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RAMAN SPECTRA OF GRAPHITE AS INDICATORS OF DEGREE OF METAMORPHISM

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ABSTRACT

This study demonstrates the usefulness of Raman microspectroscopy in an evaluation of the crystallinity of graphite in natural samples. The sensitivity obtained is at least as good as that for X-ray diffractometry. Laser Raman microprobe analyses of graphite separates, mostly from suites of regionally metamorphosed carbon-bearing pelites (Grew 1974), show that 1) the spectra of graphite accurately reflect the degree of crystallinity in terms of the (001) in-plane crystallite size, 2) the same spectral features and changes with crystallinity occur in the spectra of natural graphite as in those of synthetic samples, 3) the Raman spectrum is a sensitive monitor of changes in graphite crystallinity, reflecting conditions from greenschist- to granulite-facies metamorphism, 4) significant changes in the Raman spectral profile coincide with transitions in the metapelites that delineate the chlorite, biotite + garnet, staurolite + kyanite + andalusite, and sillimanite zones, and 5) the graphite structure apparently records only the peak metamorphic temperatures and does not recrystallize under retrograde conditions.

Keywords: graphite, crystallinity, Raman spectroscopy, metamorphism, metapelites.

SOMMAIRE

Nous démontrons ici l'utilité de la microspectroscopie de Raman pour évaluer le degré de cristallinité du graphite provenant d'échantillons naturels. La sensibilité de la méthode est au moins équivalente à celle de la diffraction X. L'analyse par spectroscopie Raman de concentrés de graphite, prélevés surtout de pélites carbonacées qui ont subi un métamorphisme régional, a été effectuée par microsonde au laser. Les spectres illustrent bien le degré de cristallinité en termes de la dimension des domaines cristallins dans le plan (001). Les mêmes caractéristiques du spectre et les mêmes dépendances sur le degré de cristallinité sont présentes dans les échantillons synthétiques. Le spectre de Raman est sensible aux changements de cristallinité subis lors d'un métamorphisme allant du facies schistes verts jusqu'au facies granulite. Les changements importants dans les profils coïncident avec les transitions dans les métapélites entre les zones à chlorite, à biotite + grenat, à staurotide + kyanite + andalousite, et à sillimanite. La structure du graphite semble se ré-équilibrer lors du paroxysme du métamorphisme, et ne montre pas d'effets rétrogrades.

(Traduit par la Rédaction)

Mots-clés: graphite, cristallinité, spectroscopie de Raman, métamorphisme, métapélites.

INTRODUCTION

Considerable interest has been focused on graphite as an indicator of the metamorphic grade of its host rock. Although graphite can form by precipitation from a volatile phase, most studies to date have concentrated on graphite produced by the thermal maturation (*i.e.*, graphitization) of organic matter. Because the chemical and structural properties of graphitized material apparently reflect the conditions under which it crystallized, accurate analyses of these properties can provide geothermometric data. For instance, the metamorphic grade of a carbonaceous rock can be inferred from the degree of crystallinity of its graphite or from the fractionation of carbon isotopes between coexisting graphite and carbonates (*e.g.*, Ergun 1968, Landis 1971, Grew 1974, Diessel *et al.* 1978, Itaya 1981, Valley & O'Neil 1981, Okuyama-Kusunose & Itaya 1987, Hoefs *et al.* 1988). In this work, the relationship between degree of graphite crystallinity or, conversely, disorder, and metamorphic grade will be explored by Raman microspectroscopy.

As organic matter is metamorphosed, hydrogen, oxygen, and nitrogen are expelled, and the carbon atoms become progressively organized into stacked planar arrays of 6-fold rings. During this process of graphitization, the distance between the planes (*d* value) decreases to about 3.35 Å (Fig. 1). In addition, the size of the well-ordered domains increases (*i.e.*, the crystallite size increases) in all directions, but not at equal rates. In-plane (001) growth is called sheet formation; L_a is the average length-scale of continuity within the sheets. The increase in the number of sheets in an undisturbed sequence along the *c* axis is called stack formation; L_c is the average length-scale of continuity perpendicular to the sheets (*e.g.*, Oberlin *et al.* 1980, Beny-Bassez & Rouzaud 1985). The values of L_a, L_c and *d* are the quantitative parameters indicative of crystallinity.

Three analytical techniques can provide structural characterization of graphitic materials: high-resolution transmission electron microscopy (HRTEM), X-ray diffractometry (XRD), and Raman spectroscopy. HRTEM produces images of the stacks and sheets that can be measured directly to determine the values of L_a, L_c, and *d*. Sample preparation for the HRTEM technique typically consists of total disaggregation of the host rock and bulk separation of the graphite, followed by extreme thinning of the individual grains to be analyzed. The scale of probing within the grains is on the order of hundreds of Ångströms (Oberlin *et al.* 1980, Buseck & Huang 1985, Beny-Bassez & Rouzaud 1985). In contrast, X-ray powder diffractometry is a macro-analytical technique that primarily yields quantitative *d* values. With appropriate calibrations and analytical conditions, L_c and L_a values also may be inferred (Ergun 1969). Although the host rock is disaggregated in the same way as for HRTEM sample preparation, a large number of grains is required for XRD analysis.

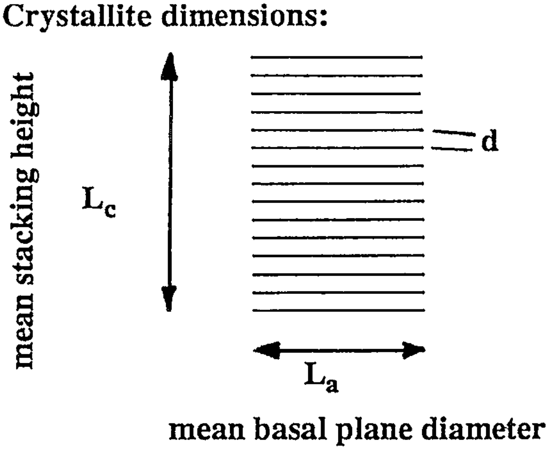

FIG. 1. Schematic representation of structure of graphite crystallite. The interplanar spacing *d* has a value of 3.35 Å in well-crystallized graphite, and in excess of 3.35 Å in disordered graphite. The "mean basal plane diameter" refers to the mean diameter of graphite platelets in the (001) plane.

It has long been recognized that the Raman spectra of graphitic materials indicate their degree of crystallinity in terms of the (001) in-plane crystallite size (*e.g.*, Tuinstra & Koenig 1970). Most work to date has focused on macro-Raman study of synthetic graphite. In principle, natural samples are equally amenable to such study, but require disaggregation, as for HRTEM and XRD analysis. An additional, and only recently used, technique for graphite analysis is laser Raman microspectroscopy (LRM). Unlike HRTEM, XRD, and macro-Raman techniques, LRM analysis need not be destructive to the sample. Although it also can be applied to grain separates, LRM analysis may be done *in situ* in polished thin-sections or wafers (with some caveats: see below) if the sample matrix provides the necessary heat-sink. For geologists, LRM provides some additional benefits. It allows the analysis of individual, microscopic grains of graphite, and because the irradiation volume of the laser beam is on the order of several cubic micrometers, the scale of probing of LRM is intermediate between the scales of HRTEM and XRD analysis. Moreover, nondestructive *in situ* analysis also permits the characterization of individual grains while preserving their petrological and textural relations. Finally, given a suitable (*e.g.*, nonfluorescent) host mineral, LRM also allows the analysis of graphite precipitated in individual fluid inclusions (*e.g.*, Guilhaumou *et al.* 1984, Pasteris & Wanamaker 1988, Pasteris 1988).

In laser Raman microspectroscopy, a monochromatic laser beam is focused into or onto a sample through an optical microscope. The same high-numerical-aperture objective is used to optically image the sample, focus the laser, and transmit the scattered radiation to a monochromator. The inelastically scattered Raman radiation is monitored by a photon detector, and is recorded in terms of intensity (number of photons) as a function of Raman shift (relative wavenumbers, Δ cm^{-1}), which reflects the difference in frequency between the exciting laser radiation and the Raman scattered radiation. The value of L_a can be inferred from Raman vibrational spectra of the covalent bonds of graphitic matter, *i.e.*, those reflecting the within-sheet properties.

Despite extensive previous study of the Raman spectroscopy of carbonaceous materials (Knight & White 1989, and references therein), most analyses have been confined either to coals or to "carbons" produced by the heating of organic compounds to 2000–3000°C (*e.g.*, Beny-Bassez & Rouzaud 1985). Thus, the applicability of observed temperature-dependent changes in the Raman spectra to geological samples has not been tested. Moreover, parameters such as complex organic precursor compounds, elevated pressures, shearing, and contact with other (changing) mineral grains add to the complexity of interpretations of the Raman spectra of natural carbonaceous materials by comparison with spectra obtained on coal and synthetic "carbons". Although some spectra of natural graphite have been published or discussed (*e.g.*, Guilhaumou *et al.* 1984, Pasteris *et al.* 1986, Hess *et al.* 1988, Wang *et al.* 1989, Knight & White 1989), to our knowledge, no systematic Raman study of a well-characterized suite of graphite-bearing rocks has been reported.

The present study addresses two points concerning the feasibility and geological applicability of LRM analysis to natural occurrences of graphite. The first concerns the changes in the Raman spectra of *natural* graphitic materials in response to progressive metamorphism: are they the same as those previously recorded on synthetically heat-treated organic compounds? The second consideration concerns the range in size of the graphite crystallites to which the Raman spectrum is sensitive, and whether it is possible to spectrally resolve changes developed in graphite under a geologically significant range of metamorphic conditions. In other words, beyond what metamorphic conditions does graphite appear completely ordered according to its Raman spectrum? This is not an unreasonable concern, given that carbonaceous materials in some pelites metamorphosed only to the upper chlorite zone have a basal spacing close to that for well-crystallized graphite (Grew 1974).

RAMAN SPECTRA OF CARBONACEOUS MATERIALS

Various empirical and theoretical aspects of the Raman spectroscopy of carbonaceous materials, including graphite, already have been treated in the chemistry and physics literature (*e.g.*, Tuinstra & Koenig 1970, Nemanich & Solin 1979). The Raman spectrum of graphite is known to be sensitive to variations in L_a between about 30 and 1000° (Tuinstra & Koenig 1970). Several features are consistently recorded by Raman analysis of non-abraded samples (*i.e.*, neither mechanically polished nor physically disrupted) using an incident laser beam oriented perpendicular to the basal plane of graphite (see Wang *et al.* 1989, Pasteris 1989, and references therein). The first-order Raman spectrum (analyzed from 1200 to 1700 cm^{-1}) of well-crystallized (L_a >> 1000 Å), pure-carbon graphite has only one band at ~ 1582 cm^{-1} (Fig. 2). The second-order spectrum (analyzed from 2350 to 3350 cm^{-1}) shows several features, most notably a feature near 2700 cm^{-1} that clearly consists of two overlapping bands.

Progressive disorder in graphite is reflected in the first-order Raman spectrum by the broadening and

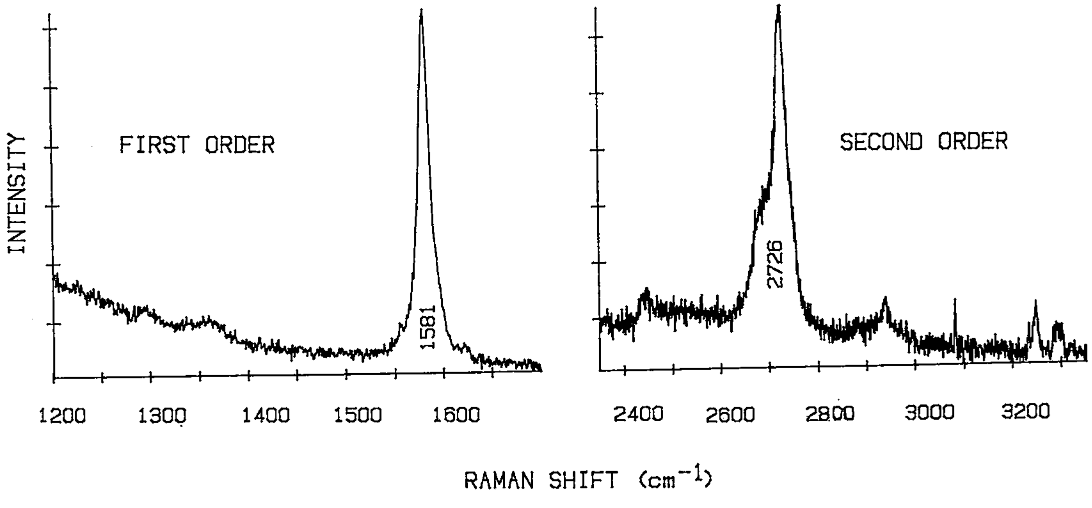

FIG. 2. First- and second-order Raman spectra of well-ordered, granulite-facies graphite from a vein deposit in Sri Lanka. Spectra not plotted to the same scale of intensities. Ref. # CEYL–1A.DAT, J77.

shifting of the 1582 cm^{-1} band to higher wavenumbers due to the development of an additional band that is usually observed as a shoulder on the high-wavenumber edge of the main band, and by the development of an additional band near 1360 cm^{-1} (Fig. 3). Tuinstra & Koenig (1970) proposed that the ratio of the intensities of the bands near 1360 and 1582 cm^{-1} is proportional to L_a. Features in the second-order spectrum of disordered graphitic materials are broadened or even suppressed compared to those for well-ordered graphite; in particular, resolution of two overlapping bands in the feature near 2700 cm^{-1} is lost (Fig. 3).

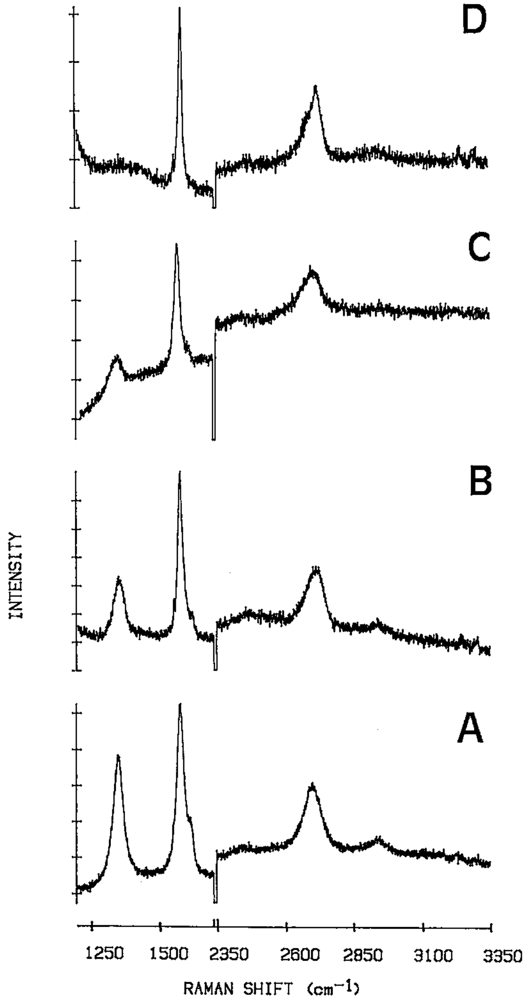

FIG. 3. Representative Raman analyses from the four spectrally recognized metamorphic categories (see Fig. 4). First- and second-order spectra plotted to the same scale of intensities. Very narrow peak on the low-wavenumber shoulder of the band at about 1582 cm^{-1} represents oxygen in the air above the sample. A) Chlorite zone (sample from Columbia Co., NY). B) Garnet zone (Stockbridge, MA). C) Staurolite zone (Worcester, MA). D) Sillimanite zone (South Kingston, RI). Ref. # 71-78A.CAT, 71-82A.CAT, 71-83A.DAT, J97, 71-51B.DAT, J101.

SAMPLE DESCRIPTION AND ANALYTICAL PROCEDURE

This paper deals with a total of 21 regionally metamorphosed carbonaceous metapelites, mostly from the northeastern U.S. All samples were provided as graphite separates by Edward Grew, who had studied the mineralogy of the host rocks and had done extensive XRD work on the same graphite separates (Grew 1974). HRTEM analysis was subsequently done on a subset of these graphite suites by Buseck & Huang (1985).

Seven of the samples were collected from the Mississippian to Late Pennsylvanian Narragansett Basin in Rhode Island and Massachusetts, which is comprised of coal-bearing, non-marine (alluvial-fan) clastic sediments (*e.g.*, Grew 1974, Grew & Day 1972, Murray 1987, Mosher *et al.* 1987). This basin illustrates well the effects of the Alleghanian Orogeny in New England, because it has undergone two major prograde metamorphic episodes, and has preserved abundant evidence of retrograde metamorphism in the southwest. The metamorphic conditions represented by the basin samples range from about 400–500°C at 3–4 kbar pressure in the chlorite zone to about 600°C at 4.5–5 kbar pressure in the sillimanite zone (Grew & Day 1972, Murray 1987). The Narragansett suite is particularly useful in the present study. Firstly, the reaction isograds are well mapped. Secondly, the metasediments preserve an excellent record of the response of coal and other dispersed organic matter to a wide range of conditions of metamorphism and deformation (Grew 1974, Murray 1987).

Five samples originate from regionally metamorphosed, highly carbonaceous, nonmarine sediments of Pennsylvanian age and marine sediments of pre-Pennsylvanian age in the Worcester and Ayer areas of central Massachusetts. The sediments were metamorphosed under conditions ranging from the chlorite zone to the sillimanite – K-feldspar zone (Grew 1973). In contrast to the Barrovian-type metamorphism (kyanite–sillimanite) undergone by the Narragansett and western New England sediments (see below), the Worcester area underwent lower-pressure, Buchan-type (andalusite–sillimanite) metamorphism (Thompson & Norton 1968).

Three samples are taken from the Lower Paleozoic Stockbridge and the Ordovician Walloomsac Formation in the Taconic Range in the western Massachusetts – northwestern Connecticut – eastern New

York region. According to Zen (1981), these rocks underwent two major episodes of metamorphism, resulting from the Taconian (Ordovician) and Acadian (Devonian) orogenies. The second metamorphic episode apparently reached higher grade than the first, and determined the mineral assemblages of the samples that were studied. The metamorphic assemblages in this region (from below the chloritoid zone into the kyanite–staurolite zone) indicate conditions from 400 to 600°C at about 4 kbar pressure (Zen 1981).

Most of the other samples originate from pre-Pennsylvanian rocks elsewhere in the northeastern United States. Two chlorite-zone samples are taken from Shunga, Karelia, in the USSR (Grew 1974).

The graphite grains analyzed in this study range in size down to a few micrometers. Although Raman analysis of nonopaque samples usually is nondestructive, many of the (opaque) graphite grains laid directly on a glass slide disintegrated owing to heating and consequent combustion in the laser beam of the Raman microprobe. Careful pressing of the graphite grains into gold foil mounted on an aluminum SEM stub, however, provided heat conduction away from the sample and permitted nondestructive analysis. The smallest grains afforded the most efficient heat conduction *via* the gold foil. This procedure of sample preparation also assured that most grains were oriented with their basal plane perpendicular to the laser beam.

The Raman analyses were done at Washington University, using a 1983 model RAMANOR U-1000 (Instruments SA, Inc.) single-channel (scanning) Raman microprobe with an Olympus microscope. For each of the 21 mounted samples, one or more Raman spectra were recorded in the regions 1200–1700 and 2350–3350 cm^{-1}. Excitation was provided by the 514.5-nm line of a 5-watt argon-ion laser (Coherent, Inc.), which delivered 3–10 mW laser power at the sample surface. Incident and scattered radiation was focused with a 40× Nachet objective with a numerical aperture of 0.75. The stepping interval was 1 cm^{-1}, and the dwell time was 10 seconds per point. Under these conditions, each scan required about 4.5 hours. In some cases, multiple scans were summed to provide a better signal-to-noise ratio. Repeated scans on some grains also served as a test for reproducibility.

RESULTS AND DISCUSSION

The observed variations in the Raman spectra of our graphite samples from several metamorphic suites (Fig. 3) are analogous to published data on synthetically produced "carbons" of various degrees of crystallinity. In order to test the applicability and significance of the Raman analyses to natural materials, all the spectra were visually compared and sequenced by degree of crystallinity of the graphite, evaluated according to the spectral criteria discussed in the literature and summarized above. When the spectra subsequently were labeled with the metamorphic mineral zones from which they originated, three important observations were made. 1) Recognizable changes are evident in the Raman spectra of graphitic matter over the entire metamorphic range from the chlorite zone through the sillimanite zone. 2) With the exception of two samples (from Ayer, Massachusetts and Mt. Cube, Vermont), the spectrally derived sequence is in agreement with the mineralogically determined metamorphic grade. For each of the two exceptions, the Raman spectrum indicates a higher metamorphic grade than does the silicate mineralogy, *i.e.,* sillimanite instead of andalusite zone and biotite instead of chlorite zone, respectively. 3) In addition to the expected progressive changes in spectral features, which reflect an increase in crystallite size, there are recognizable breaks in the progression, such that the spectra can be divided into four groups. The divisions between these spectrally recognized groups coincide almost exactly with the isograds separating the following groups of metamorphic zones: A) chlorite, B) biotite and garnet, C) staurolite, kyanite, and andalusite, and D) sillimanite.

Multiple Raman analyses on the same graphite grains produce very similar spectra. In most cases, although spectra of separate grains from the same host-rock sample do show some differences, the latter are not sufficient to change the order of the sample in the spectral sequence. In addition, the *specific* sequence almost exactly matches that inferred from independent XRD (Grew 1974) and HRTEM (Buseck & Huang 1985) analyses that were done on subsets of this group of samples.

The availability of HRTEM, Raman microspectroscopic, and XRD data on the same suites makes possible an evaluation of the homogeneity of the individual graphite samples over a range of scales. Grew's (1974) XRD data on bulk grain separates did not show evidence of the coexistence of graphites of different degrees of crystallinity within samples, although XRD analyses have revealed such inhomogeneity in other suites of graphite (Landis 1971). HRTEM data (Buseck & Huang 1985) on Grew's (1974) suite of graphite showed considerable grain-to-grain and even within-grain inhomogeneity within individual samples, especially for those of low metamorphic grade. Such findings are consistent with the several-Ångström resolution of this technique. Raman analyses of the present suites show marked inhomogeneity in only one sample. The host rock in this case is a black slate from the chlorite zone (Portsmouth, Rhode Island), and this particular sample also revealed a large degree of inhomogeneity in the HRTEM study (Buseck & Huang 1985). Given these tests for homogeneity at three different scales of probing, it appears that Grew's (1974) samples are moderately homogeneous on the scale of a few micrometers (resolution of the Raman microspectroscopic analyses).

Figure 3 shows representatives from the four spectrally recognized groups, which correlate with metamorphic grade. The greatest amount of within-group spectral variation occurs for samples from the chlorite zone, analogous to Grew's (1974) XRD-based findings. For graphite within the chlorite zone, the major spectral change with increasing crystallite size is a decrease in the ratio of the first-order Raman peak intensities, I(~ 1360 cm^{-1}):I(~ 1582 cm^{-1}), as seen in Figure 4. The band at about 1582 cm^{-1} also develops from a broad symmetrical peak to a more narrow peak with a shoulder on the high-wavenumber side (Fig. 3A). The transition from the chlorite zone to the biotite through garnet zones is reflected in an abrupt change to a ratio of peak intensities less than 0.5 (Fig. 4). Progressive increases in graphite crystallinity within this group produce relatively minor changes in the spectra, *i.e.*, a slight decrease in the intensity ratio (Figs. 3B, 4). The transition to the staurolite + kyanite + andalusite zones is marked by the development of asymmetry in the second-order band at about 2700 cm^{-1} (Fig. 3C). Within this group, an increase in crystallite size is reflected in a decreasing ratio of intensities of the first-order peaks. The transition to the sillimanite zone is recognized by the virtual nonexistence of the 1360 cm^{-1} band (Figs. 3D, 4) and the increased asymmetry of the 2700 cm^{-1} band (Fig. 3D). The best indicator of increasing size of crystallites within this group is no longer the intensity ratio of the first-order peaks (Fig. 4), but rather the resolution of the two spectral bands that comprise the feature at about 2700 cm^{-1} (Fig. 3).

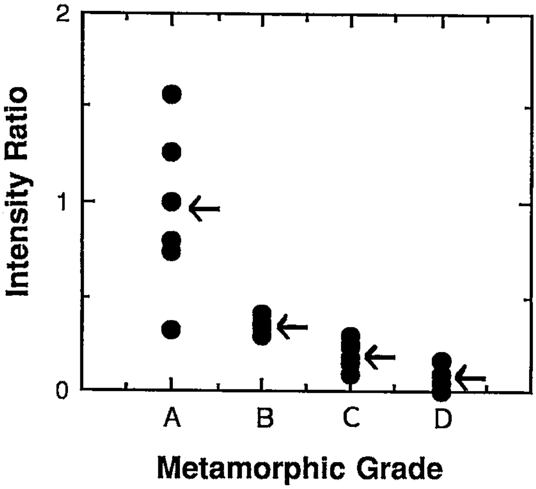

FIG. 4. Plot of the intensity ratio of Raman peaks I(~ 1360 cm^{-1}): I(~ 1582 cm^{-1}) of all the graphite samples from the metapelite suite under study, grouped according to their spectrally recognized metamorphic categories. Arrow indicates average values of intensity ratio in each metamorphic grade. A: chlorite zone, B: biotite and garnet zones, C: staurolite, kyanite, and andalusite zones, D: sillimanite zone.

The above data demonstrate that the Raman spectrum of natural graphite is a sensitive indicator of the degree of metamorphism of its host rock, over the interval from chlorite to sillimanite zone. Of further interest is the degree of spectral sensitivity for the higher-grade samples. From its Raman spectrum, sample #71–51 from South Kingston, Rhode Island (shown in Figure 3, spectrum D) is clearly recognized as the most perfectly crystalline graphite in this group of samples. Of note is the fact that sample #71–51 was collected essentially at the contact with the Narragansett Pier Granite, which is further evidence that this sample is the highest-grade one in the suite. [The Narragansett Pier Granite is a large Permian igneous body that was emplaced during the time interval between the major metamorphic episodes recorded by the Narragansett metapelite suite. It apparently was intruded into the highest-grade portion of the regional metamorphic sequence, and cross-cuts the isograds (Murray 1987).] In addition, comparison of this spectrum of sillimanite-zone graphite with that of the granulite-grade graphite shown in Figure 2 demonstrates that distinctions between even higher grades of metamorphism can be recognized in the Raman spectrum of graphite. By comparison, XRD analyses (Grew 1974) show that a *d* value [derived from the (002) peak position] almost as small as that for "good graphite" is attained by the upper chlorite zone; even the XRD peak width for the (002) reflection does not show a clear distinction between sillimanite-zone graphite and granulite-facies graphite. Results of bulk-chemical analyses of carbonaceous materials for C, H, N, O and S also are not distinguishable among samples of the highest metamorphic grades. Grew's (1974) analyses show essentially pure carbon graphite once the staurolite zone is reached.

Despite the useful correlations and sequences inferred by "eyeballing" the Raman spectra, attempts at quantification of the spectral parameters were not so successful. Correlations among most of the measurable spectral parameters (*e.g.*, ratios of peak intensities or peak areas, peak positions, peak widths) are poor on a sample-to-sample basis. For instance, the data appear scattered and not well correlated in two-parameter (X–Y) plots, and plots of one parameter *versus* metamorphic grade show considerable overlap among values for individual samples from different groups (Fig. 4). However, the *average* parameter values from the four spectrally recognized categories of metamorphism usually are different; the trends shown by these average values as a function of metamorphic grade do match those in published analyses of synthetic "carbons" (Fig. 4).

Overall, Raman microspectroscopy compares very favorably to the other analytical techniques used to characterize the degree of crystallinity of graphite. Moreover, the data from this study on grain separates can be applied to *in situ* LRM analysis of grains in thin sections or polished wafers. Such grain-by-grain analysis may be very important in the evaluation of the homogeneity of the graphite in a sample, and of the relationship between graphite crystallinity and host mineralogy (Wopenka *et al.* 1988) or rock texture, such as strain features (Ross & Bustin 1990). The latter evaluations may be essential, for instance, in the interpretation of carbon isotopic data of mineral pairs involving graphite.

Also of concern, irrespective of the technique used to analyze the graphite, is the question of how closely the structure of graphite actually reflects its thermal history. It is known that different organic precursor materials will graphitize to different extents under the same conditions (Oberlin *et al.* 1980, Beny-Bassez & Rouzaud 1985). It is also clear that there is a vast difference between the temperatures required to form well-crystallized graphite in 1-bar, short-time laboratory experiments (2000–3000°C) and in the geological environment (450–600°C), with its accompanying pressure, shearing, long periods of heating, and possible catalytic effects of the enclosing matrix. The inability to calibrate for, or even to determine, the effects of the above parameters in rocks suggests that graphite may not be a reliable indicator of metamorphic grade.

The present study, like the original study of Grew (1974), provides a means of evaluating this apparent limitation. For the samples analyzed, it is reasonable to assume a similar organic precursor for all the graphite samples from the Narragansett Basin suite. Thus, under ideal conditions, variations in the degree of crystallinity of graphite should mimic changes in the metamorphic silicate mineralogy of the Narragansett Basin samples. Although the rest of the samples also are metapelites, they differ from the Narragansett suite in their original sedimentary lithology (both marine and nonmarine sediments) and consequently in the nature of their precursor organic matter. The pressure regime of the samples also differed (both Buchan and Barrovian sequences). It is, therefore, of particular geological significance that the Raman spectra of graphite samples from localities both within and outside the Narragansett Basin show the same very good correlations with the metamorphic mineralogy of their host rocks. As indicated above, the distinctions among the Raman spectra of the 21 analyzed samples reflect only their metamorphic grade and not their locality.

It has been previously recognized, or at least inferred, however, that the host lithology may affect how readily graphite crystallizes under given conditions (Landis 1971, Grew 1974). Although the present paper addresses only metapelite-hosted graphite, we have investigated samples from other lithologies. In cases in which the samples were studied by Raman and by XRD (Grew 1974), both types of analysis showed, for a given grade of metamorphism, that the crystallite size for graphite is larger in calcareous than in pelitic host-rocks.

Based on the above Raman data on several metapelite lithologies, some further speculation seems reasonable. The fact that breaks in the progression of spectral changes in graphite coincide with breaks between metamorphic zones suggests a relationship between the changes in crystallinity of graphite and the changes in silicate mineralogy of the host rock. Two products of metamorphic silicate reactions, which might induce this apparent relationship, are the release of fluids (conducive to graphite re-equilibration and recrystallization) and changes in grain size and texture of the host rock (producing localized stresses on carbonaceous grains).

Graphitization is an irreversible and, in many cases, disequilibrium process. The irreversibility means that the highest degree of crystallinity attained by graphite will be retained during retrograde metamorphism. This statement is confirmed by both Grew's (1974) XRD and our Raman analyses of graphite in a sillimanite-zone mica schist in which sillimanite has been replaced by sericite. Moreover, the only two Raman spectral exceptions in this study indicate metamorphic grades *higher* than those inferred from the accompanying silicate mineralogy. It is possible that these two samples had undergone higher grades of metamorphism before their final re-equilibration.

There are obvious advantages to such an indicator mineral as graphite, especially in terranes like the Narragansett Basin, in which there has been significant retrograde metamorphism. Moreover, its quantifiable degree of crystallinity makes graphite one of the few single-mineral indicators of metamorphism. Because graphite is a common phase in several metamorphic lithologies, it is useful to include it among the minerals that are used to evaluate metamorphic grade. On the other hand, the disequilibrium development of much of the graphite can complicate geological interpretations. In particular, the effects of shear stress may be very significant in the crystallization of graphite (Ross & Bustin 1990). Wherever possible, the determination of graphite crystallinity should be combined with information on the assemblage of coexisting minerals in order to evaluate the complete metamorphic history of a rock.

CONCLUSIONS

The Raman spectrum of graphite provides a sensitive indicator of its degree of crystallinity, and of its conditions of formation in the range from greenschist facies (chlorite zone) to granulite facies. The level of sensitivity to progressive metamorphism is comparable to or better than that of the XRD technique, previously used to infer metamorphic grades. The Raman spectra of 21 grain separates of graphitic material from regionally metamorphosed pelitic suites show the same types of spectral features and the same trends (as a function of degree of crystallinity) as spectra taken of artificial "carbons" produced by heat treatment of organic compounds. Although numerous Raman spectral features can be quantified and compared, for the suites investigated in this study, the best method of inferring the degree of metamorphism is by visual comparison of the individual spectra. With few exceptions, the Raman spectra of graphite samples analyzed in this study permit not only a proper ordering of their metapelite hosts, but also a correct grouping according to metamorphic grade. With some caveats, the degree of crystallinity of graphite can be a useful metamorphic indicator (as also concluded by Grew 1974), and Raman microspectroscopy is a reliable means of its structural characterization.

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