

EXPERIMENTAL DETERMINATION OF THE KINETICS OF Tb TO IaA NITROGEN AGGREGATION WITH APPLICATION TO NATURAL Ib-IaA DIAMONDS

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Introduction: Natural type I diamonds contain up to ~4000 atomic ppm of substitutional nitrogen impurities which were initially incorporated in a singly-substituted form (C-defect-centres) at the time of diamond growth. Diamonds containing only C-defects are known as type Ib and most synthetic diamonds, grown from metal catalysts, are of this type. During residence of diamond at high temperatures in the mantle, the early-formed C-defects aggregate to form A-defect centres (type IaA diamond); further aggregation yields B-defect centres and platelets (type IaB diamond). Natural diamonds from kimberlite and lamproite pipes are generally mixed type IaAB stones consistent with long-term mantle storage at ~1050-1250 °C. Because most diamond populations have had long-term histories at high temperature, type Ib or mixed Ib-IaA diamonds are comparatively rare in nature and if present must represent a young diamond population and/or one which grew and resided under relatively cool conditions (<1050°C). Some natural diamonds of very low nitrogen content may also contain Ib nitrogen. Type Ib-IaA diamond from kimberlitic sources (e.g. Yakutia, Zaire) typically occur as cuboid overgrowths (coats) on octahedral diamonds or as individual crystals of cuboid habit. Such diamonds are characterized by a yellow, yellow-green or orange colour. Type Ib-IaA microdiamonds also occur in crustal host rocks in some metamorphic belts such as the Kokchetav massif in Kazakhstan (Finnie et al., 1994).

In order to evaluate the thermal history of type Ib-IaA diamonds the kinetics of the aggregation process need to be accurately determined. There have been several previous high-P,T investigations of the kinetics of the Ib to IaA transformation which showed that the aggregation process is consistent with 2nd order kinetics. These studies, however, have yielded a wide range of different values for the activation energy (E_a) and Arrhenius constant (A) (see Kanda et al., 1990). At least part of this variability may relate to sector-dependence of the Ib aggregation rate in the cubo-octahedral synthetic diamonds used as starting materials. Satoh et al. (1990) found that nitrogen aggregation was enhanced in the octahedral (111) sectors compared to the cube (100) sectors, possibly due to higher concentrations of lattice vacancies in the (111) sectors. If the extent of aggregation is not determined by a microanalytical technique capable of distinguishing between the sectors, then an average value for the kinetic parameters will be obtained. For application to natural Ib-IaA diamonds, which are almost invariably of cube or cuboid habit, the aggregation rate determined on the cube sectors will be most relevant.

Methods: Fourteen high-P,T experiments were carried out over the range 6.5 to 9.5 GPa and 2200 to 1350°C using multi-anvil presses at the Bayerisches Geoinstitut, Bayreuth and the High Pressure Laboratory, Edmonton. Run durations varied from a few minutes at the highest T to 44 hours at the lowest T. Starting materials consisted of <2mm size DeBeers and GE synthetic Ib diamonds of either conventional cubo-octahedral form or of largely cubic form in which the octahedral faces were poorly developed, together with some natural Ib-IaA cubic diamonds (including a Kokchetav cube) with high nitrogen contents. The synthetic diamonds were confirmed to be pure type Ib diamonds by infrared (IR) spectroscopy. Following a high pressure run, aggregation state and nitrogen contents were determined separately on cube and octahedral faces using a Bruker IR microscope with a 120 μm aperture. Spectra were baselined, scaled to a constant thickness of 1 mm and deconvoluted into Ib and IaA components. In some runs, the cube faces of synthetic diamonds were lightly graphitized and this was removed by acid treatment prior to IR determinations. Total nitrogen contents of the diamonds were determined using the Ib and IaA absorption coefficients recommended by Kiflawi et al. (1994).

Results: The results are illustrated on Arrhenius plots (log of second order rate constant k_2 versus reciprocal temperature) shown in Figs 1A and 1B for spectra determined on cube and octahedral faces, respectively. At temperatures $\leq 1500^\circ\text{C}$ no discernible conversion was detectable for cube sectors of synthetic diamonds and natural cubes. Within error limits, the data show a linear dependency (regression coefficients >0.9) consistent with 2nd order kinetics. There is no discernible pressure effect on the aggregation rate and consistent results were obtained from the natural and synthetic cubes. Determined activation energies show a large difference between cube sectors (6.0 ± 0.2 eV) and octahedral sectors (4.4 ± 0.3 eV) in agreement with the findings of Satoh et al. (1990). The two different activation energies are in excellent agreement with theoretical calculations of Mainwood (1994), who obtained 6.3eV for nitrogen migration involving direct interchange of atoms, and 4.5 eV for a vacancy-assisted mechanism, though the reason for sector dependence is not obvious. The data points of Kanda et al. (1990) have been recalculated with new absorption coefficients and plotted in Fig. 1B for comparison. Although some of these data points fall on or close to the (111) regression line, many of the points scatter toward the (100) line. It appears that although Kanda et al. made efforts to measure only (111) faces, some overlap with cube sectors occurred resulting in an array of points that define a mixing line between differently aggregated sectors.

Discussion: In previous investigations of natural Ib-IaA diamonds an activation energy of 5 eV from Evans and Qi (1982) has usually been employed in kinetic calculations. Our results suggest that a value of 6eV is more appropriate for natural Ib-IaA cubes which implies such diamonds have experienced higher temperatures and/or have longer residence times at depth than previously proposed. By way of an example, Finnie et al. (1994) calculate a very short (~ 0.2 - 0.4 Ma) high-P residence time for Kokchetav microdiamonds assuming an average temperature of 900°C . Using the new activation energy, a high-P residence time of between 7 and 15 Ma is obtained. This longer residence period is in good agreement with geochronological studies which suggest a subduction to exhumation history of ~ 15 - 20 Ma for the Kokchetav massif (Jagoutz et al., 1990). The new kinetic parameters can also be used to place constraints on the timing of growth of yellow Ib-IaA cubes such as that described by Talnikova (1994) from the Udachnaya pipe. This diamond contains ~ 1000 atomic ppm nitrogen and is $\sim 80\%$ aggregated. If it grew and resided in the mantle under cool conditions, say in the range 1050 to 950°C , then it would have formed in the interval 0.1 to 7 Ma before kimberlite eruption. Thus it appears that yellow cubes of this kind formed during a very late lithospheric diamond growth event that immediately preceded kimberlite eruption.

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FIG. 1A

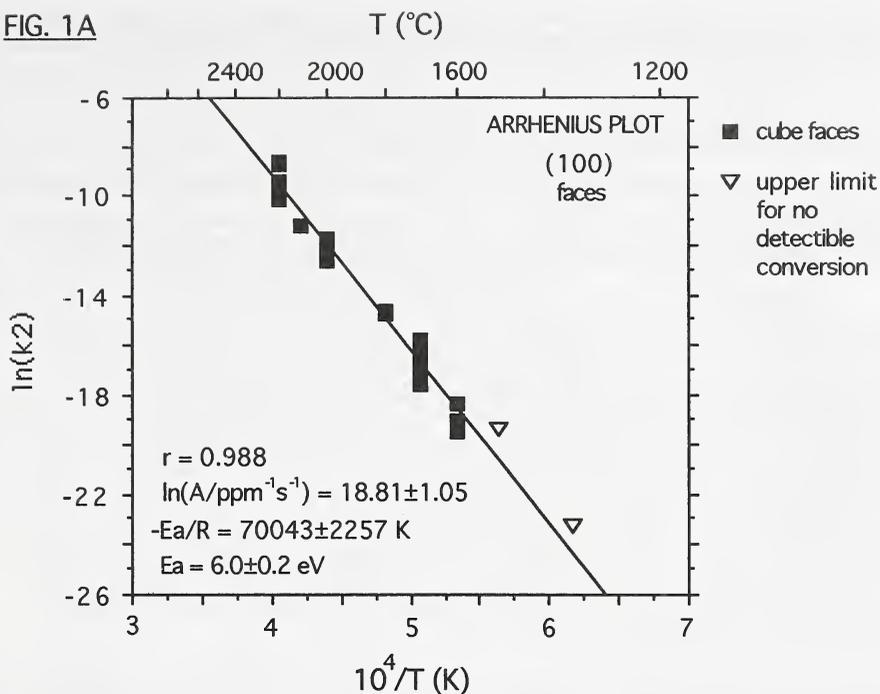


FIG. 1B

