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Research Article

Carbon in mineralized ultramafic intrusions, caledonides, northern Britain

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ABSTRACT

Graphite in Ordovician ultramafic intrusions through Neoproterozoic country rocks in West Aberdeenshire, NE Scotland attests to the mobility of carbon into subduction-related magmas. Pelites in the country rock contain up to 5% organic carbon, and are consequently also sulphide-rich. This occurrence is one of many examples of graphite in ultramafic intrusions. The sedimentary origin of the graphite carbon is indicated by carbon isotope compositions (mean − 19.7‰) in the same range as in the country rocks (mean − 21.6‰). The graphite is spatially and temporally associated with nickel-bearing sulphides, whose precipitation was strongly influenced by incorporation of the carbonaceous, sulphidic country rocks into the intrusions. Raman spectra for graphite in the intrusions show it is fully ordered, deposited from fluid in the magma. Preferential intrusion into pelitic country rocks facilitated the ready assimilation of carbon. In this case reworking of carbon from the crust into intrusions occurred 200 million years after sedimentation, a much longer timescale than most cycling of carbon in subduction zones.

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1. Introduction

Subduction is a critical process in the long-term carbon cycle (Brovarone et al., 2016; Dasgupta and Hirschmann, 2010; Galvez et al., 2013; Hayes and Waldbauer, 2006; Keleman and Manning, 2015; Martin and Hermann, 2018; Schwarzenbach et al., 2018). Previous studies have focussed on the removal of carbon by subduction, and it's outgassing through arc volcanoes, but there is increasing realization that more carbon is recycled at the Earth's surface than hitherto understood (Keleman and Manning, 2015). A neglected aspect of subduction in the carbon cycle is the role of partial melting of the crust. Very extensive mafic-ultramafic rocks occur in the deep crust of orogenic belts, derived from subduction-related magma, where they interact with the crust. This allows reworking of deep crustal carbon into magma that is conveyed to the shallow crust.

There is an opportunity to investigate the origin and behaviour of carbon in subduction-related magmas in the Caledonian orogenic belt of northern Britain. The largest graphite deposit in Britain is in subduction-related Ordovician andesites in Borrowdale, England (Ortega et al., 2010). The next most graphitic deposit is in NE Scotland, where graphite-bearing Ordovician intrusions in West Aberdeenshire cut through Neoproterozoic Dalradian Supergroup country rocks.

Investigation of the Aberdeenshire graphite was directed at determining:

1. Is the carbon of juvenile origin, or remobilized from assimilated sedimentary rock?
2. Characterisation of the graphite, i.e. is it partially or fully ordered carbon?
3. What genetic (spatial or geochemical) relationships can be determined between carbon and mineralization?

1.1. Geological setting

The Grampian Highlands terrane of NE Scotland consists of three main units: Proterozoic basement, Ordovician to Devonian intrusions, and Devonian sedimentary rocks. The basement is formed by metasediments of the Dalradian Supergroup, deposited c. 800 to 595 Ma (Halliday et al., 1989; Thomas et al., 2007). The Younger Basic intrusions of West Aberdeenshire were emplaced during the Grampian event of the Caledonian Orogeny (~470 Ma), accompanied by the conclusion of amphibolite facies metamorphism of the Dalradian Supergroup country rocks (Oliver et al., 2008). Intrusion was related to subduction in central Scotland, which instigated partial melting of the upper mantle (Oliver, 2001; Thompson et al., 1984), and the incorporation of partially melted crustal rocks of the Dalradian Supergroup within the intrusions. Emplacement occurred at a depth of about 16 km (Droop et al., 2003). These rocks were subject to the earliest studies of partial

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melting and assimilation, based especially on field and microscopic evidence of the incorporation of pelites (Droop et al., 2003; Gribble and O'Hara, 1967; Read, 1923a, 1935). Isotopic studies have confirmed the contribution of partial melting to the composition of the intrusions (Fletcher et al., 1989; Pankhurst, 1969).

The Younger Basic rocks are predominantly mafic and ultramafic cumulates (Gunn et al., 2015; McKervey et al., 2007; Munro, 1984; Wadsworth, 1988), including peridotite, picrite, troctolite, pyroxenite, gabbro and norite, serpentinized to varying degrees. The cumulates occur in the Argyll and Appin Groups (700–600 Ma) of the Dalradian Supergroup (at outcrop and depth respectively), which includes numerous beds of both graphitic pelites and limestones. Rocks rich in cordierite and wollastonite-actinolite-tremolite formed from these progenitors during high grade metamorphism, and occur especially in xenolithic partial melted metasediment in the cumulates. The cumulates include low-grade Ni-Cu-PGE mineralization (Fletcher and Rice, 1989; Fletcher et al., 1989; Gunn and Shaw, 1992;, McKervey et al., 2007) and several occurrences of graphitic carbon, in pyroxenites that cut gabbros and norites. Mineralization occurs particularly in the Huntly district of West Aberdeenshire (Fig. 1), and is best exposed and studied in graphitic pyroxenite through olivine gabbro at Bin Hill Quarry (National Grid Reference NJ 498430).

1.2. Organic matter and graphite

The Proterozoic Dalradian Supergroup country rocks contain graphitic schists (Fig. 1), representing the deposition of organic-rich sediments in deep sea and outer shelf marine environments. The graphite-bearing cumulate rocks occur predominantly in such schists rather than limestones. The graphitic schists occur in beds up to 10+ m thick, cumulatively 100 s m thick, in the Argyll and Appin Groups of the Dalradian Supergroup, and can be traced for over 400 km strike length across Scotland and Ireland (Anderton, 1976; Harris and Pitcher, 1975; Stephenson et al., 2013). The schists were formerly shales with hydrocarbon source rock potential as in younger sequences (Bata and Parnell, 2014). Contents of organic carbon commonly exceed 1%,

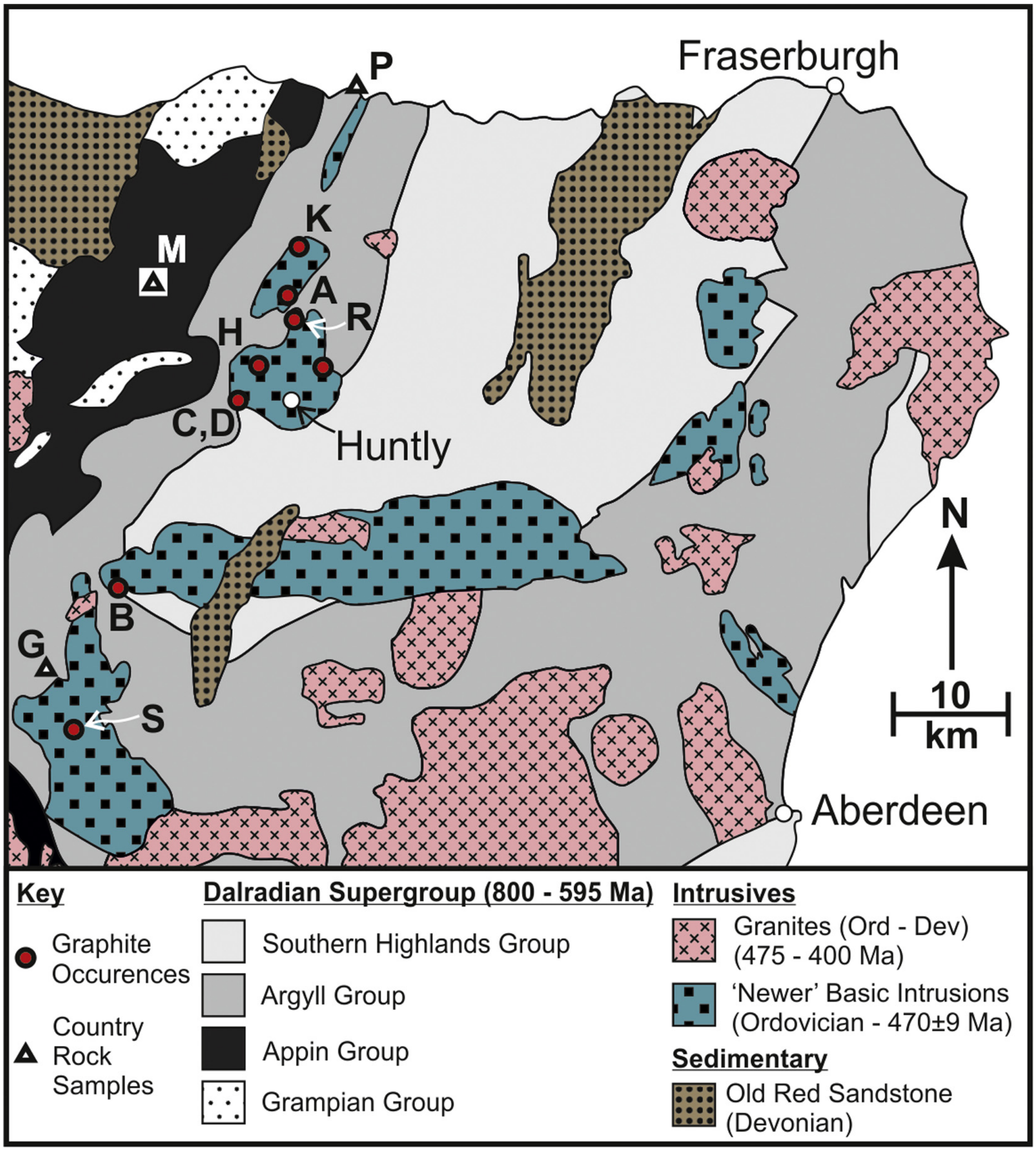

Fig. 1. Map of north-east Scotland, showing occurrences of graphite in Newer Intrusions, and localities of country rock used for Raman spectroscopy. Map after Stephenson et al. (2013) and Droop et al. (2003). Graphite: A, Auchincrieve; B, Bodiebae; C, Cairnie; D, Dunbennan; H, Bin Hill; K, Knock; S, Strathdon; R, Rothiemay. Country rock: G, Glenbuchat; M, Mortlach; P. Portsoy.

and contributed enough oil to fill turbiditic sandstones comparable in size to commercial oil reservoirs. The Proterozoic age of the rocks implies that the organic matter is all of microbial origin.

There is widespread evidence for the neoformation (Fig. 2) of graphite, including:

(i) Graphite incorporated within metamorphic minerals that grew in pelite (cordierite, andalusite) and also rarely in limestone (actinolite) country rocks.
(ii) Xenolithic metasediment incorporated in cumulate rocks, rich in graphite and sulphide minerals.
(iii) Graphite within pyroxenite pegmatite dykes cross-cutting the cumulates.
(iv) Veins of graphite cross-cutting the cumulates, large enough to have been mined in historical times.

The evidence of former graphite mining near Huntly and Portsoy was summarised by Strahan et al. (1917) and Read (1923b), who also reported graphite veins at Bodibae, Rothiemay Station and Knock (Fig. 1). A vein of width 4 ft. (1.3 m) was recorded in Strathdon (Statistical Account, 1843).

2. Methodology

Graphite samples from the intrusions in NE Scotland, and graphitic sediments from the Dalradian Supergroup country rock succession, were characterized by electron microscopy (Fig. 3), carbon isotope composition (Fig. 4) and Raman spectroscopy (Fig. 5). Sampling localities are shown in Fig. 1, and grid references recorded in Table 1.

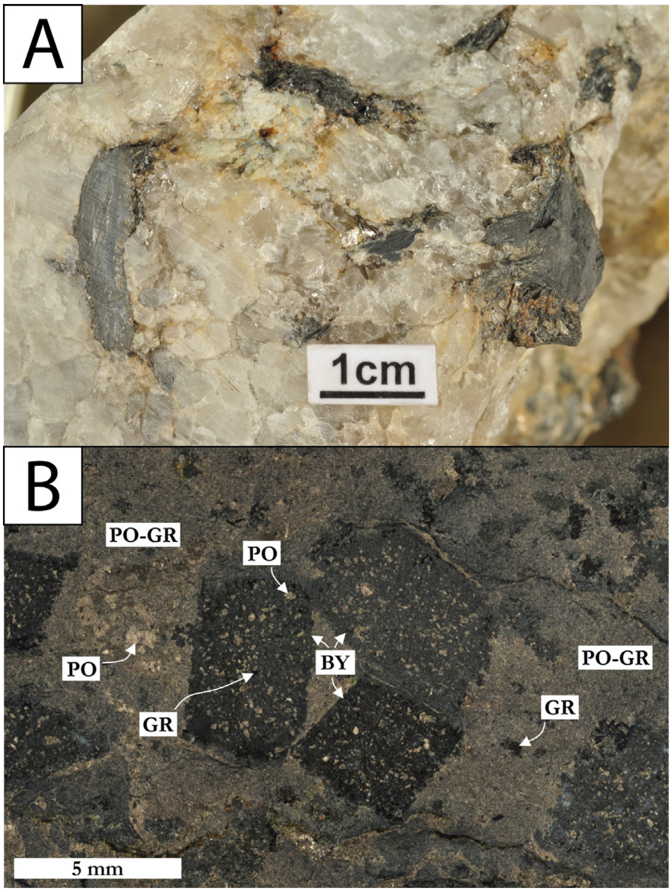

Fig. 2. Occurrences of graphite in hand specimen. A, Pegmatite, Cairnie, containing masses of graphite (grey) among quartz and feldspar crystals; B, Graphitic pyroxenite, Bin Hill Quarry, showing preservation of feldspar crystal shapes despite high content of admixed graphite (see Fig. 3B). Bytownite plagioclase (BY) includes graphite (GR) and pyrrhotite (PO), all in groundmass of pyrrhotite-graphite (PO-GR).

Scanning electron microscopy (SEM) was conducted in the Aberdeen Centre for Electron Microscopy, Analysis and Characterisation (ACEMAC) facility at the University of Aberdeen using a Carl Zeiss GeminiSEM 300 VP Field Emission instrument equipped with Deben Centaurus CL detector, an Oxford Instruments NanoAnalysis Xmax80 Energy Dispersive Spectroscopy (EDS) detector, and AZtec software suite. The operating voltage was 15 kV for EDS analysis, 8 kV for backscattered analysis.

Stable carbon isotope analysis was conducted on graphitic samples digested in 10% HCl overnight to remove trace carbonate. Samples were analysed by standard closed-tube combustion method by reaction in vacuo with 2 g of wire form CuO at 800 °C overnight. Data are reported in per mil (‰) using the δ notation versus Vienna Pee Dee Belemnite (V-PDB). Repeat analysis of SUERC's laboratory standard gave δ^{13}C reproducibility around ±0.2‰ (1 s). Data are recorded in Table 1 and Fig. 4.

Organic carbon and sulphur contents in country rocks were measured using a LECO CS225 elemental analyser, after decarbonatization with hydrochloric acid, to a precision of ±0.05%. Data for pelites at Portsoy (Fig. 1) are shown in Fig. 6.

The structural order of the graphitic samples was characterized by laser Raman spectroscopy, using a Renishaw inVia reflex Raman spectrometer, with a Ar + green laser (wavelength 514.5 nm). Initial analyses were based on accumulations over 3 s scan time on 10% laser power. The extended spectra in Fig. 5 were based on four spectra each, accumulated over 10 s scan time with 10% laser power. Data were collected from 3 samples of Dalradian country rock, and 5 samples of graphite in cross-cutting veins.

3. Results

Graphite occurs in the cumulate rocks as discrete graphite veins, as a mineral phase within pegmatites, and as a major phase within pyroxenite intrusions (Fig. 2) where it constitutes up to 50% (Gunn and Shaw, 1992). In graphitic pyroxenite at Bin Hill, typical samples are composed of plagioclase and pyroxene phenocrysts, distributed inhomogeneously in a groundmass (20–200 μm) of graphite, pyrrhotite, albite, augite, orthoclase, chlorite and biotite (Fig. 3a). Euhedral plagioclase (bytownite) phenocrysts occur up to 20 mm size and preserve the feldspar crystal shape despite contents of up to 50% admixed graphite (Fig. 2). Minor albite is also associated with the bytownite. Smaller pyroxene (ortho- and clino-) phenocrysts (0.5–1 mm) are abundant. Graphite occurs throughout all samples and within phenocrysts of bytownite (Fig. 3b) and pyroxene, indicating coeval crystallisation of graphite with igneous minerals. However, pyroxenes are more commonly independent of graphite (Fig. 3a). Graphite commonly occurs as elongate laths 40–100 μm, and up to 500 μm, in length (Fig. 3c,d). Pyrrhotite is the predominant sulphide, with rare pyrite. Where present, pyrite appears to be partially replaced by pyrrhotite. Pyrrhotite crystals, up to 500 μm size, are commonly intermixed with coeval lath-shaped graphite, and also form later cross-cutting veins (0.5–1 mm) independent of graphite (Fig. 3a). Inclusions of minor chalcopyrite and pentlandite occur within the pyrrhotite. Minor rutile and ilmenite are present in all samples (Fig. 3c). Chlorite alteration occurs throughout samples, commonly at the edges of feldspars (Fig. 3a). In summary, graphite was an integral component of the crystallizing magma, and in particular formed mixtures with the sulphide mineralization.

A typical mineralogy for the mineralized rock is: pyrrhotite 30%; bytownite 20%; graphite 20%; pyroxene 7%; chlorite 5%; augite 5%; albite 5%; rutile 2%; ilmenite 2%; pentlandite 2%; orthoclase 2%; pyrite, chalcopyrite, pentlandite, quartz and biotite all <1%.

The isotopic compositions for carbon in the graphite hosted in the intrusions (Table 1, Fig. 4) have the same range (−14.1 to −24.9‰) as carbon in the graphitic country rocks (−16.4 to −26.5‰).

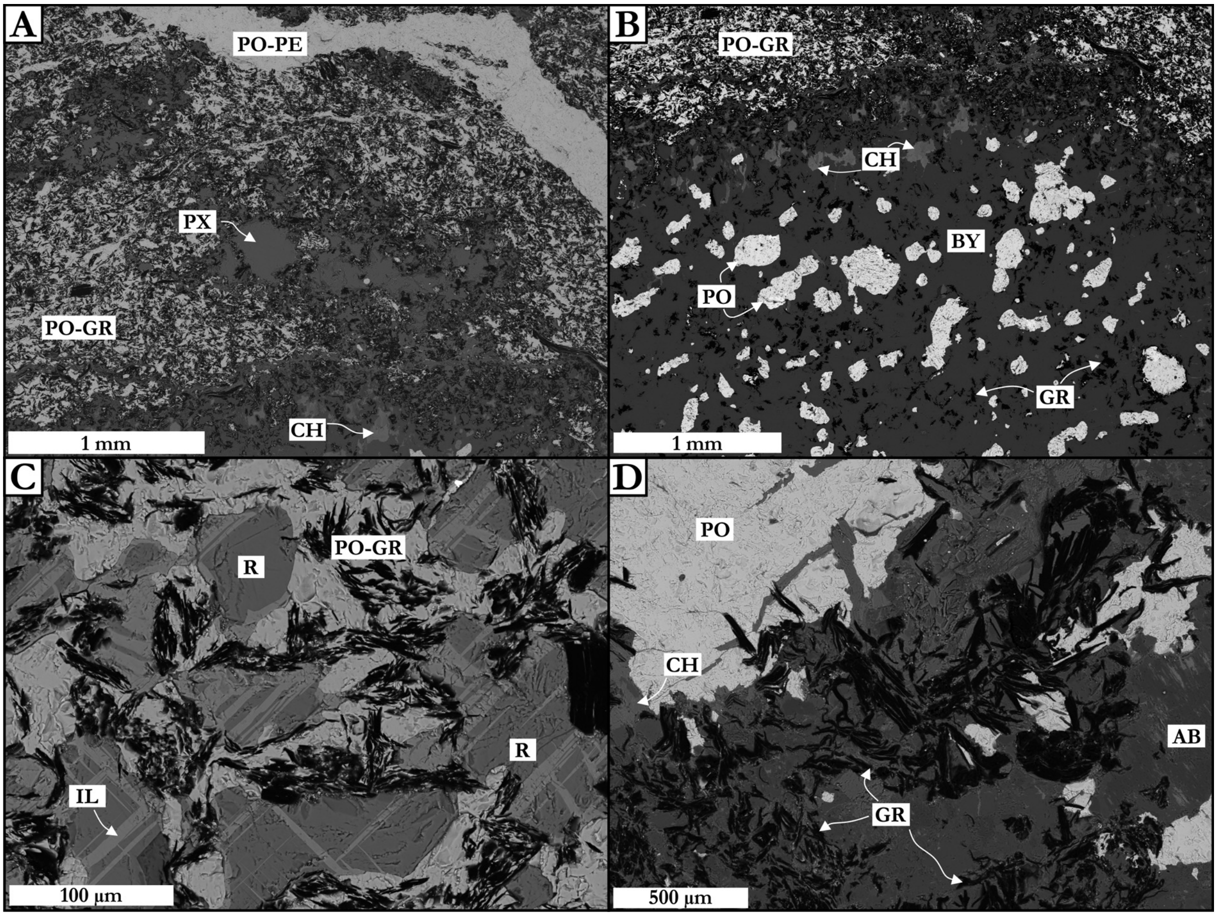

Fig. 3. Photomicrographs of mineralized pyroxenite, Bin Hill Quarry. A, Groundmass of pyrrhotite and graphite (PO-GR), enclosing phenocrysts pf pyroxene (PX), cross-cut by vein of pyrrhotite-pentlandite (PO-PE), locally altered to chlorite (CH); B, Large phenocryst of bytownite plagioclase (BY) in groundmass of pyrrhotite and graphite (PO-GR). Bytownite contains inclusions of pyrrhotite (PO) and graphite (GR), and is locally altered to chlorite (CH); C, Detail of pyrrhotite-graphite (PO-GR) groundmass, containing graphite-free rutile (R) and ilmenite (IL); D, Graphite (GR) laths in albite (AB). Albite locally altered to chlorite (CH). Pyrrhotite (PO) is relatively graphite-free.

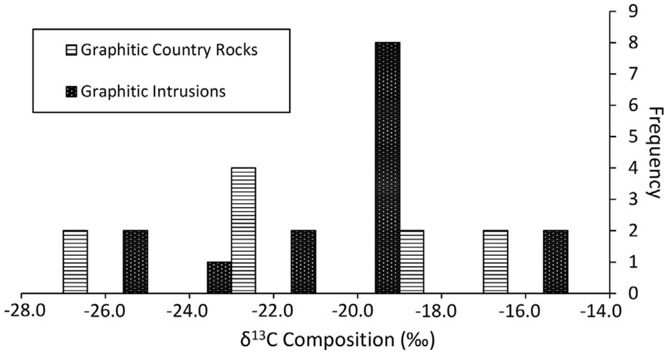

Fig. 4. Isotopic compositions for carbon in graphite hosted in Ordovician intrusions and in the Dalradian Supergroup country rocks. Ranges for the two groups overlap and imply a genetic relationship, i.e. intrusion-hosted graphite is derived from Dalradian Supergroup.

Raman spectra were successfully collected from 8 samples (Fig. 5). The graphite samples measured from Dalradian country rocks at Glenbuchat, Mortlach and Portsoy show a pronounced order (G) peak and a weakly developed disorder (D) peak. The graphite samples from cross-cutting veins at Bin Hill, Dunbennan, Auchencrieve, Rothiemay and Strathdon similarly show a well-developed G peak, but only the sample at Rothiemay shows a very limited D peak (Fig. 5).

Carbon and sulphur contents for pyritic pelite samples from the Neoproterozoic country rocks at Portsoy range up to 4.8 and 6.8% respectively, and on a cross-plot (Fig. 6) exhibit S/C ratios close to, and in some cases more S-rich than, the marine reference line of Berner and Raiswell (1984).

4. Discussion

4.1. Origin of carbon

The carbon contents of magmas are too low to allow graphite precipitation (Pawley et al., 1992), and as in other examples of volcanic-hosted graphite (Mackenzie, 1988; Mcconnell et al., 2002; Pedersen and Larsen, 2006) the source of carbon can be found in immediately available (meta)sedimentary country rocks. The isotopic compositions for carbon in the graphite within the intrusions have a similar range as carbon in the graphitic country rocks. The mean values are −19.7‰ and − 21.6‰ respectively, much lighter than the typical values for magmatic carbon in the range − 4 to −7‰ (Deines, 2002; Horita and Polyakov, 2015; Luque et al., 2012). This strongly suggests that the intrusion-hosted graphite was derived from carbon in the pelitic host rocks, and that the carbon was not a primary component of the magma. The origin of the carbon was ultimately biological, and had been recycled from older rocks rather than introduced from a juvenile source. The evidence for an origin in kerogen of the Dalradian Supergroup is consistent with 100 years of research on the assimilation of pelitic rocks into the Ordovician mafic and ultramafic intrusions. There is no evidence for graphite in the Younger Basic intrusions where they are distant from the graphitic country rocks, in the east of the region

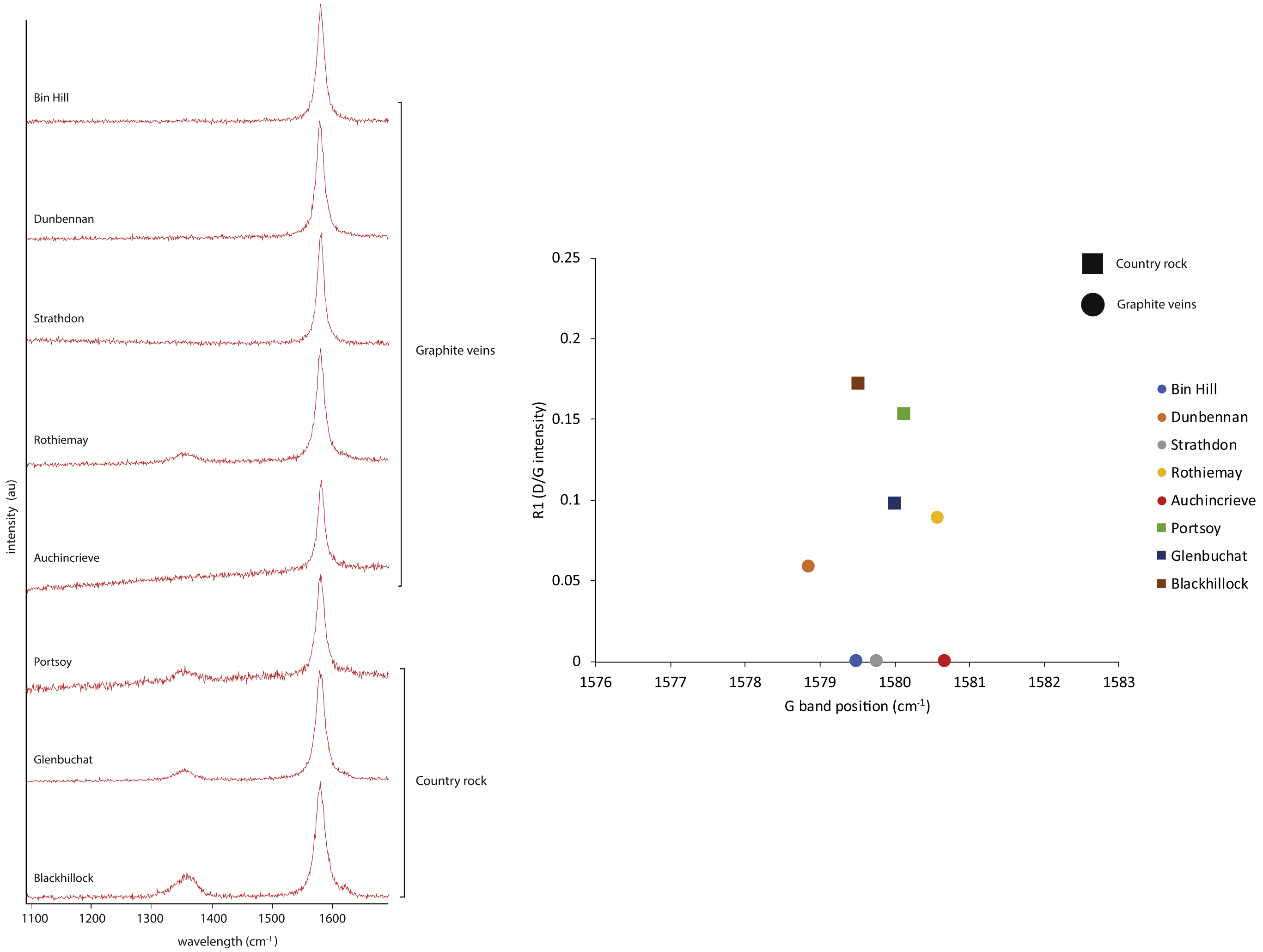

Fig. 5. Raman spectroscopy spectra for graphite veins and graphitic country rocks. All samples show well-defined graphite order peak (G) at ~1605 cm^{-1}. Country rocks additionally show minor graphite disorder (D) peak at ~1350 cm^{-1}. Cross-plot of D/G ratio and G peak position emphasizes distinction in samples.

(Read, 1923a; Read, 1935). Thus, both isotopic and petrographic data support a biological origin for the carbon.

The Raman spectra indicate that the vein graphite in the cumulate rocks is mostly fully ordered. The spectra from graphite in the Dalradian country rocks also indicate a high degree of ordering, but they indicate a greater degree of disorder than in the vein graphite shown by the D peak development, and are closer in composition to kerogen (Wopenka and Pasteris, 1993). The contrast is evident in the cross-plot of G peak position against D/G ratio (Fig. 5). The Raman data alone could be explained by increased heating of graphite by the cumulate bodies, but the occurrence of graphite in veins/pegmatites implies that it was deposited from fluids in the magma. The high ordering in the vein graphite is comparable to well-ordered graphite measured by Raman spectroscopy in other cumulate rocks, including examples in India (Rajesh et al., 2009), Spain (Crespo et al., 2006), Italy (Montanini et al., 2010) and North Africa (Pearson et al., 1994). Graphite crystals are a range of sizes up to 500 μm. The smaller graphite crystals are mixed with sulphides (Fig. 3), while the largest crystals are not. There are no cross-cutting relationships between different graphite crystal sizes, which probably formed at progressive stages of cooling.

Evidence from the mineralization in the intrusions has yielded mixed evidence for the origin of carbon, sulphur and trace elements in the melt. The isotopic composition of sulphur in sulphides is comparable to magmatic values (Fletcher et al., 1989). However, sulphides in the Dalradian Supergroup country rock have been shown to contain anomalously high contents of tellurium, selenium and gold, which would contribute to the mineralization (Parnell et al., 2018a, 2018b). Tellurium and selenium are both concentrated in the graphitic pyroxenites (Armstrong et al., 2019). Average S/Se ratios of the graphitic pyroxenites at Bin Hill Quarry are higher than the mantle maximum ratio (McKervey et al., 2007; Queffurus and Barnes, 2015), indicating a crustal component. The evidence from the graphitic component therefore favours an important role for the assimilated country rock.

Table 2 illustrates the diversity of occurrences, in time and space, of graphite-bearing ore deposits in mafic-ultramafic rocks worldwide. Most were emplaced at a depth of about 10 km or greater, including the graphite in NE Scotland. In most cases, despite the depth a source of abundant carbon was available in sedimentary/metasedimentary rocks, into which the intrusions were emplaced. In these examples, the intrusions clearly assimilated some of the host rock, which had been incorporated into the melt before the carbon recrystallized as graphite. The consistent sedimentary origin of the cumulate-hosted graphite is evident from carbon isotope data (Fig. 7). Most documented occurrences have isotopic compositions that are within the range for sedimentary carbon of −20‰ and lighter. This reflects biological preferred use of the lighter carbon-12 isotope, manifested in kerogen formed from microbial organic matter and derivatives from it including crude oil, and graphite in sedimentary rocks. The values are lighter than

Table 1
Carbon isotope composition of graphitic samples, NE Scotland.

Sample group	Location	Grid Reference	Setting	Lab no.	Composition
Proterozoic host	Glenbuchat	NJ 336177	Pelite	WAB13	−22.4
	Allt Nathrach	NJ 1510	Amphibolite	WAB10	−19.8
	Portsoy	NJ 585685	Pelite	AW1	−26.5
	Cairn of Claise	NO 185795	Pelite	WAB38	−23.0
	Mortlach	NJ 442482	Pelite	WAB34	−26.1
	Mortlach	NJ 442482	Pelite	WAB35	−18.5
Metamorphic	Coulins Burn	NJ 325187	Chiastolite	WAB16	−22.9
	Coulins Burn	NJ 325187	Chiastolite	WAB17	−23.8
	Altanower Forest	NO 0882	Actinolite	WAB4	−16.4
	Altanower Forest	NO 0882	Actinolite	WAB5	−16.5
Intrusions	Dunbennan	NJ 498405	Graphite vein	WAB1	−19.0
	Dunbennan	NJ 498405	Graphite vein	WAB2	−18.8
	Dunbennan	NJ 498405	Graphite vein	AW4	−14.1
	Strathdon	NJ 3315	Graphite vein	WAB3	−22.2
	Rothiemay	NJ 530460	Graphite vein	WAB6	−19.0
	Rothiemay	NJ 530460	Graphite vein	WAB7	−19.2
	Rothiemay	NJ530460	Graphite vein	AW3	−15.5
	Knock	NJ 525515	Graphite vein	AW2	−18.2
	Bodiebae	NJ 3924	Graphite vein	AW5	−19.1
	Auchincrieve	NJ 517478	Gossan	WAB8	−18.2
	Auchincrieve	NJ 517478	Gossan	WAB9	−19.4
	Bin Hill Quarry	NJ 498430	Sulphide ore	WAB11	−21.8
	Bin Hill Quarry	NJ 498430	Sulphide ore	WAB12	−21.2
	Cairnie	NJ 4844	Pegmatite	WAB14	−24.9
	Cairnie	NJ 4844	Pegmatite	WAB15	−24.4

Table 2
Age, emplacement depth and carbon isotope composition of graphite in mineralized cumulates (see Fig. 7 for data sources).

Deposit	Age	Emplacement	δ^{13}C (‰)
Stillwater, USA	2.7 Ga	10–15 km	−26 to −24
Voisey's Bay, Canada	1.33 Ga	9–11 km	−25 to −8
Duluth, USA	1.1 Ga	36 km	−37 to −19
Achankovil, India	470 Ma	>15 km	−10 to −7
Aberdeenshire, UK	470 Ma	16 km	−25 to −18
Bruvann, Norway	437 Ma	10 km	−21 to −14
Duke Island, USA	226 Ma	3–9 km	−28 to −26
N. Apennines, Italy	186 Ma	12–25 km	−5 to −4
Ronda, Spain	20 Ma	>30 km	−21 to −15
Hidaka Belt, Japan	10 Ma	23 km	−23 to −19
Hoggar, Algeria	~1 Ma	20–30 km	−25 to −14

the typical range for mantle-derived carbon of −4 to −7‰ (Luque et al., 2012), and which are recorded in mantle nodules and diamond (Deines, 2002; Luque et al., 2012). The light compositions also confirm the origin

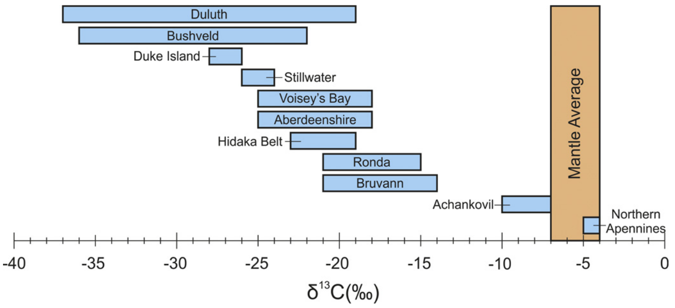

Fig. 7. Carbon isotopic compositions of graphite in Ni-Cu-PGE mineralized ultramafic intrusions. Data from Buchanan and Rouse (1984), Crespo et al. (2006), Fuex and Baker (1973), Lerouge et al. (2001), Montanini et al. (2010), Rajesh et al. (2004), Ripley and Taib (1989), Ripley et al. (2002), Thakurta et al. (2008), Tomkins et al. (2012), Wei et al. (2019) and unpublished.

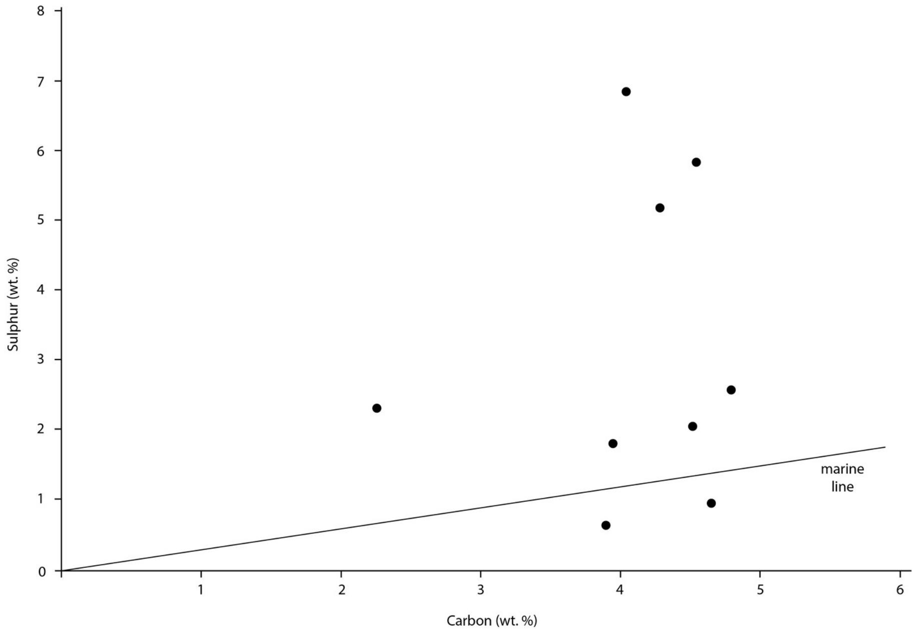

Fig. 6. Cross-plot of carbon and sulphur contents for pelitic rocks, Portsoy. Marine reference line from Berner and Raiswell (1984).

of the carbon in kerogen-rich sediments rather than limestones, which characteristically have a heavier, near-zero composition.

Elsewhere where carbon has been assimilated into intrusions from the country rock, commonly there has been only a short time gap between sedimentation and assimilation, for example in young metamorphic rocks in Japan (Tomkins et al., 2012). In other cases, the carbon experienced a history exceeding 100 million years and may have been already metamorphosed to an ordered state before assimilation. The host rock for graphite-bearing nickel deposits at Duluth, USA, is Palaeoproterozoic but was intruded and assimilated about 800 million years later (Ripley, 2014). Similarly, at Voisey's Bay, Canada, there was a delay of about 500 million years between sedimentation and assimilation into a mineralized cumulate intrusion (Ripley et al., 2002). The carbon in the Bin Hill intrusion had been deposited in the Dalradian Supergroup about 200 million years earlier before it was incorporated in the magma. Most cycling of carbon in subduction zones occurs within 10 Myr of subduction (Keleman and Manning, 2015), but clearly, the carbon cycling within intrusions can occur over a much longer timescale. The delay would not influence the assimilation of carbon into the melt. The longer timescale reflects the addition of carbon that was already incorporated in the crust rather than subducted from the ocean floor.

4.2. Role of carbon and sulphur in mineralization

The occurrence of graphite in cumulate rocks in NE Scotland is one of many such occurrences globally, most commonly associated with Ni-Cu-PGE mineralization as at Bin Hill Quarry (Table 2). Ultramafic rocks become mineralized by the segregation of an immiscible sulphide liquid, into which Ni, Cu and PGE fractionate and then precipitate during cooling (Barnes et al., 2017; Begg et al., 2010; Naldrett, 1999; Robertson et al., 2015). The interaction of these melts with crustal rocks helps to segregate the sulphide liquid, which may incorporate much of its sulphur content from assimilated crust. The consistent spatial relationship between carbon (as graphite) and Ni-Cu-PGE deposits, in varied time and space, indicates that it must also play a genetic role, most probably as a reductant. A reductant to induce low oxygen fugacity is an essential requirement of the genesis of Ni-Cu-PGE deposits, regardless of setting (Naldrett, 1999; Ripley, 2014), but especially in the relatively oxidizing magmas related to subduction. Although carbon has direct potential as a reductant, carbonaceous sediments are very often also sulphidic, as the anoxic sedimentary environments that preserve carbon are also conducive to the precipitation of syndiagenetic sulphides, especially pyrite, by microbial sulphate reduction (Berner and Raiswell, 1984). Microbial sulphate reduction to precipitate pyrite in the Dalradian Supergroup is evident from sulphur isotope studies (Hall et al., 1994; Parnell and Boyce, 2017). In the study area, high sulphur/carbon ratios in pelites at Portsoy (Fig. 6) confirm the availability of sedimentary sulphur to the cumulate melt. Assimilation of the sulphidic sediment into melt liberates hydrogen sulphide that can also contribute to reduction, and it may cause sulphide saturation so that sulphide minerals precipitate out. The petrographic evidence (Fig. 3) for an intricate mixture of platy graphite crystals with sulphides in the pyroxenites indicates precipitation from a melt rich in both carbon and sulphur. Graphite precipitates readily from carbon-sulphur melts due to a low solubility of carbon (Palyanov et al., 2006). The sulphides include pentlandite, representing nickel mineralization. Sulphide precipitation is fundamental to the mineralization process, by pulling metals including nickel out of the melt (Peltonen, 1995; Pina et al., 2006; Samalens et al., 2017). Semi-metals Te and Se enriched in the carbonaceous sediments are also assimilated in the melt, in which tellurium can precipitate elements including PGEs as tellurides (Parnell and Armstrong, 2019). The contents of semi-metals show very strong correlations with sulphur and organic carbon (Fig. 8) in the graphitic pyroxenites. This indicates the current residence of much of the semi-metals, particularly in sulphides whose distribution is controlled by the carbon. The low oxygen

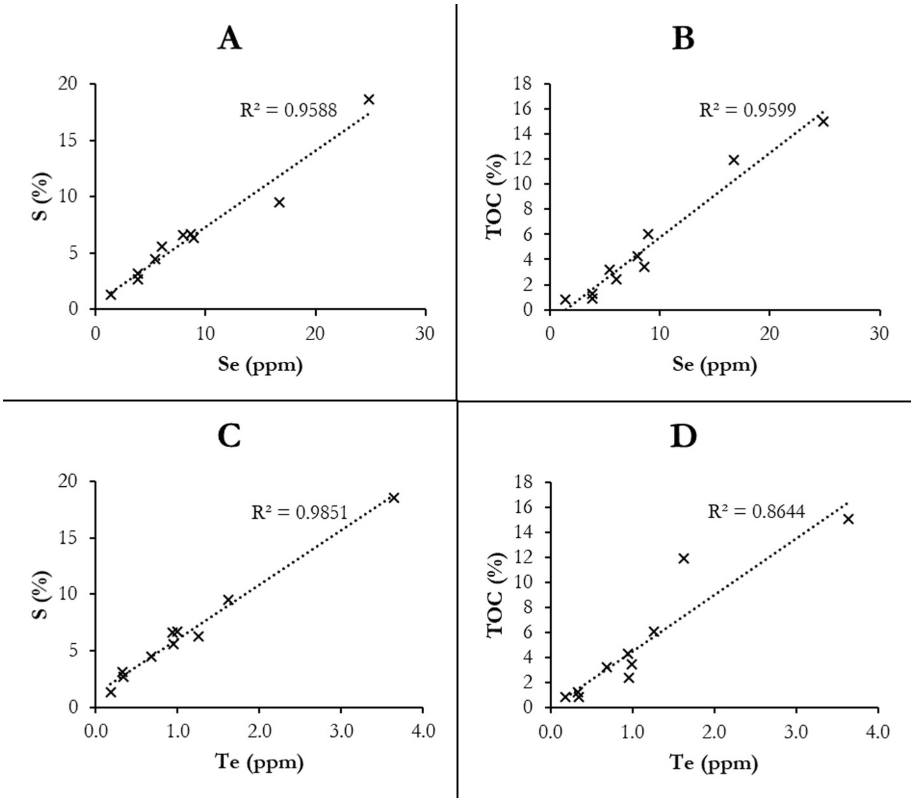

Fig. 8. Cross-plots of (A, B) Se against S and TOC, and (C, D) Te against S and TOC, for measurements of graphitic pyroxenites, showing very strong correlation.

fugacity that accompanies carbon causes low solubilities of PGE, and their resultant precipitation.

Ores in cumulate rocks formed in a range of geological environments, including subduction-related magmatism, intraplate magmatism and flood basalt, representing a range of depths, but those with evidence of graphite melt are typically from 10+ km. At such deep levels, the influence of graphite on local oxygen fugacity was strong, and loss by oxidation to carbon dioxide and degassing was very limited. Most extensively mineralized cumulates are graphite-bearing, including world-class ores at Stillwater, Bushveld and Duluth ores (Fuex and Baker, 1973; Ripley et al., 2002; Ripley and Taib, 1989). The mafic-ultramafic nature of the melts is critical to the spatial relationship. These melts are relatively high temperature, causing a high degree of melting of magma. This allows both much Ni, Cu and PGE to be released to the melt, and also much assimilation of the country rocks to yield carbon to the melt. Large volumes of magma are required to yield enough metal to reach ore grade, and for assimilation of enough sulphur to reach sulphide saturation. Such melts also have low viscosity, enhancing the separation of the ore-forming sulphide from the silicate liquids.

The interaction of carbon, sulphur and oxygen fugacity is complex. Modelling of moderately oxidized arc basalts shows that low (< 1%) graphite contents are enough to reduce oxygen fugacity and stimulate sulphide saturation (Tomkins et al., 2012). The sulphur content of a pyritic carbonaceous shale is likely to be greater than the magmatic sulphur content of an intrusion, so assimilation would increase sulphide saturation (Peltonen, 1995). Carbon in the melt also lowers the melting temperature of sulphides incorporated from country rock, and hence enhances sulphide saturation in the melt (Dasgupta et al., 2009). Thus, multiple drivers combine so that intrusion into sulphidic carbonaceous shale would cause widespread sulphide supersaturation and coalescence of ore sulphides (Tomkins et al., 2012). The precipitation of graphite may be induced in several ways, including isobaric cooling, reduction in oxygen fugacity, and reduction of an oxidized carbon-bearing fluid by sulphides. Montanini et al. (2010) emphasize the potential role of sulphides, which are readily available where shales are assimilated.

4.3. Carbon in large-scale intrusions

The distribution of kilometre-scale plutons belonging to the Younger Basic intrusions of West Aberdeenshire is strongly controlled by the pelitic Argyll and Appin groups of the Dalradian Supergroup (Fig. 1). The relatively weak fine-grained country rocks preferentially permitted emplacement of the intrusions, and also allowed relatively high yields of melt (Petford et al., 2000). They are also preferentially graphitic, as they were deposited in low-energy environments where organic matter could accumulate. Thus, the cumulate rocks were predisposed to exposure to, and assimilation of, organic carbon. This relationship is repeated in many other parts of the world, and is responsible for the numerous records of assimilation of carbon into intrusions (Table 2), and consequently contributed to the mineralization of the intrusions. The maximum possible assimilation is probably a one-for-one incorporation of country rock into melt, which in the case of the Dalradian Supergroup pelites is about 1% organic carbon. The 20–50% organic carbon in pyroxenite intrusions indicates that fractions of the melt can concentrate the carbon. However the close spatial relationship between graphitic cumulate rocks and graphitic country rocks shows that mobility of carbon, and hence homogenization, in the melt was limited.

The assimilation of country rock can create huge volumes of graphite within intrusions, for example a granite-hosted deposit estimated at billions of tonnes of graphite is recognised in China (Ai et al., 2018), and graphite exploration is being undertaken in heavily graphitized granite in Australia (Mackenzie, 1988). An estimated 250 million tonnes of graphitic carbon occurs in Palaeocene intrusive volcanic rocks in west Greenland (Pedersen and Larsen, 2006). In Britain, the Bin Hill graphite is second in graphite abundance only to the graphite in Ordovician andesites at Borrowdale, England (Ortega et al., 2010). The Borrowdale andesite magma was subduction-related (Mcconnell et al., 2002) but followed sedimentation of the assimilated organic-rich sediments by about 20 million years rather than the 200 million years in Scotland.

The Ordovician of Britain and Ireland offers a window on the interaction of volcanic rocks and organic carbon at several stages (Fig. 9). This reflects the co-occurrence of plate margin volcanism and black shale sedimentation at this time (Vaughan and Scarrow, 2003). Firstly, sea floor basalts incorporated organic carbon through intrusion into the black shales and colonization of the cooled basalts by microbial colonies (Parnell et al., 2015). Secondly, subduction-related arc volcanism incorporated the black shale carbon on a large scale (Barrenechea et al., 2009; Ortega et al., 2010). Then finally, as evident in Aberdeenshire, deep-seated subduction-related volcanism assimilated much older carbonaceous crust. In a wider context, further deep-seated subduction-related fluids, which did not assimilate organic carbon and had higher oxygen fugacity, formed Silurian carbonatites in the Northern Highlands of Scotland (Young et al., 1994).

The assimilation of carbon into magma can lead to metal ore deposition from large-scale intrusions on a commercial scale. This is most widely evident in the nickel ore bodies cited here, and is directly evident for example at the carbon-contaminated margin of the Duluth Complex (Ripley and Taib, 1989). However, several other metals become concentrated in this way, and ore deposition occurs when the host magma has appropriate carbonaceous geochemistry. Sulphide precipitation occurs similarly in granites which deposit tin/tungsten ores when carbon gives them a reduced character (Frost and Frost, 2013), including

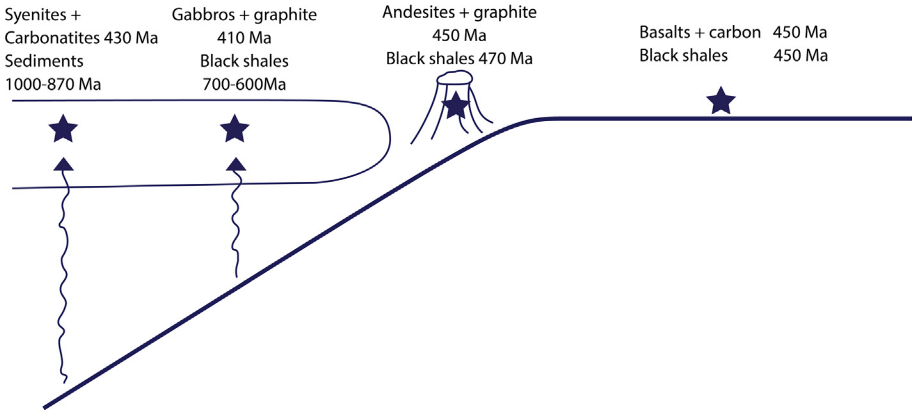

Fig. 9. Schematic occurrence of carbon-bearing rocks associated with Ordovician-Silurian subduction at margins of Iapetus Ocean, including sea floor basalt in black shales (Parnell et al., 2015), arc-related andesites with graphite (Ortega et al., 2010), deep-seated ultramafics with graphite (this study) and deep-seated carbonatites (Young et al., 1994). Ages for source sediments and mineralization increasingly separated with progress of subduction.

commercial deposits in Brazil (Sirqueira et al., 2018), Spain (Chicharro et al., 2016) and China-Vietnam-Thailand-Malaysia (Linnen, 1998; Pašava et al., 2003; Vladimirov et al., 2012). Carbon in granites can also cause contamination without forming sulphide ores, including uranium (McKechnie et al., 2013) and gold (Mackenzie, 1988). The range of metals concentrated in this manner suggests that the assimilation of carbon in intrusions could become a more prominent factor in future exploration models.

5. Conclusions

Graphite in West Aberdeenshire, NE Scotland, exemplifies carbon mobility in cumulates. Gabbros and pyroxenites host graphite-sulphide mineralization emplaced ~470 Ma into late Neoproterozoic graphitic metasediments at a depth of ~16 km. The metasediments were partially melted and were a source of carbon. The availability of carbon was enhanced by preferential intrusion into pelitic sediments which are now graphitic schists. Carbon and associated sulphide contributed to a low oxygen fugacity, which engendered precipitation of reduced organic carbon. Characterisation of the carbon in West Aberdeenshire graphite shows:

(i) The carbon is fully ordered graphite.
(ii) The graphite carbon exhibits isotopic fractionation to a composition similar to that of the country rock kerogen.
(iii) The carbon forms an intimate mixture with nickeliferous and other sulphides, suggesting that the carbon contributed to a reducing environment for mineralization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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