NITROGEN AGGREGATION, INCLUSION EQUILIBRATION TEMPERATURES

AND THE AGE OF DIAMONDS

T. Evans

Department of Physics, University of Reading,
Berkshire, RG6 2AB.

J.W. Harris

Department of Applied Geology, University of Strathclyde,
Glasgow, G1 1XJ.

INTRODUCTION

Most diamonds contain significant amounts of nitrogen as a major impurity and the commonest are termed Type I(a).   The nitrogen is present in several distinct aggregation states.   Pairs of nitrogen atoms are called A-centres, N3 centres contain three nitrogen atoms and B-centres consist of four nitrogen atoms and a vacancy.   Transmission electron microscopy as well as infrared absorption techniques also indicate that Type I(a) diamonds usually contain platelets present in the cube planes.

When synthetic diamonds containing nitrogen are grown (at about 1500°C and 5GPa), the nitrogen is incorporated in the diamond lattice as single substitutional atoms.   In the same way, it is assumed that nitrogen atoms were similarly sited when natural diamond grew.   If an extended period of residence in the Upper Mantle then follows, the nitrogen would diffuse to form the various types of aggregate.   The amount of aggregation that occurs would depend upon the initial nitrogen concentration, the temperature that was encountered in the Upper Mantle and the time spent at that temperature before quenching by eruption to the Earth's surface.

The work presented here shows how the nitrogen aggregation characteristics obtained from infrared spectroscopy, can be linked through kinetic equations and activation energy values to either the temperature of equilibration or the geological age of a diamond.

THE AGGREGATION PROCESS, THE KINETICS AND INFRA-RED SPECTROSCOPY

Evans and Qi (1982) studied the aggregation process in the laboratory by heating synthetic diamonds containing dispersed nitrogen at temperatures between 1500°C and 2500°C under stabilizing pressures.   All the types of nitrogenous aggregates that are found in Type I(a) natural diamonds were reproduced and a sequence of aggregation proposed.

$$\text{Singles} \rightarrow \text{A-centres} \rightarrow \text{B-centres} \searrow \text{Platelets}$$
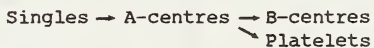
Initially, single substitutional nitrogen aggregates to form A-centres with an activation energy of 5eV.   The process obeys second order kinetics according to the formula.

$$\frac{dC}{dt} = -K\, C^2 \quad \text{where} \quad K = A\exp\left[-\frac{E}{kT}\right] \quad \text{and} \quad Kt = \frac{1}{C} - \frac{1}{C_o}$$

K = the rate constant; A = a constant; E = activation energy; C = the single nitrogen concentration after heating at the temperature T for time t; C_o = the initial single nitrogen concentration.   Values of K were determined at different temperatures.

The A-centres, in turn, aggregate to form B-centres and a side reaction is the formation of N3 centres.   Unfortunately, an activation energy for this process could not be determined in the laboratory owing to the unreliability of the temperature measurements above 2200°C, although using natural diamonds in heating experiments, some rates of aggregation were determined between about 2500°C and 2800°C.

Both the A- and B-centre nitrogen in Type I(a) diamond absorb infrared radiation in the so-called one phonon region between $7\mu m$ (wavenumber 1417cm^{-1}) and 10μm (wavenumber 1000cm^{-1}). A perfect diamond would be transparent in this region. Using the method described by Clark and Davey (1984) the absorption characteristics of Type I(a) diamond in this region can be decomposed into three spectra, named A and B, with a minor component D, the latter probably due to platelets (Woods 1986). The nitrogen concentrations in the A- and B-centres is found by using the formulae

$$\mu^A_{1282} = 300\ N_A \quad \text{and} \quad \mu^B_{1282} = 80\ N_B$$

where μ^A_{1282} and μ^B_{1282} equals the absorption coefficient in cm^{-1} due to the A- and B-centres respectively, at the wavenumber 1282cm^{-1} (equivalent to 7.8μm) and N_A and N_B are the concentrations respectively of nitrogen atoms present in the A- and B-centres in atomic percent (Kaiser and Bond (1959), Evans and Qi (1982)). Thus the total nitrogen concentration can be determined. In addition the A/B ratio at 1282cm^{-1} can be obtained and this ratio is a measure of the conversion of nitrogen in A-centres to nitrogen in B-centres. For example, diamond with an A/B ratio of 1, has about 80% of A-centres aggregated to form B-centres.

RESULTS

Four diamonds were investigated. F13 and F39 are 'peridotitic' suite diamonds from the Finsch Mine (see Gurney *et al.* 1979); diamond XM48 was released from a common coarse-grained garnet lherzolite xenolith with that designation, also from Finsch (Shee *et al.* 1982) and the fourth diamond was recovered from a Type II eclogite xenolith XRV247 from Roberts Victor (Robinson (1977)).

For the Finsch diamonds, an equilibration temperature of 1130°C and a pressure of 5 to 5.3GPa was assigned (Shee *et al.* 1982) with a model age of 3300Ma (Richardson *et al.* 1984). For F39 these pieces of information were used in conjunction with the nitrogen aggregation results to determine an activation energy for the aggregation of A-centres to B-centres assuming that this aggregation process obeys second order kinetics. An A/B ratio at 1282cm^{-1} of 8.05 was measured from the decomposed infrared absorption spectrum and a nitrogen concentration of 0.02 at.% determined. An activation energy of 6.83eV was calculated. To see if this value is reasonable, a temperature of equilibration for F13 was determined. The infrared absorption spectrum gave an A/B ratio of 15.3 with nitrogen concentration of 0.015 at.%. Assigning a model age of 3300Ma and an activation energy of 6.83eV an equilibration temperature of 1120°C was obtained in good agreement to the proposed equilibration of 1130°C given by Shee *et al.* (1982).

A temperature of 1130°C was also determined for the equilibration of xenolith XM48 from Finsch (Shee *et al.* 1982). Thus the age of the diamond from XM48 could be compared to the 3300Ma age obtained for the 'peridotitic' diamond suite at that mine. From the infrared absorption spectrum an A/B ratio of 4.7 was measured with a nitrogen concentration of 0.097 at.%. Using the equilibration temperature of 1130°C a model age of 1100Ma was determined. (If a model age of 3300Ma was assigned, then an equilibration temperature of 1050°C would result which is rather a large discrepancy from the suggested 1130°C). Thus it appears that XM48 has a younger model age than such 'peridotitic' diamonds as F39 or F13.

For the Roberts Victor eclogite xenolith XRV247, an equilibration temperature of 1024°C at 3GPa or 1115°C at 6GPa was calculated using the method of Ganguly (1979) with a minimum theoretical temperature at the diamond-graphite intercept at 1062°C. Taking the method of Ellis and Green (1979) temperatures for the same pressures were 985°C and 1088°C respectively with the diamond-graphite intercept occurring at 1027°C. As there is no pressure calibration available there are two ways of considering the probable temperature. An average of the two minimum temperatures is 1045°C. On the other hand, if it is assumed that, as at Finsch, the diamond grew at a pressure of 5GPa the average temperature obtained by the two equilibration methods is 1069°C. The age of the eclogite xenoliths at Roberts Victor have been determined by Kramers (1979) as 2465Ma. Although HRV247 was not one of the xenoliths to be age-dated, it is likely to have an age of 2465Ma in view of the very wide selection process in which five of the six xenoliths chosen were Type II; similar to HRV247. From the infrared absorption spectrum an A/B ratio of 11.1 was obtained with a nitrogen concentration of 0.11 at.%. Using the age of 2465Ma and activation energy of 6.83eV, a calculated equilibration temperature of

1087°C was obtained.   Thus it appears reasonable that the growth and equilibration took place at a pressure of slightly above 5GPa, say between 5.5 and 6.0GPa at a temperature of about 1090°C.

CONCLUSIONS

The examination of these four diamonds shows that it is reasonable to relate the aggregation of nitrogen in Type I(a) diamonds to geological information.   Some caution, however, must be exercised in using this relationship.   It is based upon the assumption that total nitrogen concentration can be obtained from infrared absorption data and that the A-centre to B-centre aggregation step obeys second order kinetics.   There is mounting evidence that at later stages of the aggregation sequence further reaction, other than those described here, takes place and that some of the nitrogen becomes optically inactive.   It is suggested that fairly reliable information about equilibration temperatures and/or geological ages can be obtained by considering the aggregation of nitrogen in diamond providing that the A/B ratio at 1282cm^{-1} is greater than 2.   This ensures that no optically inactive nitrogen is present and the aggregation process described above is appropriate.   This limitation is not serious as a large majority of African diamonds have an A/B ratio of greater than 2.

REFERENCES

CLARK, C.D. and DAVEY, S.T., 1984. One-phonon infrared absorption in diamond. **Journal of Physics, C17**, 1127-1140.
DAVIS, G.L., 1977.   The ages and uranium contents of zircons from kimberlites and associated rocks.   Extended Abstract.   2nd International Kimberlite Conference, Sante Fe, Mexico.
ELLIS, D.J. and GREEN, D.H., 1979.   An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. **Contributions to Mineralogy and Petrology, 71**, 13-22.
EVANS, T. and QI, Z., 1982.   The kinetics of the aggregation of nitrogen atoms in diamond. **Proceedings Royal Society London, A381**, 159-178.
GANGULY, J., 1979.   Garnet and clinopyroxene solid solutions and geothermometry based on Fe-Mg distribution coefficient. **Geochimica Cosmochimica Acta, 43**, 1021-1029.
GURNEY, J.J., HARRIS, J.W. and RICKARD, R.S., 1979.   Silicate and oxide inclusions in diamonds from the Finsch kimberlite pipe.   In: Boyd, F.R. and Meyer, H.O.A. (Eds.): **Kimberlites, Diatremes and Diamonds.**   American Geophysical Union, pp. 1-15.
KAISER, W. and BOND, W.L., 1959.   Nitrogen a major impurity in common type 1 diamonds. **Physical Review, 115**, 857-863.
KRAMERS, J.D., 1979.   Lead, uranium, strontium, potassium and rubidinum in inclusion-bearing diamonds and mantle-derived xenoliths from Southern Africa. **Earth and Planetary Science Letters, 42**, 58-70.
RICHARDSON, S.H., GURNEY, J.J., ERLANK, A.J. and HARRIS, J.W., 1984. Origin of diamonds in old enriched mantle. Nature, 310, 198-202.
ROBINSON, D.N., 1977.   Diamond and graphite in eclogite xenoliths from kimberlite. **Extended Abstract.** 2nd International Kimberlite Conference, Santa Fe, Mexico.
SHEE, S.R., GURNEY, J.J. and ROBINSON, D.N., 1982.   Two diamond-bearing peridotite xenoliths from the Finsch kimberlite, South Africa. **Contributions to Mineralogy and Petrology, 81**, 79-87.
WOODS, G.S., 1986.   Platelets and the Infrared absorption of type 1a diamonds. **Proceedings Royal Society London, A, In Press.**