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LETTERS

Interstratification of carbonaceous material within illite

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ABSTRACT

We here report the first recognized natural occurrence of a clay mineral with interstratified carbonaceous material that, in places, approaches graphite in its structural ordering. Using high-resolution transmission electron microscopy (HRTEM), we found that carbonaceous material in an early stage of graphitization occurs in extremely thin (<100 Å) domains both between and interstratified within illite crystals. This material could have been trapped during the growth of the illite or have been inherited from precursor clay minerals in the host sediments during diagenesis and metamorphism. Graphitization in low-grade rocks involves complicated microstructural changes in the carbonaceous material as a result of its fine-scale intergrowth with clay minerals. In addition, this study demonstrates that by utilizing ion-milled specimens, in situ structures and textures of fine-grained carbonaceous samples can be investigated without the unavoidable disruption produced by crushing or grinding.

INTRODUCTION

Synthetic carbon intercalation compounds are widely used for designing desirable materials in industry (Al-Jishi 1983; Morawski and Kaluch 1996), but naturally interstratified carbons in geological environments have not been recorded. Carbon in its various forms is widespread in terrestrial (French 1964; Jedwab and Boulegue 1984; Buseck and Huang 1985; Ross and Bustin 1990) and extraterrestrial materials (Smith and Buseck 1981; Allamandola et al. 1987; Wopenka 1988). Much terrestrial carbonaceous material was derived from early organisms and, when solid, ranges from kerogen and coal to highly ordered graphite. Extensive investigations using X-ray diffraction (XRD) (Landis 1971; Wada et al. 1994), HRTEM (Buseck and Huang 1985; Buseck et al. 1988; Oh et al. 1991) and Raman spectroscopy (Tuinstra and Koenig 1970; Yui et al. 1996) have been carried out to study the graphitization process and have shown that during metamorphism carbonaceous matter progressively increases in crystallinity, trending toward graphite.

Previous HRTEM, XRD, and Raman studies aimed at observing the crystallinity and structural characteristics used materials disaggregated from their host rocks, and thus the textural and crystallographic integrity of the matrix was lost. We found that the undisrupted textural and structural states of carbonaceous materials can be investigated in situ by utilizing ion-milled specimens. Non-crystalline and poorly crystalline carbonaceous material tends to aromatize with temperature and time, producing planar structures (Buseck and Huang 1985; Buseck et al. 1988). Clay minerals also have planar structures, so there is at least the possibility that the two could form in intergrowths with their basal planes parallel. Our observations of undisrupted specimens from low-grade metamorphic rocks confirm that some carbonaceous materials were intimately interstratified within illite crystals rather than occurring entirely as discrete crystallites.

EXPERIMENTAL METHODS

We studied a carbonaceous slate of the Late Triassic–Early Jurassic Daedong Group from the Jeongok area, Korea (Yu et al. 1992), which was subjected to subgreenschist facies metamorphism. Thin sections retaining the original textural integrity of the host rocks were prepared with orientations perpendicular to the foliation. Following optical and electron microprobe observations, 3 mm washers were attached to selected areas. Washer-mounted specimens were ion-milled, lightly coated with carbon, and examined at 400 kV with a JEOL JEM-4000EX transmission electron microscope equipped with a top-entry stage having tilting angles of ±15°, a spherical aberration coefficient (C_s) of 1.0 mm, and a structure resolution of 1.7 Å (Smith et al. 1986). A 40 µm objective aperture and a 150 µm condenser aperture were used for high-resolution TEM imaging.

RESULTS

Carbonaceous material occurs primarily as thin domains between illite crystals approximately 100 Å thick (Fig. 1). In most instances, it lies parallel to the enclosing illite layers. Its interplanar spacings vary slightly, and lattice fringes exhibit "fingerprint" textures, i.e., the carbonaceous layers are somewhat

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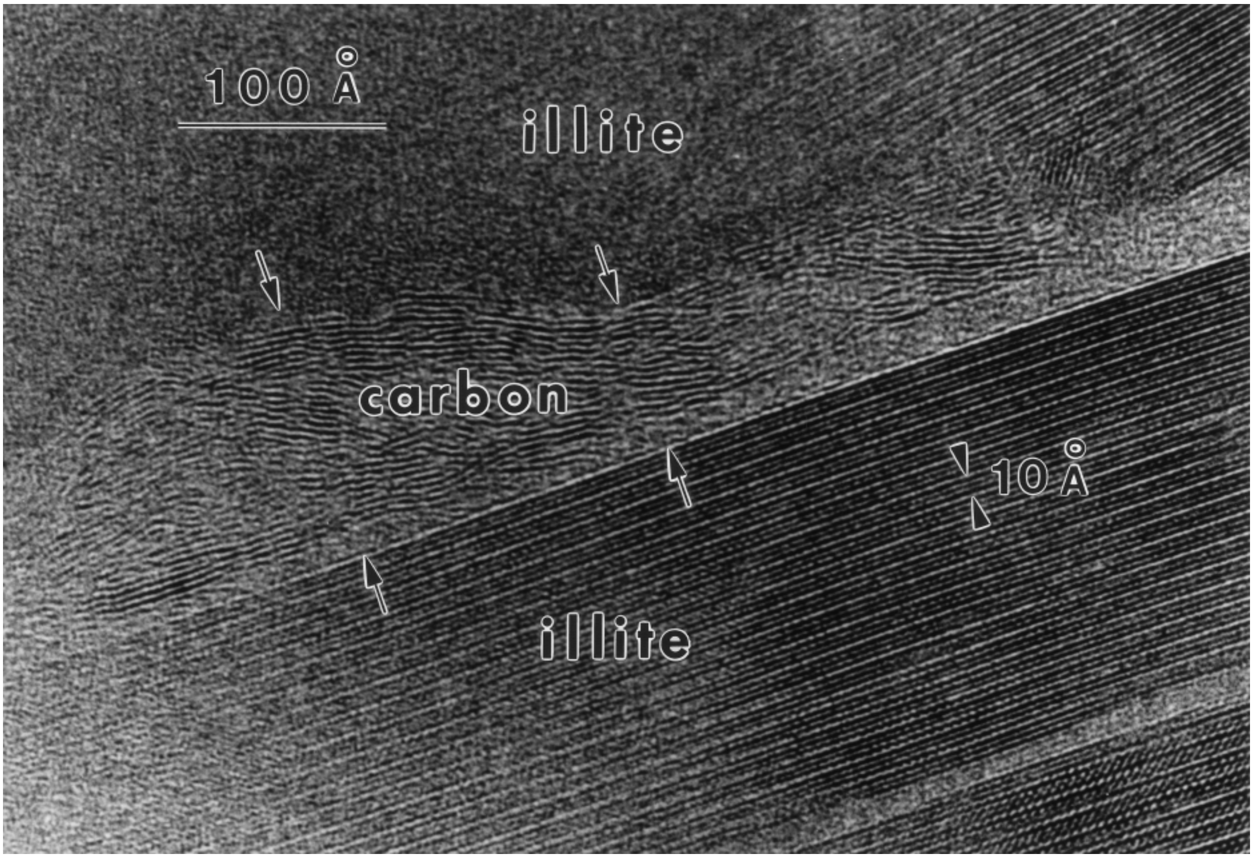

FIGURE 1. HRTEM image showing carbonaceous material between illite crystals. The carbonaceous layers show a “fingerprint” texture as a result of the wavy layer structure and edge dislocations.

wavy and discontinuous along the layers (Fig. 1). These features are characteristic of poorly graphitized carbon, a material typified by limited structural organization and abundant defects (Buseck and Huang 1985; Buseck et al. 1988; Oh et al. 1991).

HRTEM observations also show that carbonaceous material occurs in part as thin crystallites inside the illite crystals. Stacks of carbonaceous layers are observed to be scattered in otherwise pure illite (Figs. 2 and 3). The interstratified carbonaceous material is a few tens of angstroms thick, with carbonaceous layers aligned parallel to the illite layers; it generally exhibits better parallelism with illite and is in thinner units than the carbonaceous material at the grain boundaries. In places the illite layers appear to grade into carbonaceous material (Fig. 3). Isolated single carbonaceous layers within illite were not identified with certainty, but narrow stacks of carbonaceous layers could be distinguished from the sublayers of illite based on the 10 Å periodicities that are characteristic of the illite structure.

Selected-area electron diffraction patterns of carbonaceous materials show that the only reflection spots of the material occur near the 003 reflection of illite (Fig. 4). They are extremely weak and diffuse, consistent with the poor structural ordering of the carbonaceous material. They are tentatively indexed as corresponding to 002 of graphite. The interplanar spacings of the carbonaceous material are variable, but the diffraction pattern results in an average interplanar spacing of approximately 3.7 Å (Fig. 4).

DISCUSSION AND CONCLUSIONS

The extent of carbon maturation is commonly evaluated by the structural parameters, *d*(002) and *L*c, which represent the spacings between the stacked layers and the crystal thickness along the **c** axis, respectively; *d*(002) gradually decreases and *L*c increases with metamorphism (Landis 1971; Grew 1974; Itaya 1981; Wopenka and Pasteris 1993; Wada et al. 1994). The average *d*(002) value of 3.7 Å determined in this study is considerably higher than 3.35 Å, the value of well-graphitized carbon. The host rock was subjected to metamorphism below greenschist facies, and the relatively large *d*(002) value and thin crystallites are consistent with such low-grade metamorphism. Moreover, disordered structural features observed in the lattice-fringe images confirm that the carbonaceous material is only poorly graphitized (Figs. 1 and 2).

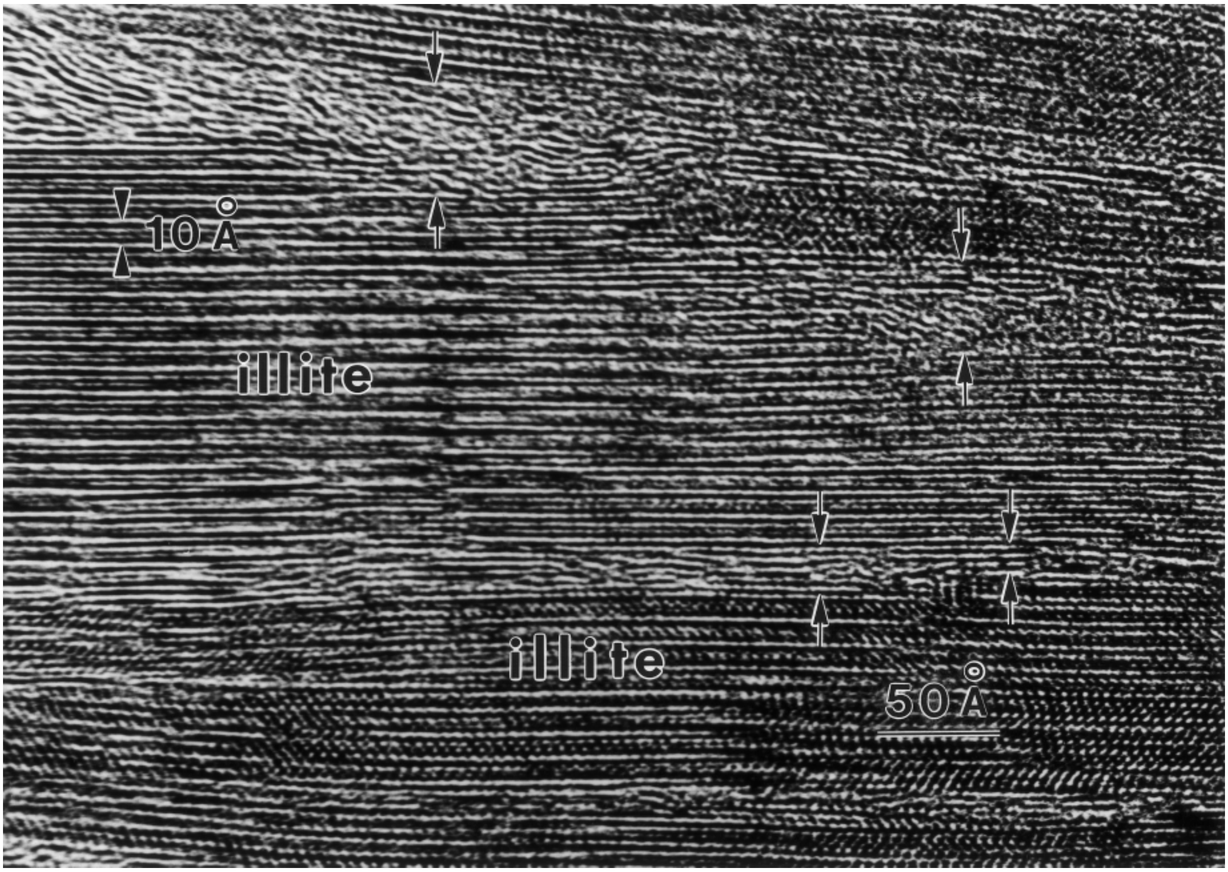

FIGURE 2. HRTEM image showing stacks of carbonaceous layers intergrown within an illite crystal. Single illite layers are resolved into three parallel sublayers with 10 Å periodicity. Discernible thin stacks of interstratified carbonaceous layers are marked by arrows.

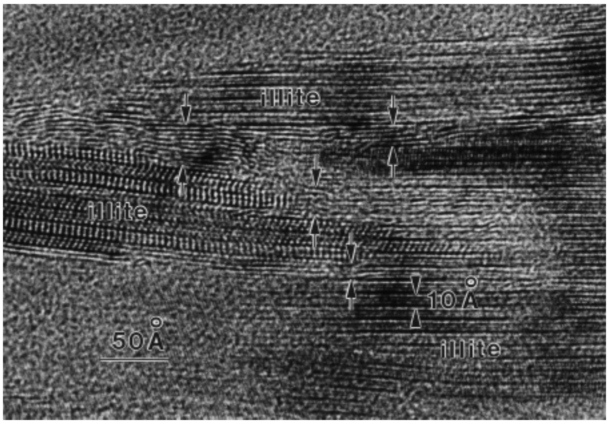

FIGURE 3. HRTEM image showing interstratified carbonaceous layers within an illite crystal. Some carbonaceous layers appear to grade into illite, and some illite layers are slightly bent. Stacks of interstratified carbonaceous layers are marked by arrows.

The graphitization of carbonaceous materials is affected by temperature, pressure, metamorphic fluids, and the lithology of the host rocks (Landis 1971; Wopenka and Pasteris 1993; Wada et al. 1994; Yui et al. 1996). Also, the types of precursor organic matter in the original sediments may influence the graphitization in low-grade rocks (Buseck and Huang 1985; Wopenka and Pasteris 1993; Yui et al. 1996). In addition to these factors, the interstratification of carbonaceous material within micas could affect graphitization. Intergrown carbonaceous material is likely to be shielded by its host illite and thus less accessible to metamorphic fluids, and therefore its structural evolution and crystal growth are likely to be more sluggish than that of carbonaceous material at grain boundaries. Previous XRD studies indicate that the decrease in *d*(002) of carbonaceous matter in metamorphic rocks is slow until the temperature reaches approximately 400 °C (Wada et al. 1994; Yui et al. 1996), which is the approximate upper limit of greenschist facies metamorphism. Interstratified carbonaceous material would eventually segregate from mica crystals, to be homogenized as discrete carbon particles with further metamorphism, and these would certainly be subjected to faster graphitization in high-grade rocks.

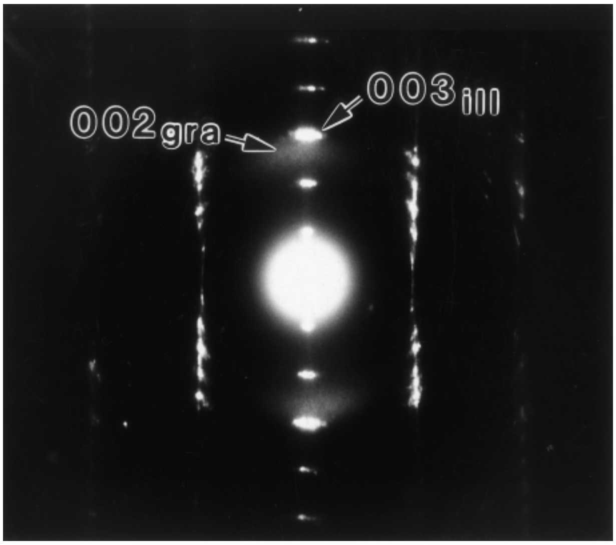

FIGURE 4. SAED pattern obtained from poorly graphitized carbonaceous material and illite. The 002 of the carbonaceous material and 003 of the illite are marked as 002_{gra} and 003_{ill}, respectively. Weak reflections from the carbonaceous material are slightly circular and diffuse.

A key question is how interstratified carbonaceous material formed within illite crystals. Illite in pelitic rocks generally evolves from smectite through diagenesis and low-grade metamorphism of the original sediments (Lee et al. 1985; Ahn and Peacor 1986; Peacor 1992), concomitant with an increase in crystallinity and crystal size. If small particles of carbonaceous material were trapped between the boundaries of illite or precursor smectite, they would appear as intergrown units within the resulting illite crystals. Alternatively, the absorption capability of smectite could result in carbon intergrowths. Smectite, which evolves toward illite and eventually muscovite through diagenesis and metamorphism, can absorb carbonaceous molecules as well as a variety of organic molecules in its interlayers (Green-Kelly 1955; Sonobe et al. 1990; Bandosz et al. 1992; Wilson et al. 1992; Putyera et al. 1994). If smectite containing the absorbed carbonaceous molecules transforms to illite, carbonaceous materials within interlayers could be partially graphitized by releasing H, O, N, and other atoms, resulting in the interstratification

This study reveals that carbonaceous material can be interstratified within minerals in the natural environment as well as in synthetic materials; such natural intergrowth is related to the illitization of clay minerals during diagenesis and metamorphism. Some crystallites as thin as several tens of angstroms that were characterized from carbonaceous concentrates separated from host rocks in previous studies may represent carbonaceous material that was actually interstratified within clay minerals. We suggest that the evolution of natural carbonaceous materials could involve such intergrowth structures and that the graphitization process, especially in low-grade pelitic rocks, can be more complex than previously recognized.

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