Origin of vein-graphite derived from metamorphic fluids in Moine (Glenfinnan Group) rocks, NW Scotland

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Synopsis

Proterozoic metasediments at Glen Strathfarrar, Inverness-shire, host a deposit of vein-graphite that is unique within the Moinian stratigraphic sequence. Carbon isotopic analysis, Raman microspectroscopy, fluid inclusion studies and volatile gas analysis were used to constrain the origin of the vein-graphite. Carbon isotopic analysis shows that the carbon is heavier than that expected for sedimentary material (δ13C value of ~14.35‰), suggesting that fractionation has taken place since sedimentation. Graphitization of sedimentary carbon in the Glenfinnan Group pelitic gneiss occurred in response to changes in both temperature and pressure arising from a series of regional metamorphic events. Scavenging of carbon by metamorphic fluids generated during amphibolite-grade metamorphism associated with the youngest, possibly Caledonian, event is the most probable source of the vein-graphite at Glen Strathfarrar. Similarities in gas composition with quartz veins occurring in Dalradian rocks show that carbonaceous sedimentary sequences consistently generate fluids rich in CO2 and N2, making volatile gas analysis a valuable tool in determining the history of metamorphic fluids. The occurrence of crystalline graphite in the pelitic gneiss at Glen Strathfarrar makes it highly likely that the carbon-rich fluids have been generated from within the Glenfinnan Group sediments rather than from Lewisian rocks at depth. Despite the assertion that graphite is uncommon in Moine rocks, the high ammonium content of biotite in these metasediments and the consistently high N2 values of fluid inclusions within the siliceous schist and quartz veins suggest that, prior to metamorphism, the sediments contained more organic matter than their present composition suggests.

Supplementary material: The results of incremental crush analysis of vein samples from localities within the Moine, Dalradian and Old Red Sandstone are available at http://www.geolsoc.org.uk/SUP18499.

Vein-graphite occurs in fractures in metasediments of Proterozoic Moine (Glenfinnan Group) rocks in Glen Strathfarrar, Inverness-shire [NH 286 384], forming a concentrated deposit that was once worked commercially, albeit on a small scale. Described by Horne & Hinxman (1914) as ‘a thin, nearly vertical, north-east and south-west vein of plumbago’, the source of the carbon has not previously been identified. This study used Raman spectroscopy to characterize vein-graphite and carbonaceous material in the host pelitic gneisses, and used isotopic analysis of the carbonaceous phases and fluid-inclusion analysis of quartz vein material associated with the graphite deposit, to determine whether the carbon was derived from the host sediments or whether it was exotic.

Metamorphism of sedimentary sequences should generate aqueous fluids commensurate with the geochemistry of the rocks and with the metamorphic grade. Volatile gas analysis of incrementally crushed samples (Norman & Blamey 2001) was used to establish the composition of fluids associated with the graphite at Glen Strathfarrar. Data from Glen Strathfarrar were compared with those from quartz veins cutting the underlying Morar and overlying Loch Eil groups of the Moine (Figs 1 and 2) and with other metamorphic quartz veins from the Dalradian of NE Scotland, allowing a metamorphic signature for the rocks to be identified. The depositional setting of the Moine and Dalradian rocks in a shallow-marine environment adjacent to a passive margin is similar (Trewin & Rollin 2002) but Dalradian sequences include graphitic facies that are not present in the Moine (Rock et al. 1986). Unmetamorphosed calcite veins from the Old Red Sandstone of Caithness provided a control dataset against which the metamorphic samples could be compared. Laminites from the Orcadian Basin are rich in organic material, allowing comparisons to be made with fluids bearing carbonaceous gases at lower (diagenetic)
temperatures. Carbon isotopic data from Dalradian pelites and associated localized occurrences of vein-graphite were also compared with carbonaceous material at Glen Strathfarrar.

The Glen Strathfarrar graphite deposit is concentrated in folded rocks of the Glenfinnan Group and has been removed by blasting at the surface. Heddle, quoted in Horne & Hinxman's (1914) Memoir for the area, states that 'in 1818 five tons (of graphite) were extracted, which sold for £93 each; the cost of raising was £13 per ton'. Hinxman speculates that the workings were 'soon abandoned ... owing to the cost of carriage and the fall in the price of the mineral'. By 1829, the landowner, Thomas Alex Fraser Esq. of Lovat, appeared to be heavily in debt, borrowing £22 100 sterling through the auspices of the Aberdeen Fire and Life Assurance Company (Highland Council Archive 1999), suggesting that either the graphite and lead workings on the estate had closed or were no longer operating at a profit. It has not been possible to ascertain when the mines were last worked or to determine how much material might have been extracted, although all the mines are shown as disused in 1872 when the area was surveyed by the Ordnance Survey. The current 1: 25 000 OS map (revised 2002) shows the mine close to a feature named as 'Tom a' Mhein', which is probably a corruption of 'Tom a' Mèinn' which translates from the Gaelic as 'knoll of the vein' (or mine or ore) (www.ordnancesurvey.co.uk/oswebsite/freefun/didyouknow/placenames/docs/gaelic_guide.pdf). The OS map also indicates that the mine is a disused lead mine, but this is erroneous. Wilson (1921) details three abandoned lead mines on the Lovat estate c. 10 km to the east in neighbouring Strathglass, suggesting that he would have included the Glen Strathfarrar mine in his report if lead had indeed been worked here. The Inverness Journal dated 10 August

Fig. 1. Map of north-west Scotland showing sample localities for quartz veins cutting Moine rocks of the Morar, Glenfinnan and Loch Eil Groups respectively.

Fig. 2. Stratigraphic position of quartz veins within the Moine succession analysed by gas mass spectrometry.
1821 (quoted in Harrison 2000) reports the death of a ‘young man employed in Lovat’s lead mine in Glen Strathfarrar’ during blasting and the Kilmorack Heritage Association surmise that this accident occurred at the graphite mine (Harrison 2000). The confusion in the historical literature arises from the use of ‘plumbago’ to refer to both lead- (Pb) and black lead- (C) bearing ores. Writing in the New Statistical Account of Scotland (Society for the benefit of the sons & daughters of the clergy 1845), the minister for the parish of Kilmorack states that ‘a black lead mine ... did not turn out profitable, the rock being exceedingly tough and hard, and the quality of the plumbago rather inferior’, again indicating that the deposit was not worked for long. The ruins of three mine buildings remain (the largest is c. 8 m × 4.5 m), as does the c. 1 m deep channel that carried water c. 40 m to/from the river for processing the ore.

The rocks of the Glenfinnan Group are a mix of pelites, semipelites, quartzites and psammites, which have been subjected to at least two episodes of amphibolite-grade metamorphism, resulting in the gneissification of the original lithologies (Strachan et al. 2002). The units are often thinly interbanded and rocks in the vicinity of the mine show upright folds along north–south axes (Fig. 2), which are interpreted as D3 structures (Rogers et al. 1998). Fracture planes with a similar orientation to the fold axes are also observed within the worked area of the mine, which covers an area approximately 250 m². Some fracture surfaces retain a thin veneer of vein material suggesting that they are linked to a late deformation event and, consequently, may be Caledonian in age. Neoproterozoic Dalradian rocks from the Banffshire coast of NE Scotland have also been subjected to amphibolite-grade metamorphism (Strachan et al. 2002) and quartz veins cutting these rocks are also likely to be associated with late-stage Caledonian metamorphism. In contrast, Devonian Orcadian basin laminites from Caithness have not been metamorphosed and contain calcite veins linked to fluid flow during diagenesis (Trewin & Thirlwall 2002).

Samples

Samples were collected from the two spoil heaps at Glen Strathfarrar (Fig. 3); the spoil is now heavily vegetated and comprises an area c. 300 m² to the NW of the workings, with a smaller area of spoil (c. 200 m²) to the SW of the worked area. Material on the larger spoil heap is predominantly quartz-mica schist (c. 80%), with some siliceous schists (c. 15%) and minor graphitic schist and vein material (< 5%). The smaller tip contains more siliceous schist (c. 20 %) and quartz vein material (c. 15 %), with minor amounts of graphite-bearing material (< 5%) still evident. The samples collected for this study included massive graphite (Fig. 4), quartz vein material edged with graphite (Fig. 5) and disseminated graphite within a quartz and orthoclase feldspar vein (Fig. 6). In all the samples, graphite is present as aggregates of thin, platy flakes, with each flake up to 1 mm in length. The graphite is intimately associated with varying amounts of biotite, muscovite, quartz and feldspar, all of which are similar in size (c. 1 mm across). Pinky-red garnets up to 2 mm in size occur in all the samples, with the graphite flakes wrapped around the garnet. The carbonaceous material was analysed using Raman spectroscopy to determine its structural order. Although...
crystalline, the structural order of graphite varies due to defects in the hexagonal rings and in the stacking sequence, largely influenced by precipitation temperature and pressure (Pasteris 1999). Polished thin sections were made from the graphite vein and from the host metasediments. The thin section of the graphite vein (Fig. 7) shows that graphite is generally aligned parallel to biotite crystals in the deposit. Both minerals occur at right angles to the edge of the quartz vein but become parallel to the vein walls nearer the vein centre. In the host metasediments, the graphite occurs as flakes up to 0.5 mm long, with some flakes reflecting the alignment of the biotite and others in random orientation. The metasediments also contain quartz, orthoclase feldspar, garnet, ilmenite, apatite and zircon. A doubly-polished wafer for fluid inclusion analysis (microthermometry) was prepared from a quartz vein edged with graphite, with additional sub-samples from the vein used for fluid inclusion volatile analysis. Samples of pelitic gneiss in the vicinity of the mine and siliceous schist from Pollcherian Bridge [NH 330 396] further downstream were also sampled. Carbon isotopic analysis of the vein-graphite and a limestone unit in the Lewisian outlier to the west of the mine was carried out in addition to analysis of three limestone samples and a calc-silicate band in Lewisian gneiss from the Loch Monar area at the western end of Glen Strathfarrar. These samples were loaned by BGS Edinburgh and are detailed in Rock (1989). Carbon isotopic analysis was carried out to determine if decarbonation of the calcite/calc-silicates had occurred, potentially providing the source of the graphite. Total organic carbon content of the graphite was also measured as a proxy for total carbon content; this shows the amount of carbon covalently bonded in organic molecules within the carbonaceous material (thus excluding inorganic carbonate) without implying a direct biological origin for the carbon.

Additional samples of quartz vein material for volatile analysis were collected from a number of localities in the Morar, Glenfinnan and Loch Eil Groups (Figs 1 and 2). Quartz veins cutting Dalradian lithologies of similar composition to the Moine samples were selected for the comparative study of volatile gases. At Portsoy, one of the Dalradian localities, quartz veins cut graphitic schists, but no carbon is observed in these veins. Calcite veins cutting laminites in three localities within the Devonian Orcadian Basin (Old Red Sandstone) were also sampled. Doubly-polished wafers were prepared from samples from Strathglass (Loch Eil Group), Portsoy (Dalradian), and Spittal (ORS) for fluid inclusion microthermometric analysis.

**Methodology**

Raman microspectroscopy

Raman microspectroscopy of the carbonaceous material was conducted at the University of Aberdeen. Raman spectra of the samples were obtained using the 514.5 nm line of an argon ion laser. A specially adapted Research Grade Leica microscope (model DMLM) was used to focus the laser light on a sample, using a ×50 lens, giving a spot size of c. 1.5 µm. The scattered light was dispersed and recorded by means of a Renishaw inVia Reflex Spectrometer equipped with a Charge Coupled Device (CCD) detector. Data were collected between 1100 and 1700 cm⁻¹, with spectral resolution less than 3 cm⁻¹. Laser output power at the source (50 mW maximum) and integration times were varied to obtain the best possible spectra relative to signal to noise ratio. Between three and six spectral accumulations were averaged and Renishaw WiRE 2.0 software was used for data processing. Spectra were smoothed and a baseline subtracted using a least-squares polynomial fit; the curve-fit option was then used to obtain spectral parameters for the peaks. Peak position and peak full width at half maximum (FWHM) are recorded in wavenumbers (cm⁻¹), a non-SI unit which records the change in vibrational frequency between the irradiating laser beam and the Raman-active molecule. Graphite shows a single peak (the G peak) between 1582 cm⁻¹ (Kagi et al. 1991) and 1575 cm⁻¹ (Makjanić et al. 1989). As the graphite becomes structurally more disordered, peaks are detected at c. 1355 cm⁻¹ (the D1 peak) and at c. 1620 cm⁻¹ (the D2 peak). The ratio between the D1 and G peak heights (R1
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Raman microspectroscopy was also used to determine the non-aqueous chemical species present in fluid inclusions in the quartz vein associated with the graphite, allowing the composition of the parent fluid to be identified. These analyses were conducted at CREGU (Centre for Research on the Geology of Mineral Commodities and Energy), Nancy, France, using a Labram (Horiba Jobin) Raman Microspectrometer equipped with an edge filter and a liquid-nitrogen cooled CCD detector. An exciting radiation at 514.5 nm was provided using an ionized Ar/Ar laser. An Olympus microscope fitted with a ×80 objective was used to focus the laser. The mole fraction of gaseous species was calculated using the procedure described by Dubessy et al. (1989).

Fluid inclusion analysis

Fluid inclusion petrography and microthermometric analyses were conducted at the Memorial University of Newfoundland, Canada, and at the National University of Ireland, Galway. Microthermometric analyses at both institutions were performed using a calibrated Linkam THMSG 600 heating freezing stage; calibration was conducted using synthetic H₂O and CO₂ standards to give precision of ± 0.2°C at −56.6°C and ± 1°C at 300°C. Following procedures outlined by Shepherd et al. (1985), the temperature of CO₂ melting (Tₘ CO₂), clathrate melting (Tₘ clath) and homogenization of the non-aqueous phases (Tₜ CO₂) were determined for three-phase (L + L + V) inclusions. In addition the temperature of total homogenization (Tₜ total) was measured. Fluid salinities were calculated using Tₘ clath and the software package CLATHRATES (Bakker 1997). Where fluid inclusions were very small (< 10 µm) only Tₜ was recorded.

Fluid inclusion volatile analysis was conducted at the New Mexico Institute of Mining and Technology. Samples were first cleaned with KOH to remove surficial biological material and products, such as organic acids, that could potentially contaminate the gases liberated from the fluid inclusions. The samples were then dried below 100°C and c. 0.1 g of material was crushed incrementally under a vacuum of c. 10⁻³ Torr, using the crush fast scan method (Norman & Moore 1997), yielding two to ten crushes per sample. The instrument was calibrated using commercial gas mixtures, synthetic inclusions filled with gas mixtures, and three in-house fluid inclusion gas standards, as described by Norman & Blamey (2001). Precision is better than 5% for major gaseous species and 0.2% for water/gas ratios, whereas the detection limit for most species is < 1 ppm based on in-house standards. CO₂/CH₄ ratios measured by the incremental CFS method correspond to ratios derived independently by microthermometry as well as by the bulk thermal decrepitation method described by Norman & Sawkins (1987), demonstrating that methane is not produced mechanically during the incremental crush process. The analyses were performed by means of two Pfeiffer Prisma quadrupole mass spectrometers operating in fast-scan, peak-hopping mode. Routinely the system analyses for gaseous species H₂, He, CH₄, H₂O, N₂, O₂, H₂S, Ar, CO₂, C₂H₆, C₃H₆, SO₂, C₃H₈, C₄H₁₀, CI⁻ and benzene; with H₂O, CH₄, CO₂, N₂ and Ar utilized in this study to characterize fluids released during diagenesis and metamorphism of carbonaceous rocks. The amount of each species is calculated by proprietary software developed by the late David Norman and Nigel Blamey to provide a quantitative analysis.

Carbon isotopic analysis

Carbon isotopic analysis of the vein-graphite was carried out at Oxford University as part of a separate study (Tsikos, unpublished data), and limestone analysis for this study was undertaken at the Scottish Universities Environmental Research Centre (SUERC) at East Kilbride. All samples were powdered and the limestones acid-digested in HCl (25 v/v.%) before analysis. The samples were pyrolysed and carbon and oxygen isotopes measured from CO₂ (gas) produced during pyrolysis. Approximately 0.4 mg of sample was placed in tin capsules (0.5 × 5 mm) and analysed by continuous flow isotope ratio mass spectrometry (CF-IRMS) using a model ECS 4010 elemental analyser linked to a Delta Plus XP mass spectrometer. Three laboratory standards were analysed for every 10 unknown samples in each analytical sequence, allowing instrument drift to be corrected. Stable isotope ratios are expressed in δ notation as parts per thousand (per mille) deviation from the international standards Pee Dee Belemnite limestone (carbon) according to the following equation:

\[ \delta X = \left( \frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000 \]

All measurements are accurate to within 0.2‰.

Results

Raman microspectroscopy

Raman analysis shows the graphite to be uniformly crystalline (Fig. 8a), with a well-developed peak at 1580 cm⁻¹ (Table 1) and only weak deformation bands at 1350 cm⁻¹ and 1620 cm⁻¹ respectively. This shows that the graphite contains minimal structural and stacking faults, indicative of precipitation by moderate fluids (Pasteris 1999). R₁ values of 0.03 to 0.26 show that crystallite size varies from c. 150–3500 Å (Zinner et al. 1995). R₂ values were obtained on three spectra, giving amphibolite facies temperatures of 515°C, 550°C and 559°C using the formula of Bysacc et al. (2002). Graphite also occurs as finely disseminated particles in the pelitic gneiss and Raman microspectroscopy confirms that this material is also highly crystalline (Fig. 8b) (Table 1). Spectra from the garnet-bearing pelitic gneiss also yield amphibolite facies
temperatures of 490°C and 565°C respectively. However, most of the graphite in the vein material and the country rocks is so highly crystalline that D2 peaks are missing from the spectra, conferring uncertainty on the temperature calculations.

Fluid inclusion analysis

Microthermometry was used to determine the minimum trapping temperature of the inclusions in the quartz vein hosting the graphite and Raman microspectroscopy was used to identify the vapour phases within the inclusions. No crystal boundaries were identified in the quartz wafer, making it difficult to determine whether all the inclusions examined were primary. Isolated clusters were assumed to be primary (Fig. 9); secondary or pseudosecondary trails had very similar degrees of fill and microthermometric data to the isolated inclusions, indicating that they are related to the same primary fluid event. This is important as it means that data from the fluid inclusions can be used as a proxy for the graphite-precipitating fluid event, although such data need to be treated with care (Touret 1977). The inclusions are two-phase at 20°C and range in size from 5 to 25 µm, with irregular, ellipsoidal or negative-crystal shapes. The results of the Raman microspectroscopy analysis are shown in Table 2; microthermometric data are summarized in Table 3.

Mass spectrometry was used to measure the gas content of the fluid inclusions, including H2O, a molecule which is not Raman active and so not analysed.

![Fig. 8. (a) Raman spectrum from graphite in the quartz-graphite vein showing a weakly-developed D-peak and narrow G-peak, indicative of a highly crystalline structure with few planar stacking or ring-structure defects; (b) Raman spectrum from disseminated graphite in the pelitic schist showing similar highly crystalline structure.](image)

![Fig. 9. Isolated cluster of presumed primary fluid inclusions in quartz in the quartz-graphite vein showing vapour bubbles trapped in the inclusions.](image)

### TABLE 1

Raman spectroscopic data for Glen Strathfarrar vein-graphite and for carbonaceous material in Moine rocks in the vicinity of the mine

| Spectra   | G-peak position | G-peak FWHM | R1  | R2  | T (°C)† |
|-----------|-----------------|-------------|-----|-----|---------|
| Glen Strathfarrar vein-graphite |                |             |     |     |         |
| 1         | 1580.02         | 17.666      | 0.064 | 830 |         |
| 2         | 1579.67         | 16.409      | 0.033 | 2010|         |
| 3         | 1580.20         | 17.573      | 0.260 | 120 | 0.204 | 550 |
| 4         | 1579.82         | 15.318      |       |     |         |
| 5         | 1580.22         | 14.445      | 0.040 | 1590|         |
| 6         | 1580.28         | 19.533      | 0.149 | 260 | 0.185 | 559 |
| 7         | 1579.87         | 17.576      | 0.055 | 1015|         |
| 8         | 1568.63         | 21.673      | 0.023 | 3350|         |
| 9         | 1579.69         | 14.641      |       |     |         |
| 10        | 1579.89         | 15.570      | 0.037 | 1730|         |
| 11        | 1580.12         | 18.311      | 0.069 | 750 |         |
| 12        | 1579.25         | 20.012      | 0.206 | 165 | 0.283 | 515 |
| Moine     |                 |             |     |     |         |
| M1        | 1579.96         | 17.899      | 0.040 | 1575|         |
| M2        | 1579.28         | 18.000      | 0.007 | 1660|         |
| M3        | 1580.80         | 15.104      | 0.011 | 8675|         |
| M4        | 1580.10         | 17.013      | 0.104 | 420 |         |
| M5        | 1580.56         | 24.754      | 0.318 | 90  | 0.340 | 490 |
| M6        | 1576.69         | 17.400      | 0.081 | 600 | 0.169 | 566 |

* Zinner et al. (1995)  
† Beyssac et al. (2002)
This technique also allows marker gases, such as Ar, to be detected and the results, plus selected gas ratios, are shown in Table 4 (gas measurements in mol%). Table 5 shows these data with water removed from the analysis, producing good agreement with the Raman data presented in Table 2.

The wider volatile fluid inclusion dataset for the Moine rocks comprises three analyses from the Glenfinnan Group and two from each of the Morar and Loch Eil Groups respectively, summarized in Table 6. Table 6 also shows the five quartz vein samples that make up the Dalradian dataset and gives details of the calcite veins cutting laminites from the Orcadian Basin which form the Old Red Sandstone dataset. The results are shown graphically in Figure 10 and numerically in the supplementary material. The Dalradian samples have a higher volatile content than the Moine samples, which have a higher volatile content than the Old Red Sandstone samples. The samples from Wick South Head (ORS) have an anomalously high volatile content and this is discussed below. Microthermometric analysis was conducted on one sample from each of the three datasets and these results are detailed in Table 3.

### Table 2
Raman microspectroscopy data for fluid inclusions in quartz-graphite vein, Glen Strathfarrar

| Sample | Inclusion | CO₂ mol% | CH₄ mol% | N₂ mol% | H₂S mol% |
|--------|-----------|----------|----------|---------|----------|
| GSF 1  | a         | 75       | 0.9      | 24      | 0.1      |
|        | b         | 75       | 0.5      | 24.5    | not determined |
|        | c         | 64       | 1        | 35      | not determined |
|        | d         | 75.7     | 1.3      | 23      | not determined |
|        | e         | 77       | 0.8      | 22      | 0.2      |
|        | f         | 77       | 0.8      | 22      | 0.2      |
|        | g         | 73       | 7.8      | 19      | 0.2      |
|        | h         | 44.5     | 1        | 54.5    | not determined |
|        | i         | 52       | 1        | 47      | not determined |
|        | j         | 45       | 1        | 54      | < 0.1    |

### Table 3
Summary of microthermometric fluid inclusion analysis

| Sample                  | Petrography                                                                 | TM CO₂ | TM clat | Salinity | T_H  |
|-------------------------|-----------------------------------------------------------------------------|--------|---------|----------|------|
| Moine Glen Strathfarrar (Glenfinnan) (quartz) n = 17 | No obvious crystal boundaries; isolated clusters assumed to be primary. Secondary trails related to primary fluid event. | –57.8 to 58.5 | 7.5–10.1 | 4.8–10.4 | 249.8–308.5 |
| Moine Strathglass (Loch Eil) (quartz) n(I) = 17 n(II) = 15 | Abundant aqueous (I) and aqueous-carbonic (II) inclusions. Either isolated or in trails within annealed fractures. | –56.5 to 57.2 | 5.1–7.8 (I) | 2–7 (I) | 212.3–247.1 (II) 280–294 |
| Dalradian (Portsoy) (quartz) n = 15 | Numerous secondary inclusions in planar arrays in annealed fractures. | | | | 220–245 |
| ORS (Spittal) (calcite) n = 10 | A small number of inclusions < 10 µm in length. | | | | 183–202 |

Because of the small size of the inclusions, only the temperature of homogenization was recorded for the Dalradian and ORS samples.

$T_{M \text{ CO}_2}$, temperature of CO₂ melting; $T_{M \text{ clat}}$, temperature of clathrate melting; $T_H$, temperature of total homogenization (non-aqueous phases).

Carbon isotopic analysis

The carbon isotopic composition of the vein-graphite averaged $\delta^{13}C = -14.35\%$ ($n = 3$); $\delta^{13}C$ values of the limestones ranged from $-2.00\%$ to $3.34\%$ and the calc-silicate showed a $\delta^{13}C$ value of $-9.27\%$ (Table 7). The spatial distribution of these samples is shown in Figure 11. The total organic carbon content of a sample of the Glen Strathfarrar vein-graphite was 7.0 wt% C, with the pelitic gneiss averaging 0.4 wt% C ($n = 4$) . Five tons (5.08 tonnes) of graphite ore at (minimum) 7 wt% C equates to 355.6 kg of graphite with a volume of 0.16 m³, based on an average density of 2.16 g cm⁻³ (www.web.mineral.com).

Discussion

The Moine rocks of Glen Strathfarrar are assumed to overlie an allochthonous slice of Lewisian basement (Strachan et al. 2002). Thus, the graphite is likely to be derived either from syn-sedimentary organic material within the Moine or from the underlying Lewisian rocks. The following paragraphs explore the possible origins of the vein-graphite.
Carbon isotopic analysis was used to constrain the possible origins of the Glen Strathfarrar vein-graphite. With an average $\delta^{13}C$ value of –14.35‰ (Table 7), the graphite is heavier than most sedimentary organic carbon ($\delta^{13}C < –25‰$) but lighter than that expected for graphite derived from the decarbonation of limestone at amphibolite-grade metamorphic temperatures ($\delta^{13}C \sim –5‰$ lighter than residual calcite at 550°C) (Valley 2001). The $\delta^{13}C$ values for calcite in the Glen Strathfarrar impure limestone/dolostone (Rock 1989) and for the Loch Monar limestones (Table 7) fall within the broad ranges expected for limestone (Rollinson 1993). Plotting these values against that of Viezer & Hoefs (1976) (Fig. 12) confirms that the Lewisian samples are within expected isotopic trends for Precambrian limestones that are largely unaffected by secondary alteration. Conversely, the $\delta^{13}C$ value for the calc-silicate (~9.27‰) appears low, suggesting that this thin band (2–3 cm wide) within the hornblendic gneiss has experienced decarbonation and that this is a very local phenomenon. Consequently, it seems unlikely that the vein-graphite originates solely from metamorphism of Lewisian carbonates. The most effective method of depositing graphite is to cool a carbon-rich fluid so that graphite becomes stable (Luque et al. 1998). As well as being generated by decarbonation reactions, carbonic fluids can be produced by dehydration of pelites during metamorphism, with the carbonic species present in the fluid controlled by devolatilization reactions in the sedimentary rocks. The isotopic composition of graphite at Glen Strathfarrarr falls within the range seen in hydrothermal deposits studied by Rumble & Hoering (1986). They ascribe similar values to the assimilation of reduced carbon (of biogenic origin) and carbonate, with precipitation being driven by fluid mixing. Derivation from metamorphic fluids of mixed composition may thus explain the occurrence of the vein-graphite at Glen Strathfarrar.

Fluid inclusion analysis
Phases identified by fluid inclusion analysis (Tables 2, 4 and Supplementary Material) were used to constrain the source of the graphite further. Carbonic species (CO$_2$/CH$_4$) may be present in both metamorphic fluids and in hydrocarbons expelled from carbonaceous source rocks. Hydrocarbon has been generated from Old Red Sandstone rocks (Hillier & Marshall 1992) and locally from Dalradian rocks during igneous intrusion (Selley 1992) but oil-bearing lithologies are not known to occur in the Moine rocks. No solid bitumen was found in fluid inclusions from any of the samples and the carbonic phases are discussed in the next section.

The high percentage of nitrogen in the inclusions (up to 54.5 mol% of the non-aqueous volatiles present) is consistent with analyses from quartz veins in other metamorphosed terranes. These studies show that nitrogen is derived from thermal maturation of organic matter in the host shales (Huff & Nabelek 2007),

### TABLE 4
Gas mass spectrometry of successive crushes of quartz-graphite vein, Glen Strathfarrar

| Crush | 7973a | 7973b | 7973c | 7973d | 7973e | 7973f |
|-------|-------|-------|-------|-------|-------|-------|
| H$_2$ | 0.0153 | 0.0057 | 0.0072 | 0.0175 | 0.0044 | 0.0017 |
| He    | 0.0000 | 0.0002 | 0.0001 | 0.0000 | 0.0002 | 0.0001 |
| CH$_4$| 0.1585 | 0.1472 | 0.1157 | 0.1356 | 0.2130 | 0.1689 |
| H$_2$O(fit) | 87.062 | 83.873 | 93.943 | 88.172 | 86.148 | 93.788 |
| CO    | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| N$_2$ | 2.7430 | 5.3016 | 2.3753 | 2.4115 | 3.7357 | 1.8538 |
| C$_2$H$_4$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C$_2$H$_6$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| H$_2$S | 0.0003 | 0.0006 | 0.0005 | 0.0002 | 0.0003 | 0.0004 |
| Ar    | 0.0040 | 0.0005 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C$_3$H$_6$ | 0.0731 | 0.0874 | 0.0299 | 0.0614 | 0.0891 | 0.0398 |
| CO$_2$ | 9.9415 | 10.5741 | 3.5239 | 9.1901 | 9.8034 | 4.1290 |
| C$_2$H$_8$ | 0.0011 | 0.0000 | 0.0001 | 0.0012 | 0.0005 | 0.0011 |
| C$_3$H$_8$ | 0.0001 | 0.0040 | 0.0000 | 0.0001 | 0.0012 | 0.0001 |
| SO$_2$ | 0.0021 | 0.0014 | 0.0015 | 0.0015 | 0.0015 | 0.0004 |
| Benzene | 0.0000 | 0.0005 | 0.0006 | 0.0000 | 0.0004 | 0.0004 |
| CO$_2$/CH$_4$ | 62.7 | 71.8 | 30.5 | 67.8 | 46.0 | 24.4 |
| N$_2$/Ar | 811.8 | 1335.9 | 1335.1 | 913.9 | 1589.2 | 1650.9 |

Gases shown as mol%.

### TABLE 5
Results of gas mass spectrometry recalculated to remove H$_2$O

| Sample | CO$_2$ mol% | CH$_4$ mol% | N$_2$ mol% | H$_2$S mol% |
|--------|-------------|-------------|-------------|-------------|
| 7973a  | 76.8        | 1.2         | 21.2        | 0.002       |
| 7973b  | 65.6        | 0.9         | 32.9        | 0.004       |
| 7973c  | 58.2        | 1.9         | 39.2        | 0.008       |
| 7973d  | 77.7        | 1.1         | 20.4        | 0.002       |
| 7973e  | 70.8        | 1.5         | 27.0        | 0.002       |
| 7973f  | 66.5        | 2.7         | 29.8        | 0.006       |

Carbon isotopic analysis
Carbon isotopic analysis was used to constrain the possible origins of the Glen Strathfarrar vein-graphite. With an average $\delta^{13}C$ value of ~14.35‰ (Table 7), the graphite is heavier than most sedimentary organic carbon ($\delta^{13}C < –25‰$) but lighter than that expected for graphite derived from the decarbonation of limestone at amphibolite-grade metamorphic temperatures ($\delta^{13}C \sim –5‰$ lighter than residual calcite at 550°C) (Valley 2001).
producing ammonium, and that NH$_4^+$ substitutes for K in mica (Jai & Kerrich 2000). Boyd & Philippot (1998) found ammonium concentrations of up to 1739 ppm in biotite in Glenfinnan Group rocks near Kinloch Hourn, with increasingly lower concentrations found in muscovite, K-feldspar and plagioclase feldspar, respectively. The vein-graphite at Glen Strathfarrar is closely associated with biotite and muscovite, making it highly probable that the carbonic fluids have been generated from the same nitrogen-rich source rocks.

Evidence from volatile gas analysis of fluid inclusions

Figure 13 shows CO$_2$ plotted against N$_2$ (mol%) for fluid inclusions analysed in the three stratigraphic datasets. The fluid inclusions dominated by N$_2$ (mol% > 1) are found in quartz veins from Portsoy and Sandend (Dalradian), where the host rocks are associated with carbon (Table 6) and in veins from Glen Strathfarrar (Moine), suggesting that the latter may also have been generated in the proximity of carbonaceous sediments. The lower amount of N$_2$ in the Old Red Sandstone laminites, which also contain organic matter, indicates that lower temperatures (< ~200°C (Table 3)) are insufficient to convert ammonium to nitrogen during diagenesis. The vein from the ORS dataset with the highest concentration of N$_2$ (mol% = 0.87) is from Wick South Head, which lies to the east of a major fault that delineates an abrupt change in thermal maturity of the Orcadian Basin fill (Hillier & Marshall 1992). These rocks have generated hydrocarbons offshore and the fluid inclusions from calcite veins at Wick South Head are dominated by methane, consistent with this scenario (Figs 10 and 14). Heating of this sample has greatly

TABLE 6

| Dataset  | Locality | Stratigraphic group | Lithology | Vein material | Dominant gas phases* |
|----------|----------|---------------------|-----------|---------------|----------------------|
| Moine    | Loch Ness NH 545 309 | Loch Eil | Psammite | Quartz | CO$_2$ |
|          | Strathglass NH 357 320 | Loch Eil | Psammite | Quartz | CO$_2$ |
|          | River Callop NM 922 796 | Top Glenfinnan | Psammite | Quartz | CO$_2$/CH$_4$ |
|          | GSF – Struy NH 370 376 | Glenfinnan | Siliceous schist | Quartz | CO$_2$ |
|          | GSF – Pollicharian Bridge | Glenfinnan | Siliceous schist | Quartz | CO$_2$ |
|          | NH 330 396 | | | | |
|          | GSF – mine NH 286 384 | Glenfinnan | | Pelitic gneiss Quartz-graphite | CO$_2$/N$_2$ |
|          | Kinlochewe (1) NH 067 594 | Morar | | Pelitic schist Quartz | CO$_2$ |
|          | Kinlochewe (2) NH 046 617 | Morar | | Pelitic schist Quartz | CO$_2$ |
| Dalradian | Portsoy (1) NJ 583 664 | Argyll | Graphic schist | Quartz | CO$_2$/N$_2$ |
|          | Portsoy (2) NJ 583 664 | Argyll | Staurolite schist | Quartz | CO$_2$/N$_2$ |
|          | Sandend NJ 554 667 | Appin | Graphic schist | Quartz | CO$_2$/N$_2$ |
|          | Cullen (1) NJ 513 675 | Grampian | Quartzite | Quartz | CO$_2$/N$_2$ |
|          | Cullen (2) NJ519 677 | Grampian | Quartzite | Quartz | CO$_2$/N$_2$ |
| ORS      | Spittal (1) uncertain | Middle | Laminite | Calcite | CO$_2$ |
|          | Spittal (2) uncertain | Middle | Laminite | Calcite | CO$_2$ |
|          | Castletown Hbr ND 198 685 | Middle | Laminite | Calcite | CO$_2$ |
|          | South Head, Wick ND 376 | Middle | Laminite | Calcite | CH$_4$/CO$_2$ |

GSF, Glen Strathfarrar

* Excluding H$_2$O, which is the dominant phase in all samples. Gases shown occur at concentrations > 1 mol%.

TABLE 7

| Sample       | δ$^{13}$C$_{PDB}$ | δ$^{18}$O$_{SMOW}$ |
|--------------|------------------|-------------------|
| GSF graphite | -14.30/-14.40    | —                 |
| GSF limestone| -1.50            | 15.62             |
| Loch Monar   | 3.34/-0.20/-2.00 | 14.36/10.30/18.76 |
| limestone*   | -9.27            | 22.20             |

* BGS samples S12417, S12645 and S12423
  BGS sample S12646 (Rock 1989)
increased the volatile content of the fluid inclusions, making them appear anomalous compared to the other ORS samples (Fig. 10). The fluid inclusion data suggest that methane is generated during first heating of organic matter in sediments (ORS), with CO$_2$ becoming dominant under metamorphic conditions (as methane is lost from the system (Dalradian/Moine)). The relatively low concentration of methane in the Glen Strathfarrar samples makes it unlikely that there was a bitumen precursor to the vein-graphite. Plotting N$_2$/Ar ratio against CO$_2$/CH$_4$ ratio for the inclusion data shows that the stratigraphic datasets can be grouped together by metamorphic history, lithology and/or OM content (Fig. 15). This indicates that metamorphic fluids generated in Glen Strathfarrar had a broadly similar geochemical composition to fluids associated with Dalradian metamorphosed graphitic sediments, despite the Glenfinnan Group apparently containing little carbon and their different tectonic and metamorphic histories (Strachan et al. 2002). Fluid inclusion data show that the carbonic inclusions in the Moine samples (Table 3) have higher total homogenization temperatures (> 250°C) than the Dalradian samples (< 245°C), suggesting that temperature may have controlled graphite precipitation.

Metamorphic conditions

The fluid inclusion data show an average total homogenization (non-aqueous phases) temperature (T$_{H}$) of 289°C ± 17°C, which represents the minimum trapping temperature. The actual trapping temperature is likely to be significantly higher than this, given the metamorphic grade of the rocks. Using the technique of Beyssac et al. (2002) to derive peak metamorphic temperature from Raman spectra gives an average temperature of 536°C (Table 1), which is within the garnet zone (lower amphibolite facies).

![Fig. 11. Map showing localities and δ$^{13}$C values for samples from Glen Strathfarrar and Loch Monar.](image1)

![Fig. 12. Scatter diagram of δ$^{13}$C versus δ$^{18}$O for Precambrian limestones (redrawn from Vieux and Hoefs (1976)) and for limestones from Glen Strathfarrar and Loch Monar and a clc-silicate band in Lewisian gneiss.](image2)

![Fig. 13. Crossplot showing CO$_2$ (mol%) against N$_2$ (mol%) for fluid inclusions in veins from the Moine, Dalradian and Old Red Sandstone datasets. Veins dominated by N$_2$ (mol% > 1) are quartz veins associated with graphitic lithologies (Dalradian) and with Glenfinnan Group rocks in Glen Strathfarrar. (Moine n = 10; Dalradian n = 5; ORS n = 4; data points = average 6–10 incremental crushes).](image3)
Microthermometric software allows isochores to be calculated from fluid inclusion data. The software uses the homogenization temperature and pressure of the inclusions (minimum trapping conditions) to project trapping pressure at higher temperatures for a constant volume of fluid. Homogenization temperatures may also record retrograde as well as prograde events. Homogenization of $\text{CO}_2 + \text{N}_2$ to the liquid phase in the Glen Strathfarrar fluid inclusions occurred over a temperature range of 11.1–13.4°C, suggesting that fluid density varied. Homogenization to the vapour phase took place at 10.2°C, which may reflect retrograde condensation of a high density fluid (Van den Kerkhof & Thiery 2001). Using the average temperature determined by Raman microspectroscopy above, gives a trapping pressure of $\approx 6.6$ kbar at 536°C (Fig. 16), which is consistent with amphibolite facies metamorphism at a depth of 25 km (calculated for density 2.70 g cm$^{-3}$ and a lithostatic gradient of 26.46 MPa km$^{-1}$ (http://www.stanford.edu/~tyzhu/Documents/Some%20Useful%20Numbers.pdf)). Use of this average Raman temperature is supported by calculations made using the gas spectrometry data given in Table 2 and gas equilibrium equation (34) of Giggenbach (1980), which yields a geothermal equilibration temperature of 550°C.

Stratigraphic control

A major ductile fault, the Sgurr Beag Thrust, is thought to underlie the Glenfinnan Group throughout the area of NW Scotland to the east of the Moine Thrust (Holdsworth et al. 1994). The Sgurr Beag Thrust separates the Glenfinnan Group from the older Morar Group sediments, which unconformably overlie Lewisianoid gneisses (Friend et al. 1997). Further south, Lewisian inliers are tectonically emplaced along the thrust, although the Glen Strathfarrar inlier is likely to represent the core of a pre-Caledonian anticline (Holdsworth et al. 1994). The Sgurr Beag Thrust dates back to the Neoproterozoic Knoydartian event at c. 750 Ma (Tanner & Evans 2003). Rogers et al. (1998) have suggested that this event might have resulted in prolonged or episodic heating and deformation, creating a polyphase metamorphic terrain long before the Caledonian Orogeny affected the area. Because so much material has been removed from the worked area, the original relationship between the veins and foliation of the host rocks is difficult to ascertain. Blasting has fractured the rocks, with some fracture surfaces appearing to show a thin veneer of vein material, suggesting that graphite deposition is a late-stage event. The temperatures obtained from the Raman data are consistent with amphibolite-grade metamorphism, and the association of the graphite with massive quartz veins indicates that the fluids represent a prograde event (Yardley 1983). This means that the veins are likely to be Caledonian in age and that thermally mature carbonaceous material must have been present in both the Glenfinnan Group metasediments and the (presumed) underlying Lewisianoid gneisses, which include graphitic schists and marble (Strachan et al. 2002). How much fluid was generated in earlier metamorphic episodes is
impossible to ascertain, but it is highly probable that devolatilization reactions produced carbonic fluids from these rocks during previous events. This repeated metamorphism explains why the Glenfinnan rocks now contain so little carbonaceous material compared to the Dalradian schists, which formed in a similar sedimentary environment. However, the fluid inclusion analysis shows that the gas signature typical of metamorphosed organic matter (rich in CO₂ and N₂) has survived in the Moine rocks, despite their complicated metamorphic history. The pelitic gneiss still contains sufficient uniformly crystalline graphite to suggest that the immediate country rocks are the source of carbon in the Glen Strathfarrar deposit.

**Conclusions**

Carbon isotopic analysis shows that, with a δ¹³C value of −14.35‰, the graphite has δ¹³C values isotopically heavier than the estimated value for all carbonaceous sediments, suggesting that fractionation has taken place since sedimentation. Higher (i.e., less negative) ¹³C values can be obtained either by decarbonation of a limestone, which releases CO₂ with a heavier isotopic signature than the residual calcite, or through the loss of volatiles from non-carbonate rocks, which produces a heavier value in the residual carbon (Rollinson 1993). Graphitization of sedimentary carbon in the Glenfinnan Group pelitic gneiss occurred in response to changes in both temperature and pressure arising from a series of regional metamorphic events. Scavenging of carbon by metamorphic fluids associated with the youngest, possibly Caledonian, event is the most probable source of the vein-graphite. Similarities in gas composition with quartz veins occurring in the Dalradian rocks show that carbonaceous sedimentary sequences consistently generate fluids rich in CO₂ and N₂ (Fig. 15; Table 6). Microthermometric analysis indicates that precipitation of the Moine vein-graphite occurred at temperatures > 250°C. Given that the Dalradian quartz samples, precipitated at lower temperature, do not contain discrete graphite, this may indicate that a minimum temperature is required for graphite precipitation. The occurrence of crystalline graphite in the pelitic gneiss at Glen Strathfarrar makes it highly likely that the carbon-rich fluids have been generated from within the Glenfinnan Group sediments rather than from Lewisian rocks at depth. Despite the assertion that graphite is uncommon in Moine rocks (Rock et al. 1986), the high ammonium content of biotite in these metasediments (Boyd & Philippot 1998) and the consistently high N₂ values of fluid inclusions within the siliceous schist and quartz veins (see Supplementary Material) suggest that, prior to metamorphism, the sediments contained more organic matter than their present composition suggests.

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Military Aspects of Hydrogeology
Edited by E. P. F. Rose and J. D. Mather

This book, generated under the auspices of the Geological Society of London’s History of Geology and Hydrogeological Groups, contains 20 papers from authors in the UK, USA, Germany and Austria. Historically, it gives examples of the influence of groundwater on battlefield tactics and fortress construction; describes how groundwater was developed for water supply and overcome as an obstacle to military engineering and cross-country vehicular movement by both sides in World Wars I and II, and culminates with examples of the application of hydrogeology to site boreholes in recent conflicts, notably in Afghanistan. Examples of current research described include hydrological model development; the impact of variations in soil moisture on explosive threat detection and cross-country vehicle mobility; contamination arising from defence sites and its remediation; privatization of water supplies; and the equitable allocation of resources derived from an international transboundary aquifer.

Natural Hazards in the Asia-Pacific Region: Recent Advances and Emerging Concepts
Edited by J. P. Terry and J. Goff

Even a cursory glance at any map of the Asia–Pacific region makes a striking impression: in addition to the large continental landmass the region encompasses a truly vast expanse of ocean, dispersed over which are thousands of islands. Many might say that it could not be a worse time to live in this region. In the past few years we have experienced not only a number of devastating tsunamis (Indonesia, Solomon Islands, Samoa, Japan), but should not forget either the seemingly endless list of other natural hazards such as tropical cyclones and typhoons, volcanic eruptions, river floods and wildfires, amongst numerous others. This Special Publication represents an important collection of both conceptual and first-hand field investigations across the Asia-Pacific region. By highlighting some of the recent advances and emerging ideas in natural hazards research, the volume draws together these disparate lines of evidence into a clear regional focus.

Martian Geomorphology
Edited by M. R. Batme, G. Sanjeev, C. Gallagher and A. Bargery

The latest Mars missions are returning data of unprecedented fidelity in their representation of the martian surface. New data include images with spatial resolution better than 30 cm per pixel, stereo imaging-derived terrain models with one meter postings, high-resolution imaging spectroscopy, and ISAR data that reveal subsurface structure. This book reveals how this information is being used to understand the evolution of martian landscapes, and includes topics such as fluvial flooding, permafrost and periglacial landforms, debris flows, deposition and erosion of sedimentary material, and the origin of lineaments on Phobos; the larger martian moon. Contemporary remote sensing data of Mars, on a par with those of Earth, reveal landscapes strikingly similar to regions of our own planet, so this book will be of interest to Earth scientists and planetary scientists alike. An overview chapter summarising Mars’ climate, geology and exploration is included for the benefit of those new to Mars.

Human Interactions with the Geosphere: The Geoarchaeological Perspective
Edited by L. Wilson

Human impact on our environment is not a new phenomenon. For millennia, humans have been coping with – or provoking – environmental change. We have exploited, extracted, over-used, but also in many cases nurtured, the resources that the geosphere offers. Geoarchaeology studies the traces of human interactions with the geosphere and provides the key to recognising landscape and environmental change, human impacts and the effects of environmental change on human societies. This collection of papers from around the world includes case studies and broader reviews covering the time period since before modern human beings came into existence up until the present day. To understand ourselves, we need to understand that our world is constantly changing, and that change is dynamic and complex. Geoarchaeology provides an inclusive and long-term view of human-geosphere interactions and serves as a valuable aid to those who try to determine sustainable policies for the future.