。

二氧化碳的还原到一氧化碳，是还原过程的第一步，热力学上不如水的还原到氢气有利。因此，很难通过电化学方式从水溶液中还原二氧化碳。高氢过电势的电解过程涉及的电位较高。