Transformation of graphite to diamond via a topotactic mechanism

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ABSTRACT

Several mechanisms and intermediate steps have been proposed to explain the transformation of graphite to diamond. However, the mechanism continues to be debated, in part because graphite that is incompletely transformed to diamond has not been reported; although such material could be used to better understand the diamond-forming process. Here we report the discovery of nano-sized grains of interstratified graphite and diamond from Gujba, an extraterrestrially shocked meteorite. We use high-resolution transmission electron microscopy (HRTEM) data from these grains to show that diamond formed via a reconstructive, topotactic rather than martensitic mechanism. Electron diffraction and HRTEM images show the following three-dimensional crystallographic relationships between the interstratified graphite and diamond: (001)[(111)]n, (100)[(2TT)]d, and (120)[(011)]d. These relationships yield the transition matrix linking the graphite and diamond unit cells, which become coincident for graphite compressed to 7 GPa. The specific product, whether single-crystal or twinned diamond, is dictated by the initial graphite polytype and transformation route. The derivation of a three-dimensional transition matrix is consistent with a topotactic relationship between graphite and the newly formed diamond.

Keywords: Crystal structure, crystal growth, electron microscopy, meteorite

INTRODUCTION

Shock waves can convert carbonaceous materials to diamond. Products of this process occur as the result of explosive compression of powders (DeCarli and Jamieson 1961; Donnet et al. 2000, 1997; Erskine and Nellis 1991; Yamada et al. 2000), extraterrestrial impacts (Le Guillou et al. 2010; Sharp and DeCarli 2006), and impacts of meteorites on Earth (El Goresy et al. 2001; Langenhorst et al. 1999; Pratesi et al. 2003; Yelisseyev et al. 2013). Of particular interest are the recent reports of terrestrial impact-produced nanodiamonds, specifically those associated with the hypothesized Younger Dryas (YD) boundary impact event (Israde-Alcantara et al. 2012; Kennett et al. 2009a, 2009b; Kurbatov et al. 2010). These reports describe nanodiamonds, diamond, lonsdaleite, and n-diamond, in sediments of the Allerød-Younger Dryas boundary, with the lonsdaleite being presented as evidence of shock synthesis (Kennett et al. 2009a, 2009b), although the evidence for lonsdaleite in these deposits is open to debate (Daulton et al. 2010). To use the presence and characteristics of the shock-formed diamonds as indicators of specific formation processes, it is necessary to understand the mechanisms and conditions under which graphite transforms to diamond.

Graphite has been proposed to form diamond through either a martensitic or reconstructive process, whereas non-graphitic carbon such as carbon black and glassy carbon transforms to diamond by a reconstructive mechanism (Irifune and Sumiya 2004; Le Guillou et al. 2007; Sumiya et al. 2006). Static and shock-wave experiments show that the uncatalyzed, direct transformation of graphite to diamond requires pressures >15 GPa and transient T of >3000 K (reviewed in DeCarli 1995; DeCarli et al. 2002). Shock-wave experiments suggest that graphite oriented with its basal planes normal to the direction of shock-wave propagation transforms to diamond through a two-step martensitic mechanism (Erskine and Nellis 1991, 1992): graphite to lonsdaleite (also called hexagonal diamond), followed by a transformation from lonsdaleite to diamond at <2000 K, substantially below the melting temperature of graphite. Independent of the mechanism by which it occurs, the transformation results in a 61% collapse along the [001] of graphite, whereas the lateral dimensions decrease by only 2.8%. Strong covalent bonds form in diamond, and there is a dramatic density increase from 2.28 to 3.52 g/cm³. The bonding changes from planar, 3-coordinated, sp²-bonded C in sheets held together by Van der Waals forces for graphite to 4-coordinated, sp³-bonded C in diamond. Also, the planar C-C bond length of graphite increases by 0.015 nm on transforming to diamond.

A range of intermediates structures have been hypothesized to form during shock or static compression of graphite to diamond (Khalilullin et al. 2011; Le Guillou et al. 2007; Yang and Wang 2001) starting with the two major graphite polytypes: 2H (hexagonal, AB stacking) and 3R (rhombohedral, ABC stacking). 3R graphite is thought to form diamond via buckling and compression of graphene sheets, without the formation of intermediate structures, whereas diamond formation from the 2H