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A gas-chromatograph, continuous flow-isotope ratio mass-spectrometry method for $\delta^{13}C$ and δD measurement of complex fluid inclusion volatiles: Examples from the Khibina alkaline igneous complex, northwest Russia and the south Wales coalfields

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Abstract

A new method is described for on-line extraction of complex mixtures of fluid inclusion volatiles for compound specific carbon- and hydrogen-isotope determination by gas-chromatography–continuous flow mass-spectrometry. Reproducibility for multiple aliquots of gas released from single samples and for duplicate samples is generally $\leq \pm 0.7$‰ for $\delta^{13}C$ measurements of hydrocarbon and CO_2 gases to concentrations as low as 20 nmol and $\leq \pm 7$‰ for δD measurements of hydrocarbon gases to concentrations as low as 100 nmol. This approach significantly improves upon the detection limits for trace gas analysis in fluid inclusions and enables rapid stable isotope measurements of multiple gas species in a single run.

Two examples are evaluated and discussed in their geological context. First, stable isotope results for CH_4, CO_2 and C_2–C_5 fluid inclusion gases hosted in the undersaturated peralkaline igneous complex of Khibina in northwest Russia indicate that CH_4 was the juvenile magmatic gas phase ($\delta^{13}C = -13$ to -8‰, $\delta D = -120$ to -50‰). The $\delta^{13}C$ values of the C_2–C_5 hydrocarbons are lower relative to CH_4 (by up to 12‰), confirming their abiogenic origin. The $\delta^{13}C$ values of CO_2 are consistently lower than CH_4 (by up to 9‰) and the δD values of C_2H_6 are 70–100‰ lower than the δD_{CH_4} values. This pattern indicates that the CO_2 and higher hydrocarbons were generated during sub-solidus, kinetic CH_4-oxidation fractionation and polymerisation reactions.

Second, CH_4, CO_2 and C_2H_6 fluid inclusion gases were analysed from quartz veins associated with anthracite from the Nant Helen mine in the south Wales coalfields. The $\delta^{13}C$ values of CH_4 (-27.9 ± 0.1‰), CO_2 (-3.1 ± 0.8‰) and C_2H_6 (-20.7 ± 0.1‰) are typical of mature thermogenic coal-associated natural gases, as is the δD_{CH_4} values (-148 ± 1‰). Assuming equilibrium, the $\Delta^{13}C_{CO_2-CH_4}$ value (+24.8‰) suggests that temperatures may have reached ~300 °C in the anthracite zone.

Keywords: Stable isotopes; Fluid inclusions; Abiogenic hydrocarbons; Khibina; Coal-derived gas; South Wales

1. Introduction

Fluid inclusions are ubiquitous in geological samples, can host significant concentrations of gases such as CO_2,

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CH_4, N_2 and higher hydrocarbons and can provide valuable information about the physico-chemical conditions at the time of their trapping (see Roedder, 1984; Samson et al., 2003). A variety of techniques have been developed for the study of fluid inclusions, from non-destructive methods such as petrographic interpretation, microthermometry and laser-Raman microprobe analysis, which provide compositional information and the temperature and pressure at the time of entrapment (see Samson et al., 2003 and references therein), to destructive bulk volatile extraction techniques for compositional analysis of the entrapped fluids (see Salvi and Williams-Jones, 2003). The stable isotopic composition of fluid inclusion volatiles can also provide essential information about the origin and chemical characteristics of the fluids and related host rocks at the time of entrapment.

A variety of methods have been developed over the years to extract and prepare fluid inclusion volatiles for gas chromatographic and/or mass spectrometric analysis. In the past, two main off-line methods have been favoured. The first is *in vacuo* thermal decrepitation (Piperov and Penchev, 1973; Mironova et al., 1985; Barker and Smith, 1986; Jackson et al., 1988; Kesler et al., 1997). This approach can cause elevated concentrations of CO_2, CH_4, CO and H_2 to be generated, because of thermal decomposition of minerals and interstitial carbonaceous material, both of which can affect the calculated fluid inclusion gas compositions and their isotopic values (Piperov and Penchev, 1973; Mironova et al., 1985; Kesler et al., 1997). The second method involves mechanical crushing *in vacuo* or under an inert gas at <200 °C (Petersilie and Sørensen, 1970; Piperov and Penchev, 1973; Ikorskiy, 1986; Whelan, 1988; Simon, 2001; Potter and Siemann, 2004; Beeskow et al., 2006). The contributions of gases from the mineral host are minimised in this approach, but high blanks of common fluid inclusion components and high adsorption levels of polar species such as CO_2 and H_2O have been observed during crushing (Piperov and Penchev, 1973; Ikorskiy, 1986; Whelan, 1988).

A further disadvantage of off-line methods is that in most cases only a sub-sample of the extracted volatiles is transferred to the gas chromatograph and/or mass spectrometer for analysis, limiting detection levels (Salvi and Williams-Jones, 2003). Preparation of volatiles for isotopic measurement off-line can also be extremely time-consuming, requiring numerous steps to isolate and convert individual volatile species for isotopic analysis (Petersilie and Sørensen, 1970; Nivin et al., 1995; Kesler et al., 1997).

Andrawes and Gibson (1979) developed an on-line crushing technique for compositional analysis of fluid inclusion volatiles by gas chromatography. Samples were crushed in a high helium flow and sent directly to a gas chromatographic column for subsequent separation and analysis of the individual fluid components. This approach was developed further by Bray et al. (1991) and Salvi and Williams-Jones (1997a). Their procedure allows for transfer of all extracted volatiles to the gas chromatograph column, thereby improving the detection levels for trace volatiles hosted in fluid inclusions. Crushing in a helium flow at low temperatures (~120 °C) also decreases/eliminates problems such as adsorption and chemical reactions, which can arise upon crushing (Bray et al., 1991; Salvi and Williams-Jones, 1997a, 2003). However, this method requires high flow rates (>20 ml/min) because of large dead volumes within the system; high flow rates, in turn, necessitate the use of fused silica megabore (≥0.53 mm ID) and stainless steel-packed (≥3.18 mm OD) gas chromatographic columns. In contrast, low flow rates (1–2 ml/min) are required for isotopic determination by mass spectrometry and therefore gas chromatographic fused silica columns with ≤0.32 mm internal diameters are generally used. The use of megabore and packed gas chromatographic columns requires the majority of the sample to be vented for mass spectrometric analysis, with only ~1% reaching the mass spectrometer. As a result, off-line extraction and preparation of volatiles for isotopic analysis has remained the preferred approach of most researchers (Kesler et al., 1997; Beeskow et al., 2006).

Here, for the first time, an on-line gas-chromatography continuous flow-isotope ratio mass-spectrometry (GC/C-irMS) method is described and evaluated for extraction, separation and $\delta^{13}C$ and δD measurement of complex mixtures of fluid inclusion volatiles. This method incorporates the advantages of the on-line crushing method for compositional analysis (Bray et al., 1991; Salvi and Williams-Jones, 1997a). As well, a new high-flow/low-flow interface is described for moving gases extracted during crushing to the gas-chromatograph mass-spectrometer for analysis by isotope-ratio mass-spectrometry. This provides a means for rapid and efficient transfer of entire aliquots of extracted volatiles, and thus, enables the isotopic determination of, not only major, but also minor trace gases present in fluid inclusions. This approach expands greatly upon the initial ideas of Potter and Siemann (2004) for analysis of CH_4 contained in fluid inclusions from evaporites. Potter and Siemann (2004) described a means of releasing fluid inclusion gases by *in vacuo* crushing, off-line, before manual transfer to the gas-chromatograph mass-spectrometer system. Two examples are also presented here, to demonstrate the

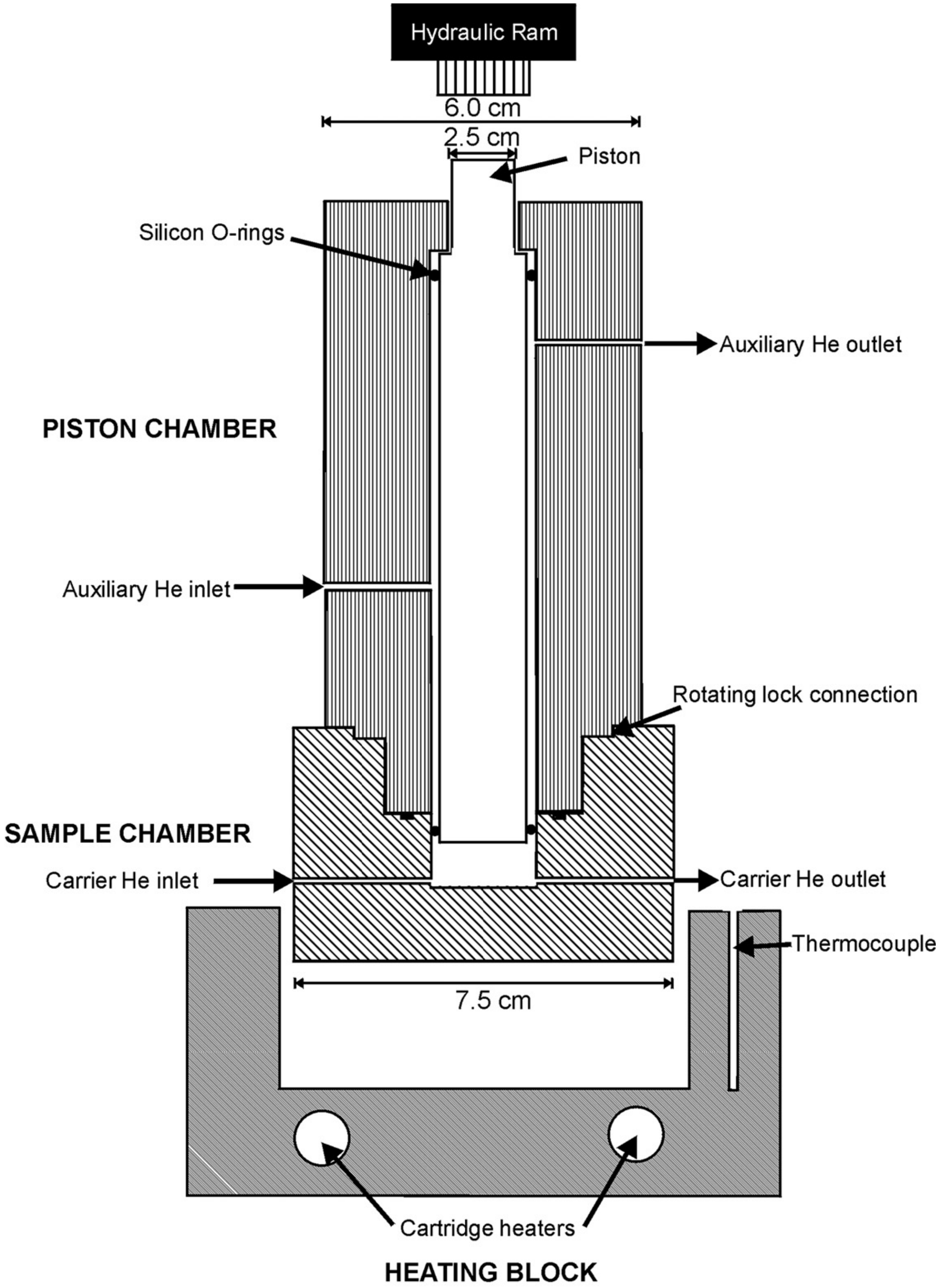

Fig. 1. Schematic drawing of a single crusher unit based on the designs of Andrawes and Gibson (1979) and Bray et al. (1991).

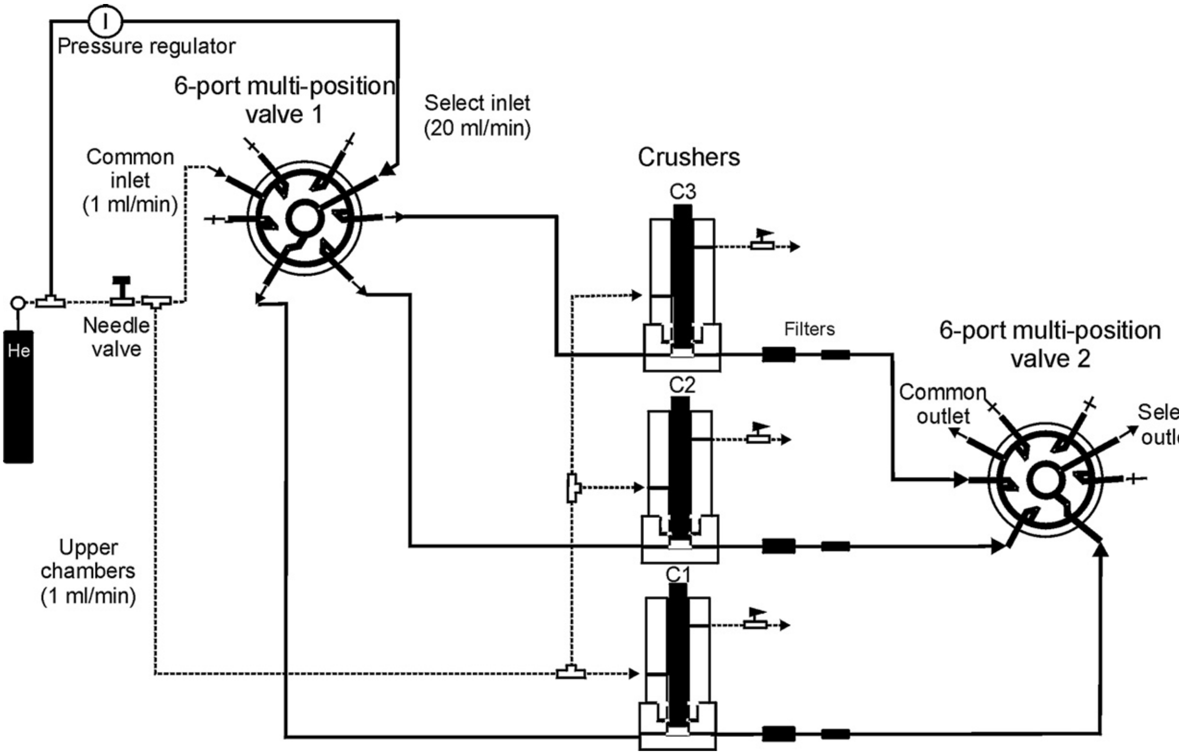

Fig. 2. Schematic drawing of the crusher line.

potential of this new method for $\delta^{13}C$ and δD measurement of fluid inclusion volatiles.

2. Analytical method

2.1. Analytical device

The crushers are largely based on the design of Bray et al. (1991) with minor modifications. Three units were assembled. A single unit comprises a sample chamber, a piston chamber and a heating block controlled by two cartridge heaters (Fig. 1). The piston and sample chambers are connected by a rotating lock and sealed by silicon O-rings (Fig. 1). Both chambers have 1/8″ stainless steel connections that attach to 1/16″ stainless steel tubing. The units are placed in a steel frame with a hydraulic ram. The hydraulic ram can be moved and locked into position above each unit when required.

A 6-port multi-position Valco® selector valve is installed before the crushers (Valve 1; Fig. 2). The 'common inlet' flow (~1 ml/min) directs flow both to (i) the sample chambers through the multi-position valve, and (ii) the piston chambers, such that the chambers can be constantly flushed with helium (Fig. 2). The 'select inlet' is set to a high flow rate (20 ml/min). This flow can be selected and directed to an individual sample chamber when a sample is ready to be analysed (Fig. 2). The lines leaving the piston chambers have 1/8″ Swagelok® two-way valves that are closed in order to seal the chamber when crushing. The lines leaving the sample chambers are equipped with first, 1/8″ Nupro® 140 μm stainless steel mesh filters to trap large rock particles and second, 1/16″ Valco® 10 μm stainless steel fret filters to trap any smaller dust particles that might escape from the sample chambers upon crushing. These lines are attached to a second 6-port multi-position Valco® selector valve. This valve has a 'common outlet' to vent helium flushing the sample chambers and a 'select outlet' to direct flow from a sample chamber to the transfer line during crushing (Valve 2; Figs. 2, 3). The lines leaving the crushers are heated to ~120 °C for efficient transfer of volatiles.

The transfer line (Fig. 3) between the crushers and the gas chromatograph comprises 1/16″ stainless steel tubing that consists of a cryogenic trap for H_2O (Trap 1; Fig. 3), a 6-port 2-position Valco® valve that switches from a high-flow *crush* configuration (Valve 3; Fig. 3A) to a low-flow *sample run* configuration (Valve 3; Fig. 3B), a molecular sieve trap for gases (Trap 2; Fig. 3), and a Thermo-Finnigan PreCon® interface (Fig. 3B). The high-flow rate *crush* configuration is required to provide rapid removal of a single plug of released volatiles from the sample

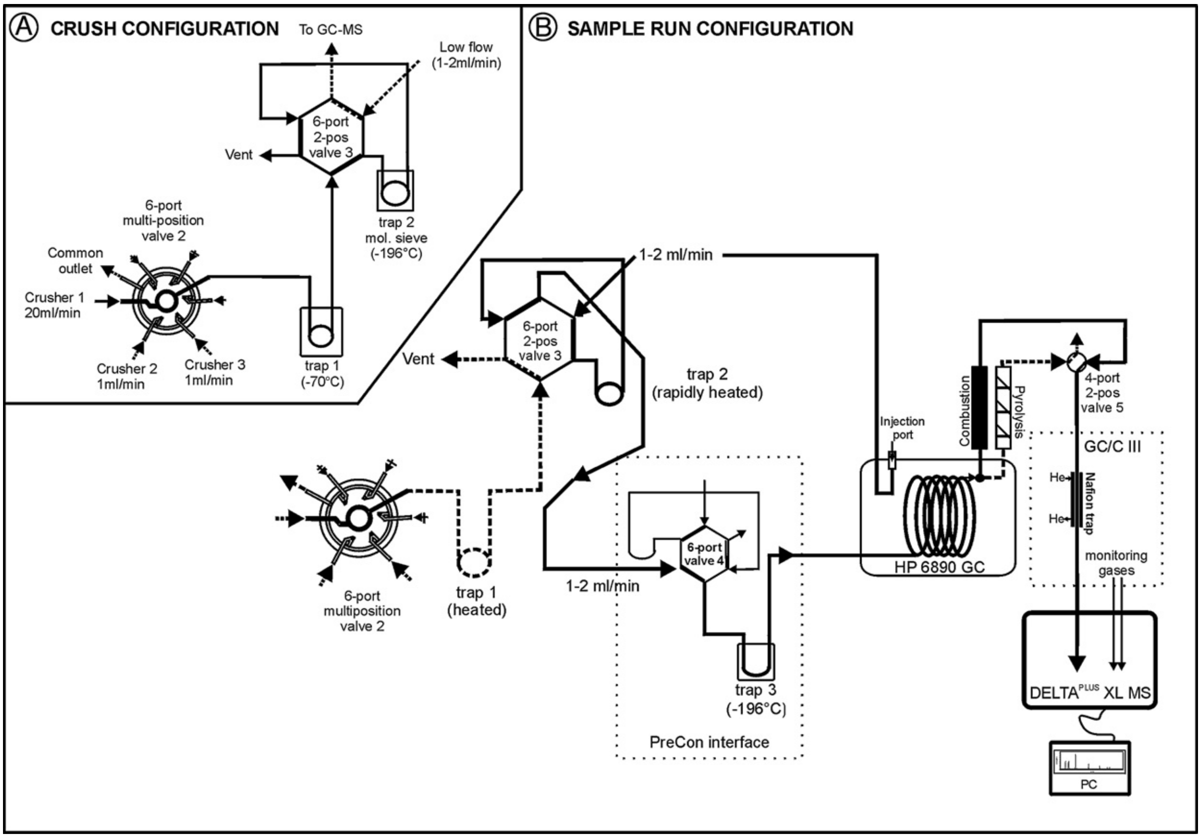

Fig. 3. Schematic drawing of the transfer line and GC/C-irMS system. (A) The transfer line in *crush* configuration when a sample is crushed. (B) The transfer line and GC/C-irMS system in *sample run* configuration during stable isotope analysis of fluid inclusion gases (see text for details).

chambers. The low-flow rate *sample run* configuration allows the gases released and trapped on the transfer line to be transferred to the gas-chromatograph mass-spectrometer. This low-flow rate enables the mass spectrometer to sample the maximum amount of the gas stream rather than venting the majority of it, as would be the case in a high-flow configuration. The purpose of the molecular sieve trap (trap 2) is to capture all gases released on the molecular sieve at −196 °C. This trap was made by inserting ~2 cm of 13 nm molecular sieve granules into ~40 cm of 1/16″ stainless steel tubing before attaching it to the line.

The low-flow (*sample run*) side of the 6-port, 2-position Valco® valve (Valve 3; Fig. 3) is connected to the injection port of the gas chromatograph oven by a 1/32″ capillary. The low flow is then directed to the PreCon® interface through another 1/32″ capillary (Fig. 3) and through the PreCon® 6-port, 2-position Valco® valve (Valve 4; Fig. 3B) to Trap 3 (used to cryofocus condensable gases at −196 °C), and into the gas chromatographic column. A Hewlett Packard 6890 gas-chromatograph oven containing a Poraplot Q® (0.32 mm×25 m) column was used to separate CO_2, CH_4 and higher hydrocarbons as well as any other species present in the inclusion gases (e.g., N_2, H_2S). The column can be connected to either (i) a CuO/NiO/Pt reactor (940 °C) for combustion of hydrocarbon gases to CO_2 for $\delta^{13}C$ measurements, or (ii) a hollow ceramic pyrolysis reactor (1420 °C) for cracking of hydrocarbons to produce H_2 for δD measurements (Fig. 3B). The gases produced from the eluting volatiles are then passed through a 4-port, 2-position Valco® valve (Valve 5; Fig. 3B). This valve directs the flow of gases from either the combustion or pyrolysis reactor to a ThermoFinnigan GC/C III® interface, which contains a nafion trap to remove water from the sample stream and permits introduction of isotope-ratio 'monitoring' CO_2 and H_2 gases to the mass spectrometer during analysis (Fig. 3B). The carbon- and hydrogen-isotope compositions of the sample and isotope-ratio 'monitoring' gases are then analysed using a ThermoFinnigan Delta^{PLUS} XL continuous flow-isotope ratio mass spectrometer.

The carbon-isotope ratios of the carbonic species, expressed in the standard δ-notation versus VPDB, are normalised to NIST reference gases (see Section 3) that

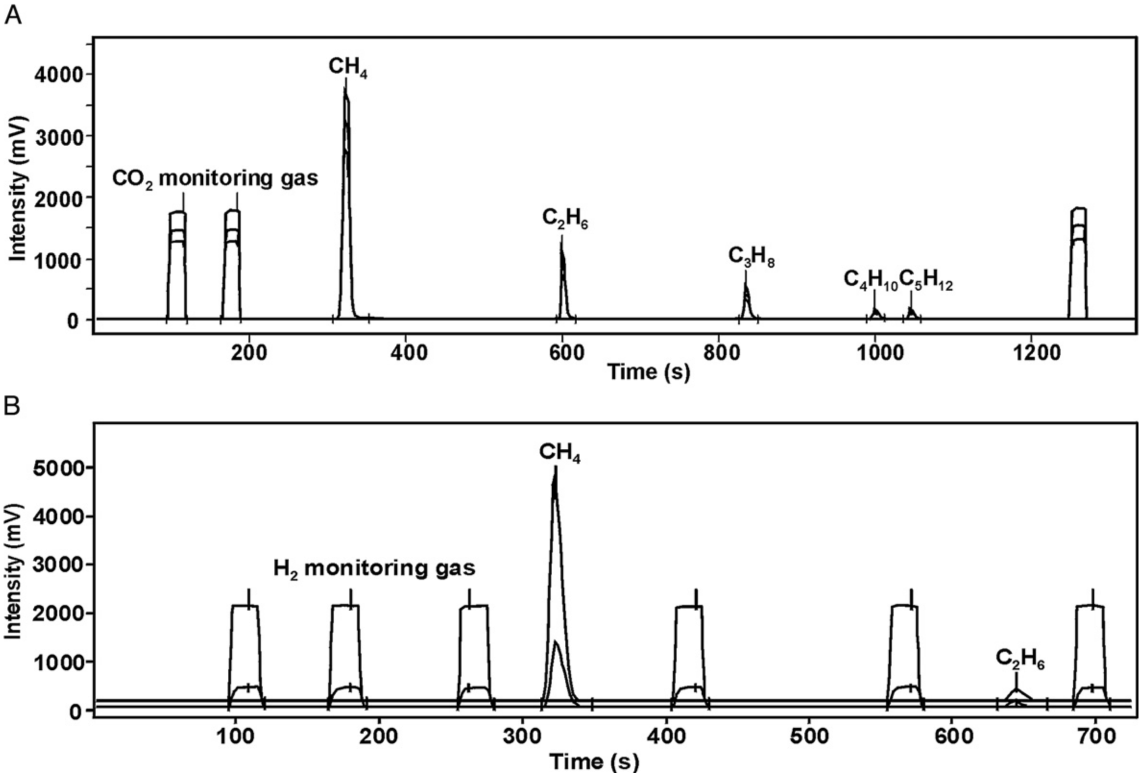

Fig. 4. Examples of typical mass-spectrometer spectra generated from samples during: (A) $\delta^{13}C$ determination, and (B) δD determination.

have been calculated against NBS 19. The hydrogen-isotope ratios of the hydrocarbon species, expressed in the standard δ-notation versus VSMOW, are normalised to NIST and alternative reference gases (see Section 3) that have been evaluated against VSMOW and VSLAP.

2.2. Analytical procedure

After characterisation of the fluid inclusion arrays in a sample, the minerals hosting the fluid inclusion population are crushed to 2–4 mm fractions and 1–2 g of material hand-picked for analysis. As a precaution, the sample is washed in deionised water and acetone to remove any surface debris and contaminants and dried at ~60 °C for 1 h. The sample is then loaded into the sample chamber, and the piston chamber is reattached. The piston is then gently pushed down into contact with the sample and the unit reconnected to the helium lines. Once all three units are in place, the helium flow is commenced and multi-position valve 1 positioned such that all three units are flushed with UHP helium at ~1 ml/min. The units are left to flush overnight at ~120 °C, which removes any surficial water and other adsorbed contaminants.

Prior to crushing samples, several in-house gas standards, evaluated against NIST natural gas standards RM 8559 and 8560, are injected at variable volumes (2–100 μl) through the line, including all gas traps, to determine any linearity correction and to measure the precision and accuracy of the system. When the samples are ready to be analysed, the hydraulic ram is moved into position over the chosen unit and ramped down into contact with the crusher piston. Multi-position valve 1 is then moved to the high-flow position for the chosen unit (Fig. 2) and the valves on the transfer line switched to the *crush* configuration (Fig. 3A), such that the high flow from the unit is directed through both cryogenic traps 1 and 2 before venting to atmosphere. An ethanol–liquid nitrogen slurry (~−70 °C) is placed on trap 1 and liquid nitrogen (−196 °C) placed on trap 2 (Fig. 3A). Once the traps are ready, the two-way valve on the piston chamber is closed and the hydraulic ram is pumped up to ~6000 Psi and released. After the released gases have been transferred to trap 2, the 6-port, 2-position valve is switched to the *sample run* configuration (Valve 3; Fig. 3B) and the high-flow regime is replaced by a low-flow regime through trap 2 in readiness for transfer of the gases to the gas chromatographic column (Fig. 3B).

At this point, the chromatographic acquisition is initiated. Trap 3 (PreCon® interface) is lowered into liquid

Table 1
Average carbon-isotope results for NIST natural gas standards

Sample	*N*	$\delta^{13}C_{CH_4}$	σ	$\delta^{13}C_{CO_2}$	σ	$\delta^{13}C_{C_2H_6}$	σ	$\delta^{13}C_{C_3H_8}$	σ
RM 8559	10	−29.2	0.2	−9.3 [a]	–	−26.1	0.1	−22.5 [a]	0.8
NIST values		−29.1	0.1	−9.2	0.8	−25.9	0.2	−22.1	0.1
RM 8560	15	−44.6	0.4	−8.3	0.5	−31.9	0.3	−25.5	0.3
NIST values		−44.8	0.1	−8.5	0.3	−31.8	0.3	−25.3	0.1

N = number of aliquots analysed.
Where the standard deviation is not reported, only one value was obtained.
[a] Amplitude of mass 44 was below 100 mV.

nitrogen. The liquid nitrogen is then removed from trap 2, which is then heated (using a heat gun) to ensure rapid release of gases from the molecular sieve. The gases are transferred to the PreCon® where condensable gases are cryofocussed on trap 3 and non-condensable gases passed through to the gas chromatographic column before condensable gases are released from trap 3.

For carbon-isotope measurement of samples, the gas chromatograph oven is held at 30 °C for 5 min before being ramped up at 20 °C/min to 150 °C and held there for 5 min before being ramped back down to 30 °C. Two minutes after the run begins, trap 3 is removed from the liquid nitrogen and the condensable gases are released onto the column. Eluting species arrive at the mass spectrometer as CO_2 at approximately 350, 450, 580, 800, 990 and 1280 s for CH_4, CO_2, C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12} respectively, as determined by injecting gases of known composition (e.g., Fig. 4A). Any other trace gases present that elute later are vented to atmosphere.

For hydrogen-isotope measurements of separate subsamples, the method described above can also be used if sufficient concentrations of higher hydrocarbons species are present. In most samples in this study, however, only CH_4 and C_2H_6 were present in sufficient concentrations for δD measurements. Moreover, an isothermal method was used for these analyses; during the heating cycle using the ramp method, it was observed that the background on *m*/*z* cups 2 and 3 could start rising, potentially causing errors in the results. The gas chromatograph oven was retained at 30 °C for 10 min and trap 3 was not used. The eluting hydrocarbons released from trap 2 are passed through the pyrolysis reactor and allowed to enter the mass spectrometer. Eluting CH_4 and C_2H_6 arrive at the mass spectrometer as H_2 at approximately 350 and 650 s, respectively, using this method (e.g., Fig. 4B). As these analyses are proceeding, trap 1 is thoroughly heated to release trapped H_2O and vented to atmosphere before the next sample is analysed.

3. Results for standard and blanks tests

Several gases of known isotopic composition were analysed to test the methods described in Section 2. Natural gas standards RM 8559 (NGS 1) and RM 8560 (NGS 2) were obtained from the National Institute for Standards and Technology. The carbon-isotope compositions of the CH_4, C_2H_6, C_3H_8 and CO_2 in these gas mixtures have been calibrated by NIST versus NBS 19 (assigned value of +1.95‰). Ranges of hydrogen-isotope compositions for CH_4 and C_2H_6 have also been reported, evaluated versus VSMOW and VSLAP (NIST report, 2004). Two gases with known δD values (CH_4 and C_2H_6) were also obtained from the Environmental Isotope Laboratory at the University of Waterloo.

The $\delta^{13}C$ values obtained in this study for the NIST standards are listed in Table 1, together with NIST reported results. The measured $\delta^{13}C$ values fall within acceptable error of published values. Reproducibility is good (± ≤0.5‰) with the exception of results for CO_2 and C_3H_8 for RM 8559. Accurate isotopic results were obtained for these trace gases (<1% volume), despite poorer reproducibility at these concentrations and it can be demonstrated that it is possible to obtain accurate and reproducible results for hydrocarbons at concentrations as low as 20 nmol (equivalent to ≤100 mV on *m*/*z* cup 44; Fig. 5A), which compares well with carbon-isotope results for CH_4 at low concentrations, reported for the method of Potter and Siemann (2004).

The δD values obtained in this study for the NIST standards and two reference gases are listed in Table 2, along with previously reported results. These values compare well with the earlier results over a range −300 to −60‰. Reproducibility is also within acceptable error (≤5‰). The large range of δD values reported by NIST in RM 8560 for C_2H_6 likely arises from its low concentration (1.3% volume). Large errors can occur (~±16‰; see Potter and Siemann, 2004) at concentrations less than ~100 nmol (equivalent of 200 mV on *m*/*z* cup 2). The result obtained here falls well within the

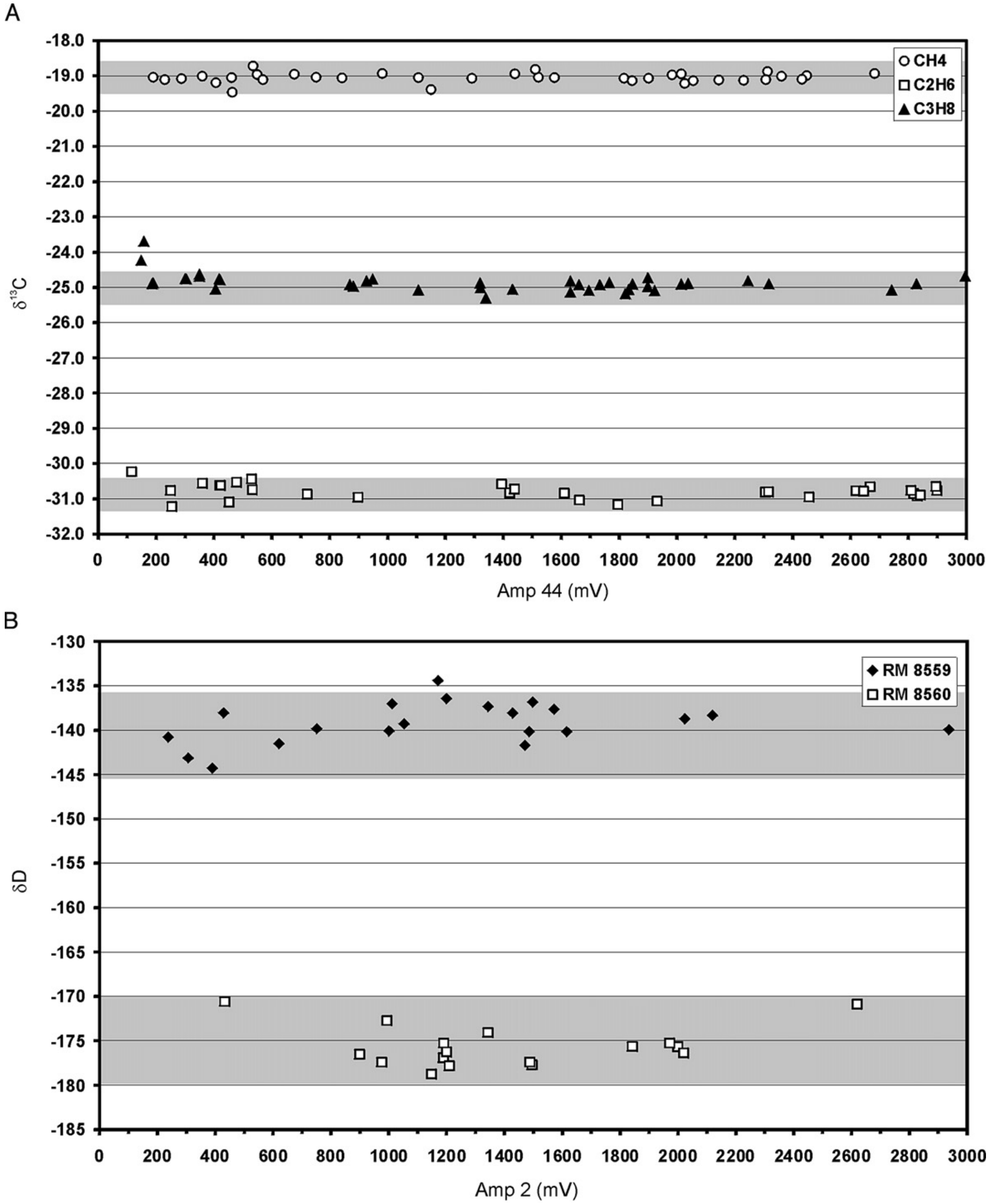

Fig. 5. (A) A plot of δ^{13}C versus amplitude on *m*/*z* cup 44. Results for three in-house hydrocarbon reference gases (CH_4 = −19.1‰; C_2H_6 = −25.0‰; C_3H_8 = −30.8‰) evaluated against RM 8559 and 8560. (B) A plot of δD versus amplitude on *m*/*z* cup 2. Results for CH_4 standards RM 8559 (−141‰) and RM 8560 (−175‰). Shaded areas are within acceptable error of ±0.5‰ for δ^{13}C and ±5‰ for δD. Note: Injection volumes ranged from 2 to 100 µl at a split ratio of 10.

$\delta D_{C_2H_6}$ reported for RM 8560 and Fig. 5B demonstrates that accurate results can be obtained for hydrocarbon concentrations down to 100 nmol using this system.

Blank tests were conducted by simulating a crush and run without a sample present. Only trace amounts of CO_2 were detected with amplitudes of 60–130 mV on

Table 2
Average hydrogen-isotope results for NIST natural gas standards and other reference gases

Sample	N	δD_{CH_4}	σ	$\delta D_{C_2H_6}$	σ	NIST values	Other reported values
RM 8559	10	−141	2			−133.7 to −141.9	−138±4[a]
RM 8560	12	−175	3			−169.4 to −175.2	−174±3[a]
RM 8560	3			−118	3	−114.5 to −128.2	
EIL 8	8	−67	1				−65±3[b]
EIL 7	5			−324	2		−325±3[b]

N = number of aliquots analysed.

[a] Results from Potter and Siemann (2004).

[b] Results from the Environmental Isotope Laboratory, University of Waterloo.

m/*z* cup 44. However, when crushing samples (see Section 4), detectable CO_2 was not observed in several runs. The CO_2 detected during the blank runs may therefore result from small reactions between the sample chamber and piston when no sample is present, as observed previously during *in vacuo* crushing (e.g., Piperov and Penchev, 1973; Whelan, 1988). Such reactions are minimised when a sample is crushed, as steel-to-steel contact is reduced. We are, therefore, confident that blanks are low in this system and do not affect the isotopic values obtained for samples.

4. Applications

4.1. Case study 1: Khibina alkaline igneous complex, northwest Russia

The Devonian Khibina alkaline igneous complex is located in the Kola Alkaline Province in northwest Russia (Fig. 6). These peralkaline igneous rocks host unusually high concentrations of reduced gases entrapped predominantly as secondary fluid inclusions (Potter et al., 1998; Beeskow et al., 2006). The gases are similar to those found in other peralkaline igneous complexes worldwide (Petersilie and Sørensen, 1970; Salvi and Williams-Jones, 1997b; Konnerup-Madsen et al., 1985; Markl et al., 2001; Potter et al., 2004). Although it is widely accepted that these reduced gases are of abiogenic origin, the mechanism and timing of their formation remains controversial (Beeskow et al., 2006; Salvi and Williams-Jones, 2006; Ryabchikov and Kogarko, 2006). Various models for gas formation have been proposed, with sources ranging from early juvenile magmatic (>600 °C) (Petersilie, 1962; Markl et al., 2001; Markl, 2005) to late-magmatic (<500 °C) (Konnerup-Madsen et al., 1985; Konnerup-Madsen, 2001; Beeskow et al., 2006) to post-magmatic (350–400 °C) (Salvi and Williams-Jones, 1997b; Potter et al., 1998; Potter et al., 2004; Salvi and Williams-Jones, 2006). Although there is now evidence for magmatic CH_4 in primary inclusions in the Khibina complex (Beeskow et al., 2006), problems remain with the hypothesis of a primary magmatic source for the complete suite of hydrocarbon species found in this and other peralkaline complexes. The significant concentrations of higher hydrocarbons, and in some cases hydrogen, cannot be explained using a simple magmatic model (Salvi and Williams-Jones, 1997b; Potter and Konnerup-Madsen, 2003; Potter et al., 2004; Salvi and Williams-Jones, 2006). Thermodynamic considerations of redox conditions during crystallisation of the Khibina intrusion suggest that the stable gas phase at >400 °C should be CO_2, and that the amounts of CH_4 and H_2 should be negligible (e.g., Ryabchikov and Kogarko, 2006). Hence, the origin of these gases may be more complex than previously suggested.

Stable isotope data for fluid inclusion-hosted hydrocarbon gases in these peralkaline complexes have been reported previously using off-line methods (Galimov and Petersilie, 1967; Petersilie and Sørensen, 1970; Galimov, 1973; Konnerup-Madsen et al., 1985; Potter, 2000; Konnerup-Madsen, 2001; Potter and Konnerup-Madsen, 2003; Beeskow et al., 2006). However, in some cases, only bulk $\delta^{13}C_{HC}$ values have been reported where a mixture of hydrocarbon gases were extracted and combusted together before being analysed (Galimov, 1973; Potter, 2000) or only $\delta^{13}C$ and/or δD values for a single gas phase have been reported, given the difficulty of separating, preparing and transferring trace gas components for isotopic determination (Galimov and Petersilie, 1967; Konnerup-Madsen et al., 1985). Beeskow et al. (2006) provided the first comprehensive report of $\delta^{13}C$ values for complex hydrocarbon gases in samples from the Khibina complex using off-line *in vacuo* crushing prior to conventional GC–irMS analysis.

Here, we present carbon- and hydrogen-isotope results for four samples (Table 3) from the Yuksporr mine at Khibina (site U; Fig. 6). These samples represent the urtite–ijolite series and the apatite–nepheline ore. They host abundant hydrocarbon gas

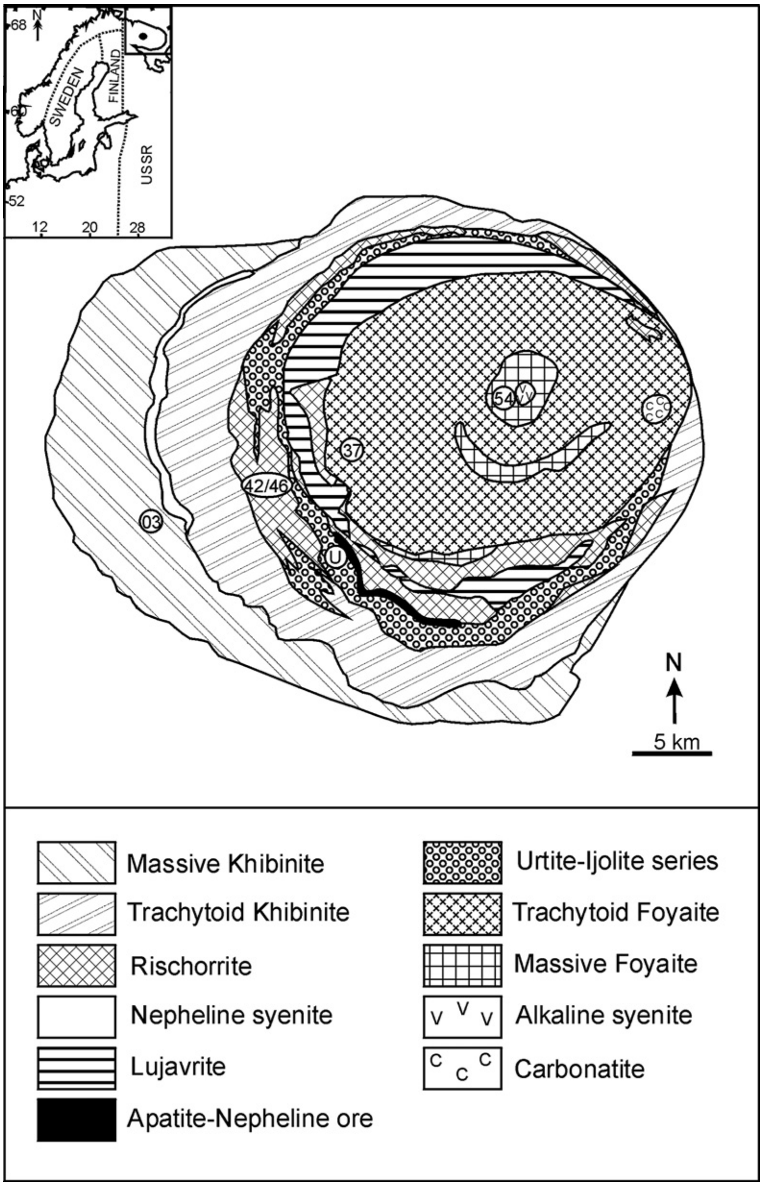

Fig. 6. A simplified geological map of the Khibina intrusive complex showing approximate sample localities for this study (U) and those from Beeskow et al. (2006) (03; 37; 42; 46; 54). After Beeskow et al. (2006). The inset shows the location of the Khibina complex in northwest Russia.

inclusions entrapped as 5–10 μm secondary inclusions along cleavage and fracture planes in nepheline and apatite. The gases comprise predominantly CH_4 (70–90 vol.%), but also contain significant concentrations of higher hydrocarbons up to C_7H_{16} (Potter, 2000). The $\delta^{13}C_{CH_4}$ values range from −13.3 to −7.6‰. Trace amounts of CO_2 were also detected. The $\delta^{13}C_{CO_2}$ values (−18.6 to −14.6‰) are lower than the $\delta^{13}C_{CH_4}$ values. C_2H_6 was detected in all samples, and has $\delta^{13}C_{C_2H_6}$ values ranging from −23.3 to −16.1‰. C_3H_8 was detected in three samples; its $\delta^{13}C_{C_3H_8}$ values (−21.3 to −14.1‰) are similar to those of C_2H_6. Only one sample contained sufficient concentrations of C_4H_{10} and C_5H_{12} for $\delta^{13}C$ measurements. These gases have a similar range of $\delta^{13}C$ values (−20.6 to −16.8‰) to C_2H_6 and C_3H_8 (Table 3).

The reproducibility of the $\delta^{13}C$ values obtained for separate aliquots of gases extracted from the same sample during multiple crushes is generally good (≤±0.5‰). However, the variation can be as high as ±1.9‰. The variation in isotopic composition for duplicate analyses of the same sample (i.e., different sub-samples were crushed)

Table 3
Stable isotope results for the Khibina alkaline igneous complex

Sample	Rock type	Wt (g)	*N*	$\delta^{13}C_{CH_4}$	σ	δD_{CH_4}	σ	$\delta^{13}C_{CO_2}$	σ	$\delta^{13}C_{C_2H_6}$	σ	$\delta D_{C_2H_6}$	σ	$\delta^{13}C_{C_3H_8}$	σ	$\delta^{13}C_{C_4H_{10}}$	σ	$\delta^{13}C_{C_5H_{12}}$	σ
KH-03-U10	Ap–Ne ore	2.0	3	−12.0	0.3	–	–	−16.5	1.9	−16.5†	0.3	–	–	–	–	–	–	–	–
KH-03-U10-dupl	Ap–Ne ore	1.7	3	−11.8	0.3	–	–	–	–	−17.1†	0.4	–	–	–	–	–	–	–	–
KH-03-U10	Ap–Ne ore	2.0	3	–	–	−118	5	–	–	–	–	–	–	–	–	–	–	–	–
KH-03-U10-dupl	Ap–Ne ore	1.9	3	–	–	−108	7	–	–	–	–	–	–	–	–	–	–	–	–
KH-03-U19	Urtite	1.0	3	−8.1	0.1	–	–	–	–	−20.6	0.8	–	–	−19.7†	–	–	–	–	–
KH-03-U19-dupl	Urtite	2.0	2	−7.6	0.3	–	–	−18.6†	0.1	−20.4	0.2	–	–	−18.3†	0.2	–	–	–	–
KH-03-U19-dupl2	Urtite	2.0	3	−8.9	0.2	–	–	−17.0†	1.2	−20.9	0.3	–	–	−18.9†	0.7	–	–	–	–
KH-03-U19	Urtite	1.9	4	–	–	−88	3	–	–	–	–	−154	1	–	–	–	–	–	–
KH-03-U19-dupl	Urtite	2.0	3	–	–	−89	4	–	–	–	–	−146	–	–	–	–	–	–	–
KH-03-U20	Urtite	1.0	3	−13.2	0.6	–	–	–	–	−23.1	0.1	–	–	−20.7	–	−16.8	–	−19.6	–
KH-03-U20-dupl	Urtite	2.0	2	−13.3	0.7	–	–	–	–	−23.3	0.1	–	–	−20.7	0.1	−16.9	–	−20.6	–
KH-03-U20-dupl2	Urtite	2.0	2	−12.4	0.1	–	–	−14.6	0.1	−23.2	0.1	–	–	−21.3	0.1	−17.4	0.1	−20.3	0.4
KH-03-U20	Urtite	1.7	2	–	–	−88	10	–	–	–	–	–	–	–	–	–	–	–	–
KH-03-U20-dupl	Urtite	1.9	2	–	–	−84	5	–	–	–	–	−175	–	–	–	–	–	–	–
KH-03-U22A	Urtite	1.2	4	−10.6	0.7	–	–	−15.7	0.5	−16.3	0.3	–	–	−17.2†	–	–	–	–	–
KH-03-U22A-dupl	Urtite	1.2	3	−10.4	0.5	–	–	−15.2	0.1	−16.1	0.2	–	–	−14.1†	–	–	–	–	–
KH-03-U22A	Urtite	1.4	3	–	–	−50	1	–	–	–	–	−121	–	–	–	–	–	–	–
KH-03-U22A-dupl	Urtite	1.7	3	–	–	−52	3	–	–	–	–	−120	–	–	–	–	–	–	–

a. *N* = number of aliquots analysed per sample.

b. Where the standard deviation is not quoted, only one value was obtained.

c. †amplitude of mass 44 was below 100 mV.

d. Ap–Ne ore = apatite–nepheline ore.

ranges from ±0.1 to ±1.6‰ with the majority differing by <±0.7‰. The higher errors observed for multiple crushes and duplicate analyses of some samples may result from (i) low concentrations of the gas species in question (e.g., CO_2 and C_3H_8 in KH03-U19; Table 3), or (ii) heterogeneity of the fluid inclusion gas compositions released between each crush (e.g., CH_4 in KH03-U20; Table 3), which may indicate slightly different fluid inclusion

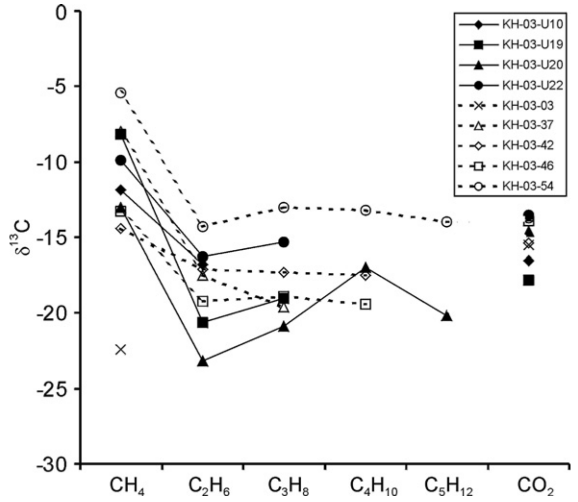

Fig. 7. The $\delta^{13}C$ values of hydrocarbon and CO_2 fluid-inclusion gases analysed in this study (solid symbols; site U; Fig. 6) and by Beeskow et al. (2006; open symbols; sites 03; 37; 42; 46; 54; Fig. 6).

generations/compositions in large and small inclusions. The fact that the majority of results have errors <0.7‰, suggests that, in most cases, fluids contained in these samples are homogeneous, and most likely represent a single fluid generation.

The hydrogen-isotope compositions of these samples were also obtained for CH_4 and in most cases, C_2H_6 (Table 3); the concentrations of the C_3–C_5 hydrocarbon species were too low for isotopic measurement. Their δD_{CH_4} values range from −118 to −52‰. The $\delta D_{C_2H_6}$ values (−175 to −120‰) are lower by 70–100‰ than those obtained for associated CH_4. The reproducibility of δD values for aliquots of gas from the same sample is variable (±10 to ±1‰), but most samples are well within acceptable error (≤±5‰). The reproducibility of results for duplicate samples is also good.

The $\delta^{13}C$ values for these samples compare well with those reported by Beeskow et al. (2006), and show the same pattern of variation amongst individual gas species (Fig. 7). The $\delta^{13}C_{CH_4}$ values (−13 to −8‰) obtained for the urtite–ijolite series and apatite–nepheline ore from site U (see Fig. 6) fall between those previously recorded (−8 to −5‰; Beeskow et al., 2006) for samples located near the centre of the complex (site 54, Fig. 6) and those located towards its edge (sites 03, 42, 46, Fig. 7; −22 to −13‰; Beeskow et al., 2006). The results are also similar to those reported by Voytov (1992) (−15 to −6‰) for free and fluid inclusion gases from apatite–nepheline deposits and ijolite–urtites from the Yuksporr mine (site U; Fig. 6) and the adjacent Rasvumchorr mine.

This pattern suggests that the original CH_4, which is preserved in the centre of the complex, had $\delta^{13}C$ values of −8 to −5‰, characteristic of a magmatic source. Subsequent migration, fractionation, secondary reactions and/or possible mixing with another source of CH_4 then produced the variation in $\delta^{13}C_{CH_4}$ values observed throughout the complex (e.g., Beeskow et al., 2006). This scenario is reasonable, given ample evidence for gas migration via fractures throughout the complex (e.g., Nivin et al., 2001) and secondary entrapment of these gases along cleavage and fracture planes within the host rock (e.g., Potter et al., 1998). The lower $\delta^{13}C$ values of the higher hydrocarbons (relative to CH_4) also suggest an abiogenic origin for these gases (Sherwood-Lollar et al., 2002), as has been proposed earlier (see Potter and Konnerup-Madsen, 2001; Beeskow et al., 2006). However, a detailed understanding of the origin (early, late or post-magmatic) and reactions (polymerisation and/or Fischer–Tropsch-type reactions) responsible for these higher hydrocarbons has remained elusive.

The δD_{CH_4} values obtained for these samples fall within the expected range for CH_4 from magmatic systems (−150 to −50‰; Kyser and O'Neil, 1984; Whiticar, 1999) and are not consistent with a thermogenic (−300 to −100‰) or bacterial (−450 to −160‰) origin (Whiticar et al., 1986; Schoell, 1988). These results are also similar to values reported previously (−72 to −56‰) for free CH_4 collected from boreholes in the adjacent Rasvumchorr mine (Voytov, 1992).

The carbon- and hydrogen-isotope data obtained for the CO_2 and higher hydrocarbons gases provides a better insight into their formation than previously possible. First, the $\delta^{13}C_{CO_2}$ values reported here and by Beeskow et al. (2006) are consistently lower than those of the associated CH_4 (Table 3; Fig. 7). Such a pattern is unusual; most CH_4 in geological and biological systems is depleted of ^{13}C relative to coexisting CO_2. The ^{13}C-depletion of CO_2 observed here can result from kinetic fractionation during abiogenic CH_4-oxidation reactions (e.g., Kiyosu and Krouse, 1989). Such an origin would have two implications: (i) CH_4 was the precursor for CO_2, indicating that CH_4 was the juvenile gas phase in the magmatic system, thus precluding Fischer–Tropsch-type reactions involving magmatic CO_2 (e.g., Potter et al., 1998), and (ii) the CO_2 was generated during sub-solidus, kinetic fractionation reactions, and not during re-equilibration of a late-magmatic fluid (e.g., Konnerup-Madsen et al., 1985).

Second, the depletion of both ^{13}C and D in C_2H_6 relative to coexisting CH_4 observed at Khibina (Table 3) is rarely observed in nature. Thermogenically derived hydrocarbons are typically characterised by ^{13}C- and D-

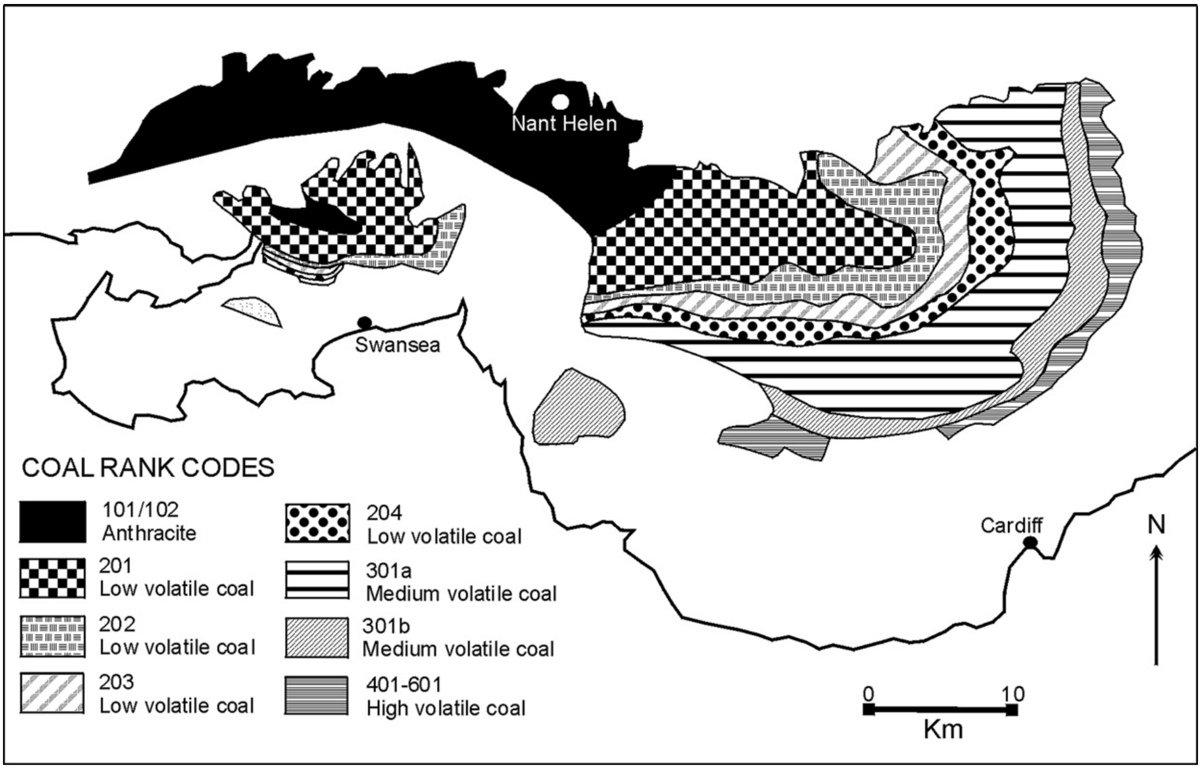

Fig. 8. A simplified geological map of the South Wales Coalfields showing coal-rank and sample location. After Alderton et al. (2004).

enrichment with increasing carbon number as the simpler hydrocarbon species are produced sequentially by thermal decomposition of their higher molecular weight biogenic precursors (e.g., Prinzhofer and Huc, 1995). Abiogenic formation of hydrocarbons via Fischer–Tropsch-type reactions, by comparison, produces ^{13}C-depletion on one hand, with increasing carbon number because of preferential incorporation of ^{12}C as the longer-chain alkanes are formed. It is also characterised, on the other hand, by D-enrichment because of preferential loss of light hydrogen upon the breaking of C–H bonds in CH_4, which accompanies generation of higher hydrocarbons (Sherwood-Lollar et al., 2002).

The cause of the coupled depletion of ^{13}C and D in Khibina higher hydrocarbons relative to methane is not fully understood. The large negative isotopic fractionations between CH_4 and C_2H_6 (up to 100‰ for hydrogen and 12‰ for carbon; Table 3), might indicate that the higher hydrocarbons were generated from the original magmatic CH_4 during lower temperature (350–400 °C?) sub-solidus reactions, as the complex cooled.

In summary, these data suggest that CH_4 in this (and other?) silica-undersaturated peralkaline complex is magmatic in origin, as suggested by Markl et al. (2001) and Beeskow et al. (2006). That said, sub-solidus, kinetic fractionation reactions have significantly altered the primary fluid composition, as suggested by Potter et al. (1998, 2004).

4.2. Case study 2: South Wales Coalfield, UK

The Carboniferous coalfields of south Wales provide an example of extreme coal-rank variations over a small area (Fig. 8). The coalfields, which extend 50 km from north-east to south-west, were formed during metamorphism that accompanied the Variscan orogeny (Gayer et al., 1998; Hower and Gayer, 2002). The coal-rank ranges from low-grade, high-volatile, bituminous coal in the south to high-grade, low-volatile anthracite in the north (Fig. 8). The thermal and fluid-flow history of the basin has been investigated using: (i) vitrinite reflectance (Bevins et al., 1996; Hower and Gayer, 2002), (ii) illite crystallinity (White, 1992), (iii) hydrogeological modelling (Gayer et al., 1998), and (iv) fluid inclusion and stable isotope studies of quartz and carbonate veins associated with fluid movement and coalification (Alderton and Bevins, 1996; Alderton et al., 2004).

Table 4
Stable isotope results for the Nant Helen mine (UK Grid Reference SN827113)

Sample	N	Wt (g)	$\delta^{13}C_{CH_4}$	σ	δD_{CH_4}	σ	$\delta^{13}C_{CO_2}$	σ	$\delta^{13}C_{C_2H_6}$	σ	$\Delta^{13}C_{CO_2-CH_4}$	T (°C)
Quartz vug	5	1.3	−27.9	0.1	–	–	−3.1	0.8	−20.6	0.1	24.8	293
Quartz vug	3	0.6	–	–	−148	1	–	–	–	–	–	–

N = number of aliquots analysed per sample.
Temperature calculated from the CO_2–CH_4 fractionation factor of Bottinga (1969).

There is generally good agreement about the temperatures reached in the low- to medium-grade parts of the basin. However, uncertainty exists concerning the maximum temperatures achieved in the anthracite zone (Alderton et al., 2004). The temperature required for anthracite formation is generally considered to be ~260–300 °C (Teichmüller and Techmüller, 1985; Hower et al., 1993; Hower and Gayer, 2002). In the south Wales basin, geothermal gradients of 50 °C km^{-1}, yielding temperatures for anthracite formation of ~300 °C, have been predicted from fluid-flow modelling (Gayer et al., 1998). In contrast, temperatures of ~200 °C were indicated from measurements of fluid inclusions hosted in quartz veins in the anthracite zone (Alderton et al., 2004). However, fluid inclusion temperature determinations were hindered by the rarity of coeval aqueous inclusions in association with hydrocarbon inclusions, an occurrence that would have enabled an exact determination of entrapment temperatures for these fluids (Alderton and Bevins, 1996; Alderton et al., 2004). Therefore, the carbon isotopic compositions of the carbonic gases provide an additional way to calculate possible temperatures reached within this zone.

A sample containing large, euhedral quartz crystals, formed within fractures in the anthracite (Alderton et al., 2004), was provided from the Nant Helen coal mine (Fig. 8) by Kingston University, UK. The quartz contains abundant CH_4–CO_2 fluid inclusions. These inclusions contain a homogeneous fluid with highly consistent phase behaviour and molar compositions (CH_4:CO_2=85:15±1%; Beeskow et al., 2005). Traces of C_2H_6 were also detected in our measurements (Table 4).

The $\delta^{13}C$ and δD values of the CH_4 (−27.9 and −148‰, respectively), and the $\delta^{13}C$ values of the C_2H_6 (−20.6‰) and CO_2 (−3.1‰) are typical of highly mature thermogenic gases derived from coal (e.g., Schoell, 1988). Reproducibility of the isotopic results for multiple aliquots of CH_4 and C_2H_6 from the same sample is good for both carbon (±0.1‰) and hydrogen (±1‰); the variability in carbon-isotope composition is higher for CO_2 (±0.8‰) (Table 4). Assuming equilibrium between CO_2 and CH_4, a temperature of 293 °C can be calculated using the carbon-isotope CO_2–CH_4 geothermometer of Bottinga (1969). This result most likely represents the temperature of generation for these gases. Re-equilibration and/or modification of the gases in the fluid inclusions at lower temperatures is unlikely, given that isotopic exchange between CH_4 and CO_2 is sluggish at temperatures below 400 °C (see Cole and Ohmoto, 1986 and references therein). Therefore, temperatures within the anthracite zone may have been at least as high as 300 °C, if not higher, at the time that these gases were formed.

5. Conclusions

The analytical method described here (crushing online in a constant helium flow) makes possible analysis of complex mixtures of fluid inclusion gases. Non-condensable and condensable fluid inclusion gases released upon crushing are captured using a 13 nm molecular sieve immersed in liquid nitrogen and then transferred to a gas chromatograph–continuous flow-isotope ratio mass-spectrometer system for compound-specific carbon- and hydrogen-isotope analysis. The CH_4, CO_2 and higher hydrocarbons (up to C_5H_{12}) have been separated for carbon-isotope measurements to concentrations as low as ~20 nmol, and CH_4 and C_2H_6 for hydrogen-isotope measurements to concentrations as low as ~100 nmol. The accuracy and reproducibility of results obtained for standards is ≤±0.5‰ for $\delta^{13}C$ and ≤±5‰ for δD, which is typical of this and other continuous-flow systems. The reproducibility of duplicate samples, and of multiple aliquots of gas extracted from the same sample during repeated crushing, are <±0.7‰ for $\delta^{13}C$ and <±7‰ for δD in most cases. These errors are somewhat larger than typical for bulk off-line extraction of fluid inclusion gases and their analysis using dual-inlet mass spectrometry (~±0.3‰ for $\delta^{13}C$ and ~±3‰ for δD). However, the new method provides for rapid, accurate and reproducible carbon- and hydrogen-isotope analysis of major and trace carbonic gases entrapped in fluid inclusions that is not possible using the other methods. The new method approach can, in fact, also provide additional information about the heterogeneity/homogeneity of fluid inclusion gases through analysis of multiple aliquots from the same sample.

Samples from the Khibina peralkaline igneous complex, Russia, and the south Wales coalfields, were used to explore the potential of the new methodology. Results for fluid inclusions from urtites and apatite–nepheline ores from Khibina suggest that CH_4 was the original, abiotic magmatic gas. Sub-solidus abiogenic CH_4-oxidation and polymerisation reactions then produced carbon dioxide and higher hydrocarbons that are depleted of ^{13}C relative to coexisting methane. Likewise, C_2H_6 is depleted of D relative to coexisting CH_4. The isotopic results obtained for CH_4, CO_2 and C_2H_6 from fluid inclusions in quartz veins associated with anthracite in the South Wales coalfields are typical of highly mature thermogenic coal-derived gases. The $\Delta^{13}C_{CO_2-CH_4}$ fractionation suggests gas and possibly anthracite formation at ~290–300 °C.

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