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A chlorite–"graphite" association

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Abstract

Black material coating fracture surfaces in the Wakefield marble exposed in the Medford quarry near Westminster, Maryland, consists of interlaminated magnesian chlorite, structure type IIb, and graphitized carbon with a low degree of metamorphism; only a single X-ray diffraction line, *d*(002) = 3.41Å, is obtained from the graphitized carbon. Scanning electron micrographs show no significant features in the surface appearance of the black component.

Occurrence

In the Medford quarry of the H. T. Campbell Sons' Company,[1] on Medford Road, 3 miles southwest of Westminster, Carroll County, Maryland, fracture surfaces in a limestone marble are covered by a shiny black coating and have the appearance of slickensided surfaces. These surfaces occur in the east end of the quarry, where the Wakefield marble is interlayered with the Sams Creek metabasalt. Both formations are probably of late Precambrian age; the geology of the area has been described by Stose and Stose (1946). The marble is closely folded throughout the quarry. In the west end of the quarry, the color is white, pale grey, and pale pink; no quartz and no crystallized silica–alumina minerals are found except occasional thin films of pale green chlorite along parting planes. Towards the east end of the quarry, the marble becomes more grey in color. Close to the east end, where the shiny black coatings are found, several tight folds of pale grey and dark grey marble occur, with a band of quartz bounded by a thin coating of grey chlorite along the bend of the folds.

The present note is concerned with the nature of the black coating material.

The nature of the black coating material

The black material is separated easily from the underlying limestone by a needle point or razor blade. When lightly ground by pestle and mortar, the material leaves a shiny black streak reminiscent of graphite, but when examined by X-ray diffraction a pattern of a well-crystallized chlorite of type IIb (Bailey and Brown, 1962) is obtained. This structure type is consistent with a metamorphic rather than a low-temperature chlorite (see Hayes, 1970) and with its occurrence in a marble. The only X-ray evidence for the possible presence of graphite is an inconspicuous band with a spacing about 3.4Å on the high-angle side of the strong chlorite reflection with *d* = 3.54Å. The strongest reflection from graphite, 002, has a spacing near 3.35Å but less well-crystallized "graphites" have spacings ranging up to 3.5Å or even higher values.

Separation of a black component from the chlorite proved unexpectedly difficult. The fine-grained black coating was dispersed in water by ultrasonic vibration and was treated with warm dilute HCl and then by hot concentrated HCl without any obvious reduction in the amount of chlorite. In fact, in the mechanical handling of the material, the "graphite" 3.4Å peak appeared to diminish in intensity with respect to the chlorite pattern. Because of this unusual reluctance of a fine-grained chlorite to dissolve in HCl, the material was treated overnight with an $HF^{-}H_2SO_4$ mixture in a platinum dish and then "fumed." The resulting black residue was entirely free of chlorite and gave a single strong reflection with a spacing of about 3.41Å; the peak was broad and slightly asym-

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[1] Division of the Flintkote Company

metric. No other diffraction characteristics of graphite were even faintly visible.

The chlorite component was obtained separately by placing a thin layer of the black material on a glass slide in a low-temperature ashing oven with a temperature around 180°C. In this device, an electric discharge in an oxygen atmosphere produces ozone and oxidizes carbonaceous material. The sample, after an overnight treatment, was almost white and gave the chlorite X-ray pattern without the "graphite" band. The chlorite itself was unchanged by this treatment.

The nature of the chlorite can be estimated from the X-ray data. The IIb-type structure has been mentioned already. The basal spacing, derived from orders up to 00.10, is 14.16 ± 0.02Å. From this spacing, an estimate of x in the tetrahedral cation composition $Si_{4-x}Al_x$ is obtained, namely $x = 1.35$ using an equation due to Brindley (1961) and $x = 1.29$ using an equation due to Kepezhinskas and Bailey in Bailey (1972). The use of these equations is discussed by Bailey (1972, 1975). From the b parameter, 9.20Å taken from the 060 reflection, an estimate of Fe(Mn) ions in octahedral positions is obtained. Various equations relating b to the number of Fe^{2+} ions have been given (Brindley, 1961; Bailey, 1972), all of which indicate that the number of Fe^{2+} ions must be very small or zero. The composition of the chlorite therefore is close to $(Mg_{4.68}Al_{1.32})$ $(Si_{2.68}Al_{1.32})O_{10}(OH)_8$, which places it in the prochlorite group of Tschermak's classification. The reluctance of this chlorite to dissolve in hot strong HCl may be related to the low iron content or possibly to a coating of carbon on the chlorite particles. Even after considerable grinding and ultrasonic dispersion of the material, however, the chlorite component still resisted hot HCl attack.

A thin section of a fragment of marble cut across the black-coated surface showed under the microscope thin bands of chlorite and the black graphitized material interlaminated with each other. Evidently the two components were formed more or less at the same time. Examination of the black-colored surfaces by scanning electron microscopy showed no characteristic features.

A subsequent chemical analysis by atomic absorption spectrophotometry on two samples after removal of carbon gave essentially identical results. The following formula was derived on the basis of anion composition $O_{10}(OH)_8$:

$$(Mg_{4.67}Fe^{3+}_{0.09}Al_{1.09})(Al_{0.94}Ti_{0.04}Si_{3.02})O_{10}(OH)_8 \cdot 0.89H_2O.$$

The amount of water, obtained from the ignition loss at 1100°C of material dried at 110°C, was slightly higher than the amount corresponding to $(OH)_8$, possibly because of imperfect removal of carbon; the samples still retained a greyish appearance. The Mg and Fe contents agree well with the X-ray derived values; the Al content is less than that estimated from the X-ray basal spacing measurements. The total octahedral cations, 5.85, are slightly less than the full complement of six cations. On the basis of these data, the mineral can be described as a clinochlore.

Discussion

Landis (1971), Grew (1974), and others (see Grew, 1974) have correlated the X-ray diffraction characteristics of graphitized carbonaceous materials, particularly the values of $d(002)$, the presence or absence of other diffractions, and the width and skewness of the 002 peak, with the degree of metamorphism. The present results indicate a very low degree of metamorphism, such that the black component can be described as a graphitized material but not as graphite. In relation to the scale of graphitization, 1, 1A, 2, 3, described by Landis, with strongly graphitized material in category 3, the present material, with $d(002)$ near 3.4Å, the diffraction peak slightly skewed, and with a total absence of other diffractions, comes close to category 1A. In relation to the data given by Grew, who plotted the 002 peak breadth versus $d(002)$, the present data, peak breadth 1.8° (2θ) and $d(002) =$ 3.41Å, lie on a linear extrapolation of most of his results rather than on the curved line which he plotted. Again the present data indicate a low degree of metamorphism.

The grey color of the marble suggested that graphitized material might also be disseminated through the rock. The marble dissolved readily in dilute HCl and yielded a small residue of finely divided black material, which, however, yielded no X-ray diffraction peaks. The chlorite was entirely absent, and the carbonaceous material was evidently not graphitized.

It is clear that the chlorite–"graphite" association occurs entirely in the surface coating, and since the components are interlaminated, their formation is probably related to the same metamorphic process in which silica-bearing solutions interacted with the carbonaceous limestone.

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