Graphite in natural and experimental carbonate systems

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Summary. Graphite occurs in the Darkainle nepheline syenite complex, Somali Republic, as small drop-like grains in an altered ankeritic carbonatite; it has been recorded previously from carbonate-bearing nepheline syenites and kimberlites. Experimental evidence indicates that siderite decomposes to a stable association of magnetite and graphite within the *PT* ranges 500 to 10 000 bars and 455 to 745° C. The graphite in carbonatite and other alkaline igneous rocks may have been formed similarly by the decomposition of siderite or iron-rich carbonates.

GRAPHITE has been reported from a steeply inclined minor carbonatite intrusion within the Darkainle nepheline syenite complex (10° 24′ N., 43° 16′ E.), Somali Republic (Gellatly, 1963*a*). It has been recorded in nepheline syenites and kimberlites from Canada, South Africa, India, and the USSR. The graphite in certain of these occurrences, including the Darkainle one, has a characteristic drop-like or bead-like form. The nepheline syenites from which graphite has been recorded are carbonate-bearing. Kimberlites also commonly contain carbonates and are generally regarded as being related to carbonatites. The occurrence of graphite in these nepheline syenites and kimberlites may thus be analogous to that in carbonatite.

The decomposition of siderite to magnetite+graphite has been investigated recently by French and Rosenberg (1965) and by Weidner and Tuttle (1965). Their results indicate that the reaction takes place between 500 and 10 000 bars and between 455 and 745° C. These temperatures and pressures are consistent, at least in part, with those suggested by Wyllie and Tuttle (1959*a*, 1959*b*, 1960) for carbonatite magmas. There thus appears to be a close parallel between the occurrence of graphite in carbonatite and other carbonate-bearing alkaline rocks on the one hand, and its occurrence as an experimental decomposition product of siderite on the other.

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Because of the wide range of temperatures and pressures applicable to the decomposition of siderite, it is of little use as a geological thermometer, but the drop-like form of the graphite may be of petrological significance.

Darkainle carbonatites. The Darkainle nepheline syenite in the north-western part of the Somali Republic is a concordant synorogenic intrusion of probable Precambrian age. It consists predominantly of subsolvus nepheline syenites (mainly litchfieldites) and saturated syenites (mainly rutterites) (Gellatly, 1963*b*). Veins and dykes of nepheline-syenite pegmatite, muscovite-syenite pegmatite, microlitchfieldite, and carbonatite cut the complex.

The carbonatites form concordant lenses and discordant dykes and veins up to 300 yds long and up to 12 ft thick. They are mainly limonite-rich sövites (calcitic carbonatites) and beforsites (dolomitic carbonatites). An isolated example of a sideritic carbonatite is also known.

The carbonatites consist mainly of calcite, dolomite, and siderite; other minerals include biotite, apatite, hematite, magnetite, limonite found both as pseudomorphs after pyrite and as finely divided specks within carbonate crystals, hydropyrite (?), plagioclase, pyrolusite, graphite, powellite, zircon, gypsum, baryte, and rare minute grains of probable pyrochlore. Many of these minerals, including graphite, have been noted only in the residues remaining after the carbonates were dissolved in HCl.

The Darkainle carbonatites are characterized by moderately high contents of La, Yt, Sr, and Nb, and their trace-element assemblage is comparable with those of other carbonatites rather than with those of sedimentary limestones (Higazy, 1954).

Graphite in igneous rocks

Carbonatite. Graphite has been found in only one of the several carbonatite minor intrusions cutting the Darkainle complex. This minor intrusion forms a concordant lens in biotite syenite, and has been traced intermittently for a distance of 105 yds with a maximum thickness of 10 ft. The contacts with the biotite syenite are sharp, and the syenite is apparently unaltered at the contact. At one end the intrusion grades into a syenite-breccia with a carbonate matrix, and it is cut locally by thin irregular veinlets of friable, off-white, translucent calcite.

The carbonatite is a coarsely crystalline beforsite with a grain-size of 2 to 3 mm, and is chocolate brown in colour. In thin section the rock is seen to consist mainly of large anhedral crystals of dolomite (79·3 %)

heavily speckled with limonite (2·7 %), subordinate amounts of limonite-free calcite (10·4 %), biotite (5·6 %), and magnetite (2·0 %), together with trace amounts of apatite and graphite. Dolomite shows well-developed crystal faces where it is in contact with calcite. Biotite is moderately abundant and consists of alternating green and brown laminae, with the green merging laterally into brown towards the crystal margins. Minor accessory minerals include apatite, magnetite marginally replaced by calcite, brown limonite pseudomorphs after pyrite, and small (0·1 mm) subspherical granules of graphite (fig. 1). The graphite granules consist of radiating flakes. Identification of the graphite has been confirmed by X-ray powder diffraction.

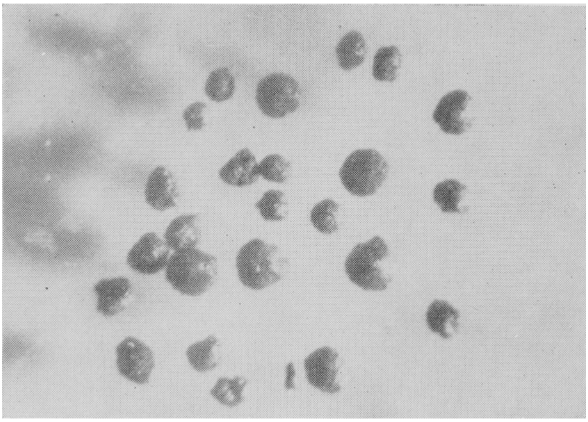

FIG. 1. Bead-like pellets of graphite, with micro-botryoidal exterior form; from carbonatite, Darkainle, Somali Republic.

Although the carbonatite in which the graphite is found contains dolomite and calcite but no siderite, the abundance of small specks of limonite suggest that the rock originally contained $FeCO_3$, probably as ankerite, and that subsequent hydrothermal alteration resulted in decomposition of the $FeCO_3$ component of this mixed carbonate.

As far as the writer is aware this is the first recorded occurrence of graphite from a carbonatite.

Nepheline syenites. The occurrence of graphite in nepheline syenites has been reported from the Haliburton–Bancroft area of Ontario (Adams and Barlow, 1910; Gittins, 1961), from Aliber in Irkutsk, USSR (Kupletsky, 1925), and from Sivamalai in India (Holland, 1901).

In each locality the nepheline syenites are associated with 'crystalline limestones', and in two of the localities—Haliburton–Bancroft and Sivamalai—the nepheline syenites contain primary calcite. Magnetite is a primary constituent in all three localities.

At Haliburton–Bancroft the graphite-bearing nepheline syenite contains calcite, which Adams and Barlow (1910) regard as primary. They record that: 'The mode of occurrence of calcite grains however is entirely different from that of a secondary constituent', the graphite occurs 'in small rounded shot-like forms consisting of minute scales of this mineral arranged in a plumose or radiating manner'. The graphite described by Gittins is in a nepheline–oligoclase–biotite–(graphite)–(calcite) gneiss. This rock is in contact with a graphitic marble, and the graphite has apparently been derived from the marble.

At Aliber the graphite 'forms large (some cubic metres) nests in nepheline syenite and is penetrated by 1 to 8 cm veins of nepheline syenite. The veins are bordered by platy selvedges of graphite, and near them there are drop-like forms of graphite embedded in the contact graphite. These drops have outer parts of calcite, orthoclase, and apatite, and internally consist of crystalline scales of graphite.' The graphite in the nepheline syenite is said to be of pneumatolitic origin and is believed to have been formed from hydrocarbons that resulted from the interaction of magmatic gases on CO_2 liberated from the limestone at the contact when wollastonite was formed (Kupletsky, 1925).

The graphite at Sivamalai occurs as flakes in a gneissose biotite–nepheline syenite containing primary calcite and magnetite. The principal feldspar is a cryptoperthite, and the rock is apparently a hypersolvus type of igneous origin.

Kimberlites. In addition to diamond, some kimberlites also contain carbon as graphite, and more rarely as bituminous hydrocarbons. Graphite has been recorded from kimberlites from South Africa (Williams, 1932), Basutoland (Dawson, 1962; Nixon, von Knorring, and Rooke, 1963), and from the USSR (Davidson, 1964).

The best-documented occurrences of graphite in kimberlite are those described by Williams (1932). He noted that diamond and graphite are found in inclusions of peridotite, pyroxenite, and eclogite, as well as in the kimberlite host-rock. Graphite forms as discrete flakes in the inclusions, whereas in the kimberlite it occurs in impure nodules containing up to 21 % of graphite. Analyses of these nodules, recalculated on a carbon-free basis, are similar to those of peridotite and pyroxenite.

In the USSR the Mir pipe in Yakutia is reported as having contained an eclogite xenolith containing both diamond and graphite (Davidson, 1964). The hydrocarbons reported from the Siberian kimberlites by Smirnov (1959) occur in calcite druses saturated with bitumen. Both the calcite and dolomite in these hydrocarbon-bearing kimberlites are stained yellow and brown by iron oxides.

The graphite from the Basutoland kimberlites has been described by Nixon *et al.* (1963) as 'slightly rounded six-sided striated crystals having a very bright metallic lustre', and makes up 0·03 % of a saxonite nodule.

The reported occurrences of graphite in kimberlite are limited in number but, according to Williams (1932), 'this may be accounted for by its softness, and therefore by the ease with which it may be destroyed'.

The main theories suggested for the origin of kimberlites postulate a close association between kimberlites and carbonatites. Von Eckermann (1961) and Garson (1962), for example, consider that carbonatites are high-level volatile-rich differentiates of a kimberlitic magma, while Bardet (1965), who also recognizes the close genetical association between kimberlites and carbonatites, regards them as early members of a differentiation sequence with nepheline syenites and related rocks as end-members. On the other hand, Holmes (1937) and Dawson (1960) regard carbonatite as a primary reactant, which by assimilation of olivine melilitite (Holmes, 1937) has given rise to kimberlite, and by assimilation of granite (Holmes, 1950) has given rise to katungite (olivine+melilite+potassic glass) and members of the olivine–biotite–pyroxene series. Dawson (1960) has extended the hypothesis of Holmes (1950) and suggests that carbonatite and granite may combine to produce kimberlite. The carbonatites necessary to produce kimberlite and its associates by reaction with granite are magnesium- and iron-rich types, such as those found locally, e.g. at Chilwa Island (Garson and Campbell Smith, 1958), Alnö (von Eckermann, 1948), and Darkainle.

Thus whether one considers kimberlites to be products of differentiation of a carbonate-rich kimberlitic magma, or a reaction product of carbonatite and silicate rocks, at some stage in their history they have contained carbonates, probably iron-rich carbonates, and elemental carbon may have been formed by dissociation reactions such as those of siderite outlined below.

Graphite in experimental carbonate systems

$CaCO_3$ and $MgCO_3$ dissociate to give the basic oxide plus CO_2, but FeO is unstable below 570° C, and the reaction $FeCO_3 \rightarrow FeO + CO_2$ is thus an oversimplification. Even if FeO were stable, it could not exist in an atmosphere of CO_2, which is oxidizing (Powell, 1965). Because of its instability FeO, once formed, will immediately react to form a higher oxide. In a closed system the most probable reaction (Powell, 1965; French and Rosenberg, 1965) is:

$$3FeCO_3 \rightleftharpoons Fe_3O_4+2CO_2+CO.$$

Ideally the gas phase produced in this reaction would have a CO_2/CO ratio of 2; such a ratio is metastable with respect to the formation of graphite between 400° and 600° (French and Rosenberg, 1965); thus graphite would precipitate from the gas phase. The combined reactions may be regarded as:

$$6FeCO_3 \rightleftharpoons 2Fe_3O_4+5CO_2+C.$$

Experimental evidence (French and Rosenberg, 1965; Weidner and Tuttle, 1965) confirms the validity of this reaction since both Fe_3O_4 (magnetite) and C (graphite) have been produced, but different results have been obtained for the *PT* ranges for which the reaction is in equilibrium.

French and Rosenberg report that small amounts of carbonaceous material, which proved to be disordered graphite, were formed during the experimental decomposition of siderite. They show that the assemblage siderite+magnetite+graphite+gas is univariant within the temperature range 455° to 465° C at moderate pressures (500 to 2000 bars). According to them siderite+magnetite+gas may exist over a temperature interval greater than 100° C, but where graphite is present, it restricts the range within which siderite and magnetite may coexist to only 10° C.

Weidner and Tuttle, however, found that the reaction is reversible at considerably higher temperatures and pressures. They report the limits 500 ± 25 bars at $500\pm15°$ C to $10\,000\pm200$ bars at $745\pm15°$ C.

No data have yet been published for melting relationships in the system $FeCO_3$–H_2O, but if it is assumed that the temperature of formation of sideritic carbonatites varies only slightly from those of calcitic and dolomitic melts (the geological evidence of the different types of carbonatite occurring in close association suggests that this is so), then the pressure–temperature stability of siderite is consistent with the occurrence of primary siderite in carbonatites, which according to Wyllie and Tuttle (1959*a*, 1959*b*, 1960) crystallize within the temperature range 640° to 740° C.

Discussion

Sideritic carbonatites and alkali rocks containing iron-rich carbonates (either siderite or ankerite) are natural carbonate systems that should approximate in their reactions, and in the pressures and temperatures of such reactions, to experimental carbonate systems. In particular, given favourable conditions of temperature and pressure, such carbonate-bearing rocks would be expected to contain magnetite and graphite, the minerals characteristic of the decomposition reaction of siderite. Both these minerals have been found in one of the carbonatites from Darkainle, and it seems to be more than coincidence that the only carbonatite to contain graphite should also be the only one from this area to contain magnetite.

The other occurrences of graphite, in carbonate-bearing nepheline syenites and kimberlites cited above, may possibly be analogous to that in carbonatite, but the graphite in these could admittedly be formed in other ways, such as by decomposition of metallic carbides, or in certain cases by the assimilation of graphite-bearing sedimentary limestones. Williams (1932, p. 206), however, states: 'Some writers have suggested that the carbon which afterwards crystallised into diamond and graphite was derived from metallic carbides, but its derivation from carbon monoxide or carbon dioxide seems more probable.'

The drop-like or bead-like form of the graphite in the Darkainle carbonatite, and in the Haliburton–Bancroft and Aliber nepheline syenites suggests some similarity in its origin. An indication of the possible significance of this bead-like form is provided by the experimental work of Noda and Matsuoka (1960) who produced beads of carbon, 1 to 3 mm in diameter, by melting charcoal and carbon black under an argon pressure of more than 100 atmospheres. The apparently exclusive occurrence in magmatic rocks[1] of these bead-like graphite pellets, and their experimental formation by melting, suggests that the graphite developed while the rock was still at least partially molten, and thus, in the case of carbonatite, at a temperature in the range 640° to 740° C (Wyllie and Tuttle, 1959*a*, 1959*b*, 1960), and in the case of nepheline syenites at about 750° C (D. L. Hamilton, pers. comm.).

Because of the change in temperature with increasing pressure of the equilibrium in the reaction $6FeCO_3 \rightleftharpoons Fe_3O_4+C+5CO_2$ noted by Weidner and Tuttle, this reaction is of no value as a geological thermometer.

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[1] Dr. O. von Knorring (pers. comm.) has, however, noted rounded forms of graphite in a skarn rock from South-West Africa.

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