RECENT ADVANCES IN THE INTERPRETATION OF THE MID- INFRARED ABSORPTION SPECTRA OF DIAMOND

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Because diamond is a centrosymmetric crystal, it should not display any one-phonon absorption in the mid-infrared (IR), but Robertson, Fox & Martin (1934) found that some diamonds showed ultraviolet (UV) and IR absorption whereas others did not, and they designated the two classes as Type I (imperfect) and Type II (perfect). Since that time, an enormous amount of effort has been expended in discovering the reasons for these differences, and as a result diamonds are now further subdivided on the basis of their absorption spectra into classes Ib, IaA, IaB, IIa and IIb. Any disturbance of local centrosymmetry will result in the appearance of one-phonon IR absorption, but effort has been concentrated in establishing a quantitative relationship between the varieties of one-phonon absorption observed in natural diamonds and the presence of nitrogen in a series of aggregation states for which activation energies can be established in HP/HT experiments. Although it has long been known that diamonds are often inhomogeneous, it is only recently that IR microscopes have made it possible to to obtain IR spectra from sub-millimetre areas of individual diamonds (Milledge and Mendelssohn 1988), while advances in mass spectrometry and diamond processing technology have permitted the measurement of carbon and nitrogen isotope data for microgram samples of diamond excised by computer-controlled lasers.

IR microscopes function most efficiently in the mid-IR (4500 - 650cm^{-1}) which is the region of interest for organic chemistry, and it happens that spectra involving hydrogen occur in the diamond 3-phonon region, where absorption is weak for all diamond types, no absorption except CO_2 occurs in the 2-phonon region except for Type IIb, which is very rare among natural diamonds, whereas three well-defined absorption envelopes corresponding to the types Ib, IaA and IaB occur in the 1-phonon region just below the Raman edge at 1332 cm^{-1}, accompanied by a peak at ~1365cm^{-1} which develops during the nitrogen aggregation sequence. Assuming that spectra for diamonds of intermediate types such as Ib/Ia or IaA/IaB are linear combinations of the end-member envelopes, it should be possible to determine both the nitrogen concentration and aggregation state in a diamond segment from its infrared absorption spectrum, and to detect the presence of other "organic" (C,O,N,H and S) species which may be present.

Two major difficulties are encountered in practice. The first concerns the nitrogen ppm concentration corresponding to a particular absorption coefficient. Different estimates may arise either from inaccuracies in the determination of nitrogen concentration by one or all of the methods used, from inhomogeneity of the specimens, or from the assumption that nitrogen alone is responsible for the observed 1-phonon absorption, and is all present in an IR-active form. The second concerns the shape of the absorption envelope for each of the Type I spectra. Envelopes for Ib obtained both from synthetic and from natural diamonds seem essentially invariant, as do IaA envelopes, but this is not the case for IaB envelopes, which show considerable variations amongst themselves and in relation to the platelet peak which usually accompanies them.

These difficulties are important in relation to the estimation of the nitrogen aggregation state for a given nitrogen concentration, because the estimates are used in conjunction with postulated mantle residence times to calculate mantle temperatures, or vice versa, in conjunction with particular values of the activation energies involved. Nppm values and IaB aggregation percentages can be superimposed on isothermal isochron charts, (see for example Taylor & Milledge 1995) which we calculated for various mantle residence time ranges for the experimentally determined value of the IaA-IaB activation energy of 7eV (Cooper 1990) and

mu[IaA](1282 cm^{-1}) = 1 for 150at.ppm nitrogen . This activation energy of 7eV was in reasonable agreement with values obtained from inclusion geothermometry (Mendelssohn, Milledge, Cooper and Meyer 1991) and has been used in current investigations. Differences in the estimates of mu[IaB](1282 cm^{-1}) = 1 range from 650 to 1000 at.ppm nitrogen, and this does affect the calculated temperatures by some 5C which is less than might have been anticipated.

Platelet peak development as a temperature indicator.

The principal bar to the usefulness of IR data which is unsupported by either time or temperature data from some other source is that it does not determine either uniquely, but only limits the combinations which are geologically acceptable. However, we propose that the state of the platelet peak may indicate the temperature at which aggregation occurred, and hence also the residence time required, so that IR data is a self-contained P/T estimate for any growth horizon involving IaA to IaB aggregation.

The rationale for this approach comes from an examination of the many thousands of Mendelssohn miniplots (Milledge and Mendelssohn, loc.cit) now extant. These miniplots were developed for displaying the results of IR mapping of diamond plates; They are 2.5 cm square plots in which the 1-, 2- and 3-phonon regions of the spectrum are superposed so that estimates of the nitrogen concentration and aggregation state can be made by inspection in relation to platelet development and the presence of hydrogen or other impurities. They are arranged in rows of 8, and produced automatically during routine data collection. and provide a convenient way of assessing groups of spectra.

From a consideration of such groups of spectra it can be seen that platelet peak development occurs at different rates relative to IaB aggregation in different specimens, or in different growth horizons within the same specimen, and that there is a continuous range of envelopes which can be represented by series involving various percentages of the IaA envelope with end-member IaB envelopes measured directly from specimens with platelet -peak ratios R = [A(P)/A(1282cm^{-1})] from 0 to 2. Fig.1 shows examples from such series for R = 0, 1 and 2. It had long been known (Evans and Qi, 1982) that the platelet peak can be destroyed very quickly in HP/HT experiments, but Cooper (loc.cit.) found that whereas for a number of diamonds for which the platelet peak development varied widely in relation to the IaB aggregation state *before* doing experiments intended to increase the aggregation, all specimens had been reduced to the *same* ratio after heating to ~2600K. Decrease of platelet peak growth with increasing temperature might be explained if the production of a 4-nitrogen IaB centre from the aggregation of two IaA centres does result in the expulsion of a carbon atom which then becomes involved in platelet development, as has been suggested, because the higher the temperature, the more likely such an atom would be to relax back into the lattice before reaching a platelet.

Whatever the reason for such behaviour may be, the validity of such a relationship, leading to a "platelet index"(PI), has been demonstrated on a number of specimens (e.g. Taylor & Milledge, loc.cit), and attempts to quantify it are in progress.
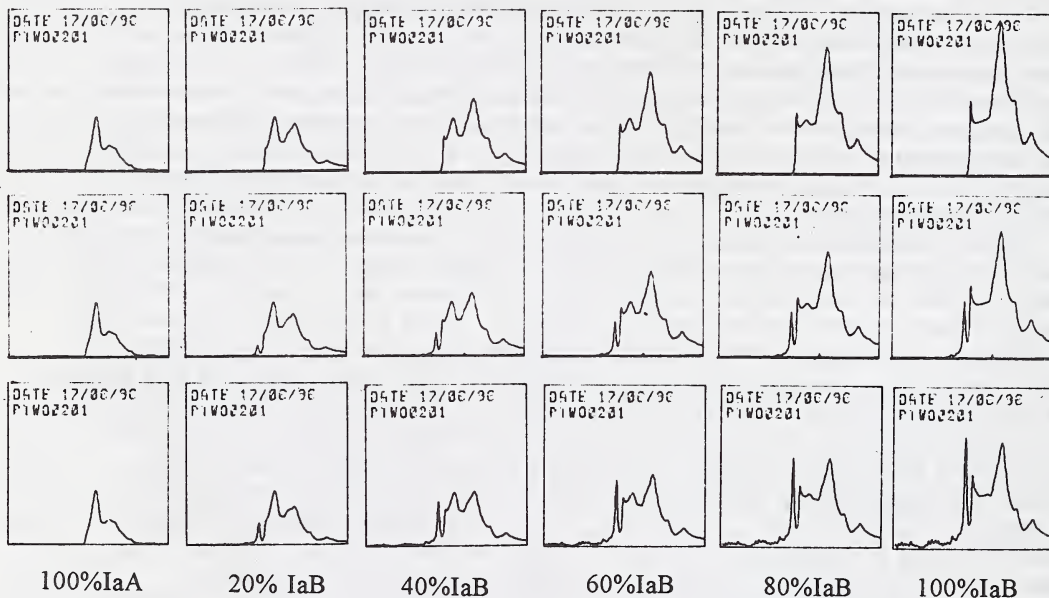
The Ib - IaA aggregation sequence

Similar considerations apply to representation of the Ib - IaA aggregation sequence, for which the end-member envelopes are sensibly invariant, but in this case it is assumed that conversion from single nitrogen to nitrogen pairs is the only process occurring, so that the size of the IaA envelope in relation to the size of the Ib envelope from which it developed can be used to obtain an estimate of the relative values of the absorption coefficients concerned. Recent values indicating that of 250 at. ppm of nitrogen give an absorption coefficient mu(1134 cm^{-1}) = 1/mm, while 160 at.ppm give mu(1282 cm^{-1}) = 1 are in good agreement with previous estimates, and have been used to calculate the Ib-IaA series shown in Fig. 2. Recent experiments (Canil, Taylor and Milledge, 1995) have confirmed previous observations that octahedral and cubic sectors of diamond aggregate at different rates, and this has an important bearing on estimates of the mantle residence times experienced by diamonds still exhibiting some Ib absorption component, as these are frequently cubes.

References

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Fig.1.

100%IaA   20% IaB   40%IaB   60%IaB   80%IaB   100%IaB

Envelopes in the IaA-IaB aggregation sequence computed for mixtures of a standard IaA
envelope with IaB envelopes showing different rates of platelet development

Fig.2.

100%Ib   20%IaA   40%IaA   60%IaA   80%IaA   100%IaA
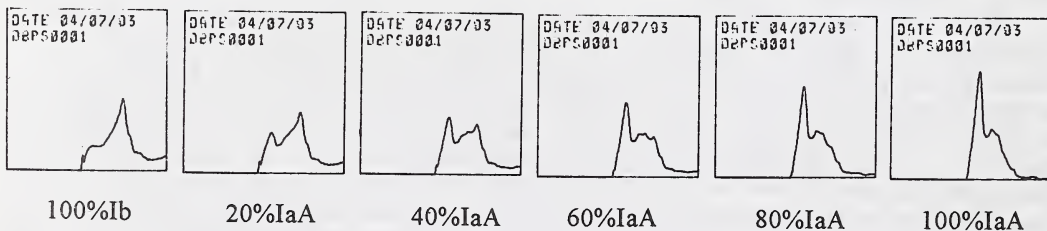
Envelopes in the Ib - IaA sequence computed for experimentally determined relative values
of the absorption coefficients involved.