Characterisation of Diamonds by Infrared Spectroscopy

M.J. Mendelssohn and H.J. Milledge

Research School of Geological & Geophysical Sciences, Birkbeck & University College London, Gower St., London WC1E 6BT, United Kingdom.

A principal objective in analysing the mid-infrared (IR) spectra of diamonds is the possibility of defining separate diamond populations with distinctive characteristics, in order on the one hand to assist in diamond exploration, and on the other to improve our knowledge of Mantle geophysics and geochemistry over perhaps 3 Ga by associating Mantle residence time/temperature estimates with other data such as isotope data and inclusion chemistry.

The first of these activities generally involves measurements on rough stones, while the second usually involves polished plates. If IR analyses are to become a routine component of exploration data, it is essential that the results be available quickly, which in turn means that it must be possible to process the spectra semi-automatically, even when they are of variable quality.

In order to achieve these objectives, hundreds of mid-infrared (IR) spectra have been measured, using a Bruker IR microscope, to obtain statistics of mantle residence conditions for various diamond populations. The spectra have been analysed using methods described in Mendelssohn & Milledge (1995), but the rate-limiting step is the extraction of relevant data from the spectra themselves, and the requirement that for spreadsheet comparisons all data from a single spectrum must be contained in a single row, and each column must have a single entry.

This problem has been solved by using specially constructed macros operating within the Bruker Opus software, to provide a few spreadsheet-friendly files for transfer to spreadsheets used for for subsequent analysis. Some of the problems and possibilities inherent in this approach will be considered.

Baselining

The main problem involved in spectra from rough stones is the variable baseline, and processing packages offer various options for baseline correction. The method used (Mendelssohn & Milledge 1995) involved the calculation of a straight baseline, which is quite satisfactory for polished plates or octahedra, but unsatisfactory for many rough stones or polished plates whose sides are not parallel. For rough stones, therefore, baselining is now being performed automatically as part of the effort to make the process as operator-independent as possible.

Diagnostics

One of the main difficulties in the automatic processing of the 1-phonon region of the diamond IR spectrum is that some features may be absent, present as a shoulder, or present as a peak, and it is necessary to know which is the case, while one number has to represent the feature in the spreadsheet. This problem has been solved in the following way:

The main macro considers 10 regions of the diamond spectrum whose boundaries have been carefully selected as a result of trial processing of five groups, each consisting of some 200 spectra, involving data from different localities where different types of diamond occur. Ideally, each region should produce

only one entry (peak or shoulder) expected in this region for any diamond spectrum. However, more than one entry may be obtained for one of two reasons: a) unexpected peaks may occur, or b) fringes may be present, and this would not be acceptable in a spreadsheet, which requires one entry per spectrum per region. The macro thus examines both peak and shoulder possibilities, and lists the number of peaks as a positive counter and the number of shoulders as a negative counter, or zero if neither is present. If more than one peak or shoulder is present, the position and absorbance of the largest peak is given. Obtaining peak positions from the macro by using the OPUS peakpick algorithms has the added advantage that the peak position is found by interpolation so that quite accurate values are obtained from the data which uses a resolution of 8 wavenumbers. Peak information is not used in routine aggregation assessment, although it has been found that the actual position of the developing 1174cm^{-1} peak gives a useful indication of the extent of aggregation, and this estimate is now included in the spreadsheet.

Nitrogen aggregation estimates

The method of estimating aggregation by comparing the ratios of various features in the 1-phonon spectrum, assuming that the shape of the end-member envelopes is known,(Mendelssohn & Milledge 1995) generally works quite well, but information about multiple peaks or off-scale data needs to taken into account, so the process is only semi-automatic, digitising the available information but still requiring assessment by the operator. In particular the temperature estimates made for a specified Mantle residence time require close attention, because of the possibility of overlapping zones, especially in rough stones. In fact the most serious systematic error so far identified in the data analysis concerns the apparent rise of temperature in low-nitrogen rims of polished plates. Higher temperatures in outer zones are not physically acceptable, and after examining expanded low-N rim spectra from a number of plates, it has become clear that the problem is due to the extension of a wedge of the internal zone into the rim, so that the shape of the envelope (and hence the estimate of %B) is the same as that found for the inner zone, but it is weaker w.r.t. the two-phonon absorption because the wedge only occupies part of the plate thickness, and thus appears to suggest the same aggregation state for less nitrogen .. i.e. a higher temperature. Once realised, this phenomenon is obvious from the traverse graph in the new spreadsheet, where it can be seen that %NasB remains constant, whereas Nppm decreases towards the rim.

Thickness calculator

Maps. Because the macros operate on any spectra which have been loaded, they can be used to process traverses extracted from maps, but attempts to do this have shown that it is essential to record the x,y values of location points on the specimen as positioned for the map, because if the increments are, say, 250 microns, the actual positions at which the spectra have been obtained relative to inclusions or zone boundaries are not known as accurately as they could have been. A further problem with maps is that the spectra have to be located at points on a regular orthogonal mesh, which usually involves significant numbers of spectra being recorded at points off the specimen altogether, or too near the edge to be acceptable. One way of discarding such spectra is to define a range of acceptable values for the 1992cm^{-1} normalising absorbance, based either on the known thickness of the plate or on the consistency of the values obtained across the specimen either before or after baselining.

Accordingly, the spreadsheet has been provided with a calculator which shows the values to be expected after baselining for a range of plate thicknesses which can be specified, and the thicknesses corresponding to the observed range of 1992cm^{-1} absorbances. A number of experiments have been made using spectra from plates whose thicknesses had been measured with a micrometer, and in all

cases calculated thicknesses were slightly less than the measured values (by ~10microns). This is probably reasonable, in that many of the plates were not completely parallel or uniform in thickness, and may not have been absolutely clean. It can also be useful when processing data from microdiamonds because values of specimen thickness, from actual measurements, using photographs or the microscope apertures and stage micrometers, can be entered in the calculator and the corresponding value of the normalising absorbance at 1992cm^{-1} can be substituted for the measured value, which is unreasonably sensitive to baselining, especially when nitrogen content is high, so that the computed value may provide a better estimate.

Automatic diagnostic graphs

It is quite obvious that platelet peak positions and intensities vary considerably within and between specimens, and do not always correlate with nitrogen concentration and aggregation results. Because platelets are precipitates, information relating to their size and distribution seems in principle to offer the possibility of investigating changes in time, temperature and impurity content, and a number of graphs relating these quantities to platelet peak position and intensity have been collected on a single page to facilitate the search for meaningful relationships.

The page also contains a graph for plate traverse data showing how scaled values of the various parameters vary across the plate, and a graph showing where the spectra have been measured if appropriate x,y data are available. The traverse graph can also be used to compare separate stones in a batch, as was done in the case of the Copeton stones (Meyer et. al.(1997), Fig.13).

Further objectives

Analysis of traverse data can in principle be used to see whether separate zones in different plates appear to have experienced the same conditions, and some of the available diagnostics, especially the data on hydrogen and carbonates, has not yet been examined in detail, and neither has the exact shape of the platelet peak, for which a separate spreadsheet is in preparation. Attempts will also be made to correlate IR data with birefringence, since both measurements involve transmission through the whole plate, whereas cathodoluminescence only refers to a few microns of the surface. A birefringence attachment has been fitted to the IR microscope so that required positions at which spectra are to be taken can be located directly.

References

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