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An appraisal of stepped heating release of fluid inclusion CO_2 for isotopic analysis: A preliminary to $\delta^{13}C$ characterisation of carbonaceous vesicles at the nanomole level

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Abstract—An appraisal of stepped heating methods for the extraction and isolation of fluid inclusion CO_2 for carbon stable isotope ratio analysis indicates that the magnitude of the system blank, and thus its influence on the resulting data, has been considerably underestimated in previous studies. The problem derives largely from the unmodified application of stepped combustion techniques originally developed for the removal of terrestrial organic matter from extraterrestrial samples. In particular, the presence of heated Pt in the sample extraction chamber, as reported in the literature, is shown to have a serious deleterious effect on the analysis of small (sub-micromole) samples. If the extracted gases are not exposed to this combustion catalyst, the magnitude of the system blank is substantially reduced. Furthermore, excellent agreement is then generally obtained between fluid inclusion $\delta^{13}C$ values determined after either stepped heating or crushing of the host mineral as the fluid extraction procedure. The release of a low temperature carbon component during stepped heating, and characterised invariably by a $\delta^{13}C$ value of ca. −25‰, is in accord with earlier studies and is attributed to surficial contamination by ubiquitous, airborne particulates of biological origin. Effective discrimination between this source of CO_2 and that derived from palaeofluid inclusions is fundamental to accurate isotopic characterisation of the latter.

Application of the revised stepped heating procedure to the extraction of hydrothermal fluid inclusion CO_2 from single quartz grains (~10–20 mg), for carbon stable isotope analysis by static vacuum mass spectrometry, is reported. Under optimum conditions, and where the isotopic composition of the sample gas is enriched in ^{13}C by less than ~20‰ relative to the associated procedural blank, 2–3 nmol of sample gas may be analysed with an attendant extraneous (blank) contribution to the $\delta^{13}C$ value that is less than the optimal analytical precision of the measurement (~±1‰, at the 1σ level).

Further progress in the application of ultra-high sensitivity mass spectrometric techniques to accurate $\delta^{13}C$ analysis of carbonaceous fluid inclusion components, particularly coexisting CO_2 and methane, is dependent on proper assessment of the associated blanks and the rigorous control thereof. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

Many crustal and sub-crustal lithologies are associated with a fluid phase in which the presence of CO_2 is recognised. Whereas mantle degassing (e.g., Mattey, 1987, and references therein; Trull et al., 1993; Zhang and Zindler, 1993) and recycling of CO_2 back into the convecting mantle (Green et al., 1993) play a fundamental role in global geochemical cycles of carbon, CO_2 is also implicated in a variety of petrogenetic processes, including the promotion of melting in the lower crust (Peterson and Newton, 1989) and examples of high-grade metamorphism (e.g., Kreulen, 1980; Lamb et al., 1987; Harris et al., 1993; Mattey et al., 1994; Mullis et al., 1994) including granulite formation (Farquhar and Chacko, 1991). Because of the low but finite solubility of CO_2 in silicic melts (Eggler and Kadik, 1979; Mattey et al., 1989; Blank et al., 1993), CO_2 is usually a major component of volatiles exsolving from ascending magmas (Stolper and Holloway, 1988) and may lead to CO_2-enrichment of magmatic-hydrothermal fluids (e.g., Miller, 1994). Except for present-day geothermal areas and submarine hydrothermal vents, however, the only means of sampling such fluids, which were originally derived from hotter and deeper regions of the Earth, is from fluid inclusions in rocks and minerals. These provide a unique source of information about the nature and composition of fluids which once formed or traversed the host (see Roedder, 1984). Published $\delta^{13}C$ values of CO_2 (and other carbonaceous components) from fluid inclusions are relatively uncommon, however, although such data provide diagnostic constraints on carbon sources and/or geochemical reactions associated with the history of the fluid.

Stepped heating, entailing either combustion, pyrolysis, or a combination of the two, has been used to release indigenous vesicular CO_2 and other carbon components from oceanic basalt glasses (e.g., Pineau and Javoy, 1983; Des Marais and Moore, 1984; Mattey et al., 1984; Sakai et al., 1984; Exley et al., 1986, 1987), upper-mantle xenoliths (e.g., Nadeau et al., 1990), amphibolite and granulite facies rocks (Jackson et al., 1988a,b), eclogites (Mattey et al., 1994), and hydrothermal vein quartz (Miller, 1994). An ubiquitous feature of such experiments is the release (as CO_2) by low-temperature combustion (<600°C) of carbon characterised by $\delta^{13}C \approx -25$ to −30‰. Although there is still not univer-

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sal agreement on the origin of this component, Des Marais and Moore (1984), Mattey et al. (1984), and Exley et al. (1986, 1987) suggested that, in the case of oceanic basalts at least, surficial organic contamination is the most probable source. This interpretation is supported by several lines of evidence, summarised by Des Marais (1986) and Mattey et al. (1989), and is now the most widely-accepted explanation. An additional complication in the case of upper-mantle xenoliths is that carbonaceous films may be present (Mathez, 1987; Nadeau et al., 1990), which are apparently not attributable to biological contamination (Tingle et al., 1990; Sugisaki and Mimura, 1994, 1995) and were possibly synthesised by reactions of volcanic gases on chemically active, fractured surfaces. These films may, in some instances, be associated with organic matter, an association that appears to be restricted to extrusive rocks (Tingle et al., 1991; Sugisaki and Mimura, 1994).

Radical improvements in the sensitivity of carbon stable isotope ratio measurement techniques since the early 1980s, either through the application of noble gas-type static vacuum mass spectrometry (Carr et al., 1986; Prosser et al., 1990; Yates et al., 1992) or recent developments of the isotope ratio monitoring approach as pioneered by Sano et al. (1976) and Matthews and Hayes (1978), currently provide the facility for isotopic analysis of CO_2 samples at the sub-nanomole level, to a 1σ precision of better than $\pm 1‰$. Whereas extraterrestrial cosmochemistry research has benefited greatly from such developments (see Pillinger, 1984, 1992), relatively few applications to terrestrial geochemistry have been reported hitherto. For the analysis of carbonaceous fluid inclusions, the improved sensitivity of isotope ratio measurement permits a greater degree of lithological control over sample selection, through use of smaller samples. A further benefit is the prospect of analysing samples which contain a very low abundance of palaeofluid carbon, arbitrarily defined for present purposes as $<0.1\ \mu mol\ g^{-1}$. In turn, this necessitated a reappraisal of procedures used to extract and isolate fluid inclusion CO_2 prior to stable isotopic ratio measurement, with particular regard to the abundance and sources of attendant carbon blank.

Stepped combustion was used by Swart et al. (1983) to remove surficial organic contaminants from extraterrestrial samples, prior to isotopic characterisation of the indigenous carbonaceous phases that combust at $> \sim 425°C$. Jackson et al. (1988a,b) and Mattey et al. (1989) applied a variation of this procedure to the extraction and isolation of CO_2 from vesicles in terrestrial samples (generally quartz, garnet, or basalt glass). Essentially, Jackson et al. (1988a,b) and Mattey et al. (1989) recommended a combustion step at 400°C in pure oxygen ($\sim 7 \times 10^4$ Pa) to remove surficial contaminants, followed by stepped heating in vacuo ($<1.3 \times 10^{-3}$ Pa), during which CO_2 was isolated for isotopic analysis. The same analytical procedure was also adopted during more recent studies of fluid inclusions in high-grade metamorphic rocks (Harris et al., 1993; Mattey et al., 1994).

Two important differences, however, distinguish the type of sample material used for fluid inclusion analysis from that for which the procedure of Swart et al. (1983) was devised. Firstly, the carbon species of interest occurs as a simple, inorganic constituent of a fluid phase (often aqueous) rather than as integral components of a refractory matrix that requires chemical alteration (oxidation) to release the carbon. Secondly, major release of fluid from many samples of hydrothermal origin, or from CO_2-rich inclusions formed in high pressure metamorphic environments, may occur below the combustion temperature ($425 \pm 25°C$) advocated by Swart et al. (1983) for the removal of organic contamination.

For the present investigation, the objectives were as follows: (1) to establish whether the carbon blank yield associated with the procedure recommended by Jackson et al. (1988a,b) and Mattey et al. (1989) permitted consistency of isotopic data from "small" ($\sim 0.1\ \mu mol$) samples of fluid inclusion CO_2, compared to results obtained using larger quantities of the same samples, where either stepped heating or crushing of the host may be used to open the vesicles; (2) to extend consistency of isotopic data down to the nanomole level using static vacuum mass spectrometry; and (3) to consider how carbonaceous fluid components other than CO_2 may be included in the experimental procedure, in particular, $\delta^{13}C$ measurements at the nanomole level on both fluid inclusion CO_2 and coexisting CH_4. For fluids containing more than one carbon-bearing component, interpretation of stable isotope data in terms of carbon sources requires characterisation of all such components, together with their relative abundances, before meaningful assessment may be made.

The present study originated from a fluid inclusion investigation of early hydrothermal mineralisation associated with component plutons of the Cornubian batholith, southwestern England (Miller, 1994). The relationship between the granite intrusives, local metasediments, and palaeofluids, as deduced from fluid inclusion and other data, will be discussed elsewhere. We report and discuss herein only those findings which relate to the extraction and $\delta^{13}C$ measurement of fluid inclusion CO_2, for applicability to a range of geochemical investigations as exemplified above.

2. MICROTHERMOMETRIC CHARACTERISTICS OF INVESTIGATED SAMPLES

All samples were of quartz and of granite-associated hydrothermal origin. CO_2 ($\pm$lesser quantities of methane) was recognised in most cases as a minor or trace constituent of the aqueous fluids, on the basis of microthermometric and/or Raman studies reported by other authors. Samples HEM-80-1, HEM-80-47, and CD-88-1 were associated with, respectively, the Hemerdon or Castle-an-Dinas (St Austell district) minor granite intrusives of the Cornubian batholith, southwestern England. For comparative purposes, samples from Carrock Fell, northwestern England (samples CF-77-39A and CF-77-79B), and Xihuashan, in the Jiangxi province of China (sample XHS-02), are also included.

Fluid inclusions associated with vein quartz from Hemerdon have been extensively studied by Shepherd et al. (1985), who recognised four inclusion types: Type 1: Two-phase liquid + vapour ($L + V$) inclusions, where $L > V$; Type 2: Two-phase vapour-rich liquid + vapour ($L + V$) inclusions, where $V > L$; Type 3: Three-phase liquid + vapour + solid ($L + V + S$) where the solid phase is halite; and Type 4: Multiphase ($L + V + S$) inclusions containing halite and up to six other daughter minerals. Types 1 and 2 predominate and are intimately associated; in some of the low salinity (<10 wt% NaCl equivalent) examples, gas hydrate develops at sub-ambient temperatures. The homogenisation temperature of these CO_2-bearing inclusions is generally ~ 400–$450°C$. Type 3 inclusions which homogenise by disappearance of the vapour phase (rather than by halite dissolution) exhibit homogenisation temperatures ranging from ~200 to >450°C. Type 3 and 4 inclusions are of high salinity (>29 wt% NaCl equivalent) and dominate the bulk salinity value of 30 ± 5 wt% NaCl equivalent (Kelley et al., 1986). As far as we are aware, no discrete (liquid) CO_2 phase has been observed in fluid inclusions from the Hemerdon locality. Detailed crush-leach analyses of samples HEM-80-1 and HEM-80-47 for fluid solute composition are reported by Miller (1994).

Examination of a polished wafer of sample CD-88-1 indicated that relatively few inclusions were visible and that the vast majority of these were very small (<2 μm) and thus inappropriate for microthermometric measurements (D. A. Banks, pers. commun.). However, as the associated mineralogy is comparable to that of the Hemerdon specimens, it was considered desirable to investigate whether the techniques reported herein could provide information on the abundance and isotopic composition of fluid inclusion CO_2 in an example where this component may be present but is undetectable by microthermometric analysis.

Vein quartz from Carrock Fell is characterised by the predominance of simple, two-phase (liquid + vapour) inclusions, the absence of daughter minerals, and a restricted salinity range of 6.8–9.6 wt% NaCl equivalent (Shepherd et al., 1976). An abundance of relatively large inclusions was noted by Shepherd et al. (1976), together with the observation that a discrete (liquid) CO_2 phase was occasionally present. Significantly lower homogenisation temperatures (~235°C) were recorded than for comparable stage mineralising fluids associated with the granites of southwestern England.

A comprehensive fluid inclusion study by Giuliani et al. (1986) of the Xihuashan palaeo-hydrothermal system showed that the inclusion systematics are complex. Essentially, however, the hydrothermal quartz veins contain aqueous and CO_2-bearing inclusions which homogenise into the liquid or vapour phase at between 150–420°C, with salinities in the region of 1–10 wt% NaCl equivalent. Raman spectroscopy results reported in the same study indicated the presence of nitrogen and methane in the fluids, but at minor or trace levels.

3. EXPERIMENTAL

3.1. Sample Preparation and Cleaning Procedures

Hand specimens of quartz were initially crushed and sieved to produce a particular grain size fraction. For isotopic measurements by static vacuum mass spectrometry, single grains of ~10–20 mg were selected for stepped heating. To meet the sensitivity requirements of dual-inlet mass spectrometry, it was necessary to use ~1000 mg of quartz; in this case, a grain size of 0.5–1 mm was used. Larger chips (~100 mg) were retained for gas release by crushing. Samples were initially examined under a low-powered binocular microscope and individual grains visibly associated with impurities were discarded. Further preparation was restricted to treatment with hot, 6 M HCl to remove any surficial traces of carbonates, followed by washing in doubly-distilled water. In the case of samples analysed by static vacuum mass spectrometry, weighed quartz grains were also subjected to ultrasonic cleaning in high purity dichloromethane (Analar® grade). An adaptation of the minimum-exposure technique of Mattey et al. (1989) was adopted, which involved loading the grains directly from storage under fresh dichloromethane into the extraction line, using tweezers pre-cleaned by dichloromethane. The high volatility of this solvent ensured that no residue was present on the sample by the time the vacuum line reached base pressure.

3.2. Fluid Inclusion Release by Stepped Heating

Two alternative analytical systems were available for the present work. For the most part, the extraction line described by Jackson et al. (1988b) and Mattey et al. (1989) was used, linked to a dual-inlet mass spectrometer (VG SIRA 24). Quartz grains were loaded directly into a degassed silica glass tube, pre-baked at ~1200°C, which was then evacuated (generally overnight) to $<1.3 \times 10^{-4}$ Pa. Stepped heating was performed either in vacuo or, if following the recommendation of Jackson et al. (1988a,b) and Mattey et al. (1989), in the presence of pure oxygen ($\sim 7 \times 10^4$ Pa) for the initial step, to combust surficial contamination. The maximum temperature of this combustion step was restricted to 350°C in the present work, rather than 400°C, to minimise loss of inclusion fluid. All heating steps were of 30 min duration. Exposure of the extracted gases to Pt foil at ~1000°C was an integral feature of the line (Mattey et al., 1989; Jackson, 1990), intended to promote the combustion of methane and other reduced carbonaceous volatiles. CO_2 was isolated from the other released fluid components (predominantly water) by multiple distillation, using a variable temperature cryogenic finger and, finally, with a slush bath of n-pentane/liquid nitrogen (−130°C). CO_2 yields were measured to within ±5% using a capacitance manometer and $\delta^{13}C$ measured to an analytical precision of better than ±0.1‰ on $> \sim 80$ nmol CO_2.

For isotopic analysis by static vacuum mass spectrometry, stepped heating was undertaken using the extraction line described by Ash et al. (1990), in conjunction with the mass spectrometer of Carr et al. (1986). A feature of this extraction line was an air-lock into which the sample was admitted; this was subsequently evacuated to $<5 \times 10^{-4}$ Pa (overnight) before transferring the sample, by aid of a magnetic slug, into the adjacent extraction tube (pre-baked at 1200°C). This procedure avoided the necessity of exposing the extraction chamber to atmosphere during sample loading, thereby permitting improved control of the carbon blank. For the present study, quartz grains were loaded into the air-lock directly, rather than being contained by a Pt envelope (cf. Ash et al., 1990; Yates et al., 1992), to minimize the carbon blank. No combustion steps were undertaken, on the basis of findings reported below; the on line CuO (sheathed in Pt foil) was maintained at a temperature of ~80°C during all heating steps, to minimize adsorption of extracted fluids whilst also ensuring no reaction with any reduced carbonaceous volatiles present. A procedural carbon blank measurement was made immediately prior to transfer of the quartz sample from the airlock, as follows. With the extraction tube at 1200°C and the online Pt/CuO finger at ~80°C, the extraction chamber was isolated from the pumping system and any evolved CO_2 collected on a cold finger at −196°C during a 30 min interval. Transfer of the quartz sample from the air-lock to the extraction tube (cooled to ambient temperature) proceeded only if the CO_2 blank yield was below the detection limit (~40 pmol) of the associated capacitance manometer. A cold finger maintained at −130°C (*n*-pentane/liquid nitrogen slush) within the extraction section prevented the subsequent transfer of water (the predominant component of the fluid inclusions) into the purification section of the line.

3.3. Fluid Release by Crushing

For the release of inclusion fluids by crushing of the quartz host, a bakeable miniature crusher constructed by modification of a Nupro SS6BK stainless steel bellows valve was used, as described by Mattey et al. (1989). A single exit port, connected by a flexible stainless steel high-vacuum coupling to the extraction line, allowed direct transfer of gas to the cryogenic purification and (subsequently) CO_2 yield measurement sections of the line. Released gases were thus not exposed to the extraction chamber used for stepped heating. For each extraction, several cleaned and weighed quartz chips (250–500 mg total) were loaded into the crusher, which was subsequently maintained at ~100°C with the aid of heating tapes, and evacuated to $<10^{-4}$ Pa. During sample crushing, the release of gas was monitored by capacitance manometer. The CO_2 component was then isolated by multiple cryogenic purification/sublimation and the yield recorded, prior to transfer to the inlet cold finger of the dual-inlet mass spectrometer.

3.4. Isolation and Oxidation of Fluid Inclusion Methane

After a satisfactory stepped heating protocol for the extraction of fluid inclusion CO_2 for isotopic analysis had been devised (as discussed below), the following procedure was used to obtain isotopic data on any coexisting methane. At the end of every heating step, residual gases (primarily methane and nitrogen) not condensed on a silica glass finger at −196°C (liquid nitrogen trap), were adsorbed onto a 5 Å molecular sieve also maintained at −196°C. After yield measurement and isotopic analysis of the CO_2 component, the methane-containing gas fraction was recovered from the molecular sieve and expanded into an evacuated section of the line. At this stage, the molecular sieve was isolated; the quantity of gas retained in the associated silica glass finger was accounted for in subsequent yield determinations. The major portion of the methane-containing gas component was then exposed to Pt foil at ~1000°C in conjunction with heated CuO (850°C) as an oxygen source. Prior to use, the CuO was purified by thermal cycling to minimize the CO_2 blank yield from this source, as described by Ash et al. (1990). CO_2 resulting from the oxidation step was isolated by multiple cryogenic distillation and the yield measured by capacitance manometer, before transfer to the inlet cold finger of the dual-inlet mass spectrometer. As methane yields were generally very much lower than those of coexisting CO_2 in the samples used for the present study, it was usually impractical to attempt carbon isotopic analysis of the methane released during individual steps of an incremental heating experiment. For this reason, methane was collected over the temperature range 300–600°C, either during a single step or as the aggregate of several consecutive heating increments.

4. RESULTS

Several hydrothermal vein quartz samples were investigated during the course of a comparison between the isotopic data given by different extraction protocols; the resulting analytical data are tabulated in full elsewhere (Miller, 1994). A common feature, however, was that fluid release was largely complete by 600°C. This is in accord with Bodnar et al. (1989), who noted that the transition of quartz from α to β polymorph (573°C at 0.1 MPa) is often accompanied by significant release of fluid, whereas release at higher temperature is usually minimal. A summary of the salient features is illustrated by Fig. 1, which refers to data obtained from different splits of sample HEM-80-1. The apparent lowering of the $\delta^{13}C$ value as the quantity of quartz sample was reduced was a characteristic feature of all samples investigated when using a stepped combustion/pyrolysis procedure as recommended by Jackson et al. (1988a,b) and Mattey et al. (1989). This result could not be attributed solely to the influence of an increasingly dominant CO_2 system blank as smaller samples of quartz were used: measurement of this component (empty extraction tube) for an in vacuo 350–600°C step showed it to be <6 nmol.

With no preliminary combustion step, and the associated Pt foil catalyst unheated throughout the duration of stepped heating, dependency of the $\delta^{13}C$ result on sample size largely disappeared. The stepped heating profile of sample HEM-80-1 under these conditions is shown in Fig. 2a. Because of the relatively large quantity of sample used in an extraction tube of only 5 mm diameter, temperature uniformity throughout the sample was unlikely to have been maintained to great accuracy. The five heating increments representative of fluid inclusion release (300–600°C), however, exhibited a notably narrow $\delta^{13}C$ range (1.5‰). If this isotopic profile was attributable entirely to mixing between indigenous CO_2 of homogeneous isotopic composition −9.5‰, i.e., the maximum value in the heating profile (denoted by **A** on Fig. 1), and a carbon blank characterised by $\delta^{13}C \approx -25$‰, simple mass balance calculation shows that the yield of the latter was at a minimum (<1 nmol) during the 400–450°C extraction and increased steadily thereafter to ~17 nmol for the 650–700°C step.

Single-step in vacuo heating from ambient temperature to beyond the $\alpha-\beta$ phase transition of the quartz host, with

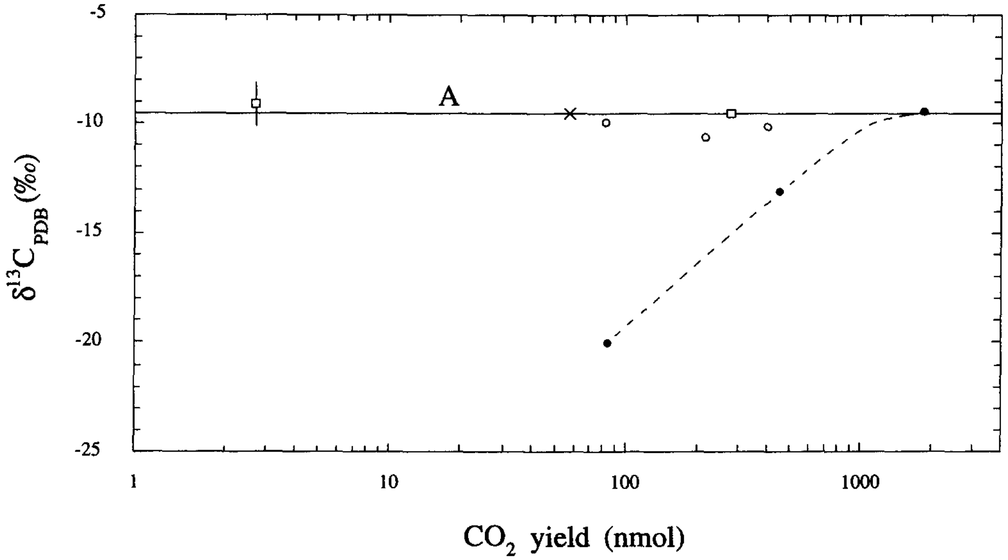

Fig. 1. An example of the dependence of measured $\delta^{13}C$ of fluid inclusion CO_2 on extraction protocol, as the host mineral sample size is progressively reduced. Data are illustrated for hydrothermal vein quartz sample HEM-80-1. Filled circles refer to data obtained using an extraction procedure based on that advocated by Jackson et al. (1988a,b) and Mattey et al. (1989): the CO_2 was collected during a single in vacuo heating step of 350–600°C, after a 350°C heating step in the presence of oxygen. Open circles represent in vacuo single-step heating from ambient temperature to 630°C, but with the on-line Pt catalytic foil at room temperature. Line **A** represents the $\delta^{13}C$ value obtained from either (1) crushing the host quartz to release the inclusion fluid (x), in which case the extracted gases were not exposed to heated Pt foil, or (2) the peak release of fluid during "high-resolution" in vacuo stepped heating (□) when the on-line Pt foil was unheated.

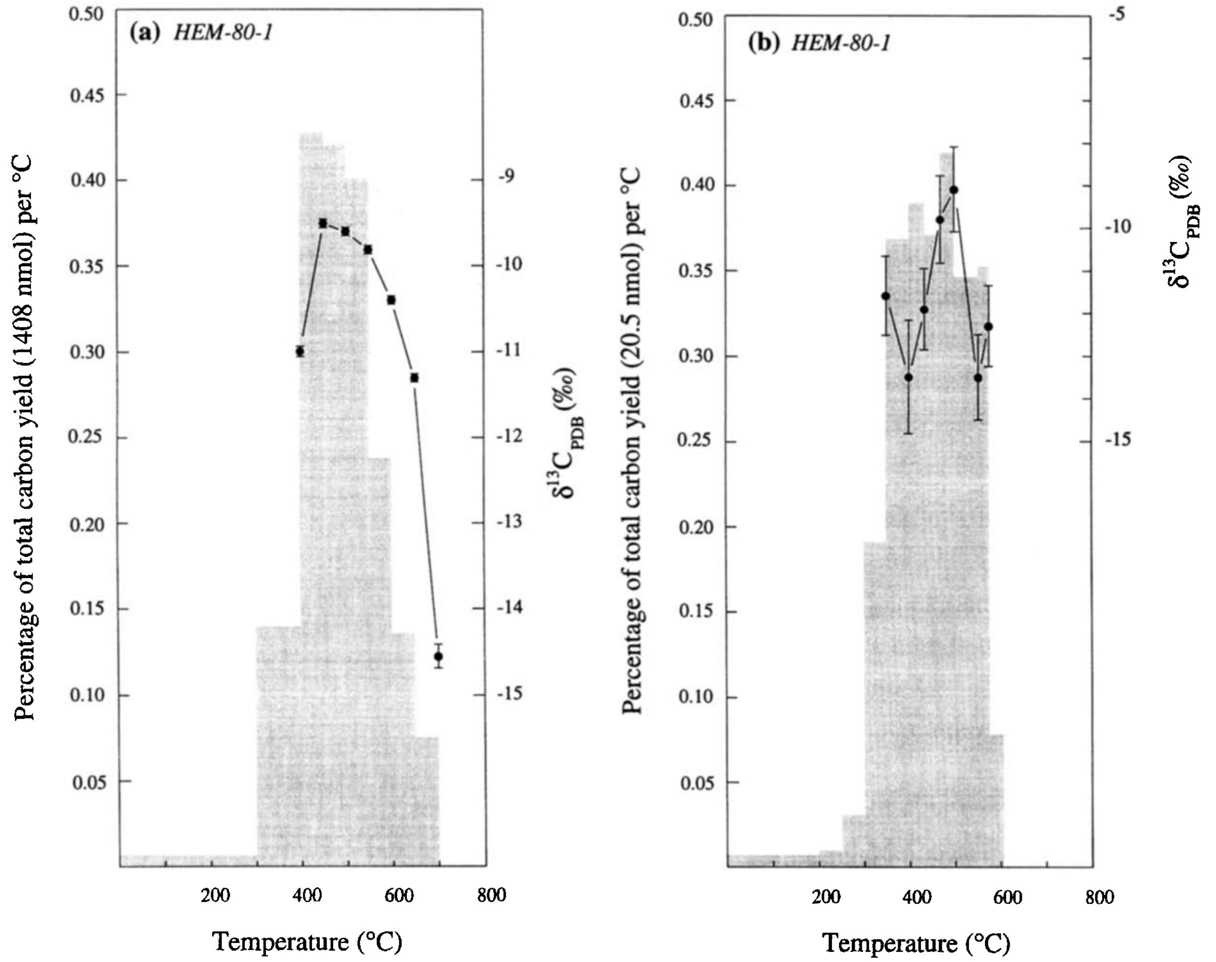

Fig. 2. Yield and isotopic composition of CO_2 extracted from hydrothermal quartz by stepped heating in vacuo: (a) 1112.7 mg of sample HEM-80-1. Released gases not exposed to heated Pt. (b) and (c): Single grains of HEM-80-1 (20.326 mg) and CD-88-1 (12.625 mg), respectively, step heated for isotopic analysis of fluid inclusion CO_2 by static vacuum mass spectrometry as described in the text.

the Pt catalytic foil remaining unheated, yielded a $\delta^{13}C$ result which, whilst 0.5–1.2‰ less than **A**, was not strongly influenced by sample size (Fig. 1). The relatively small discrepancy between these data and the "true" value was probably due to not isolating and discarding any CO_2 released below 300°C. As fluid release below this temperature was negligible (see Fig. 2a), this component would have been derived primarily from the thermal decomposition of contaminant organic matter.

Reducing the quartz sample mass by a factor of ~50 (to ca. 20 mg) and using static vacuum mass spectrometry for isotopic analysis of the CO_2, the maximum value of the $\delta^{13}C$ profile also corresponded to **A** within the limits of analytical precision, when the stepped heating was performed with the online Pt/CuO maintained at a temperature low enough to prevent oxidation of any CO or hydrocarbons. The associated profile is shown in Fig. 2b.

A further example of the application of this extraction protocol to high sensitivity isotopic analysis is shown in Fig. 2c. In this case (sample CD-88-1), the maximum CO_2 yield step (2.5 nmol at 350–400°C) was characterised by a $\delta^{13}C$ value of −8.3 ± 1.15‰, which compares favourably with −7.4‰ as obtained by dual-inlet analysis of the 300–600°C release from a substantially larger (~70×) quantity of the same sample. From Fig. 2c, it is also evident that, except for the 450–500°C step, where the CO_2 yield dropped to only 0.56 nmol (and thus contained a relatively large proportion of blank), the four increments between 300 and 600°C were associated with CO_2 yields (1.68–2.50 nmol) which were all within 2.5‰ of the maximum $\delta^{13}C$ value of the release profile.

The analytical data used to construct Fig. 2 are given in Table 1, which also illustrates the consistency of $\delta^{13}C$ value obtained from either stepped heating, a single 300–600°C step, or crushing, when all are conducted in the absence of heated Pt foil. Also evident from Table 1 is that the CO_2 yield from stepped heating of a single grain of gem quality, "inclusion-free" quartz (sample BQ), using the gas extraction and purification protocol for isotopic analysis at the nanomole level, was 270 ± 30 pmol for heating steps within the temperature range 300–1000°C. This provides a more realistic assessment of the procedural blank than is obtained from measurements on the empty extraction chamber.

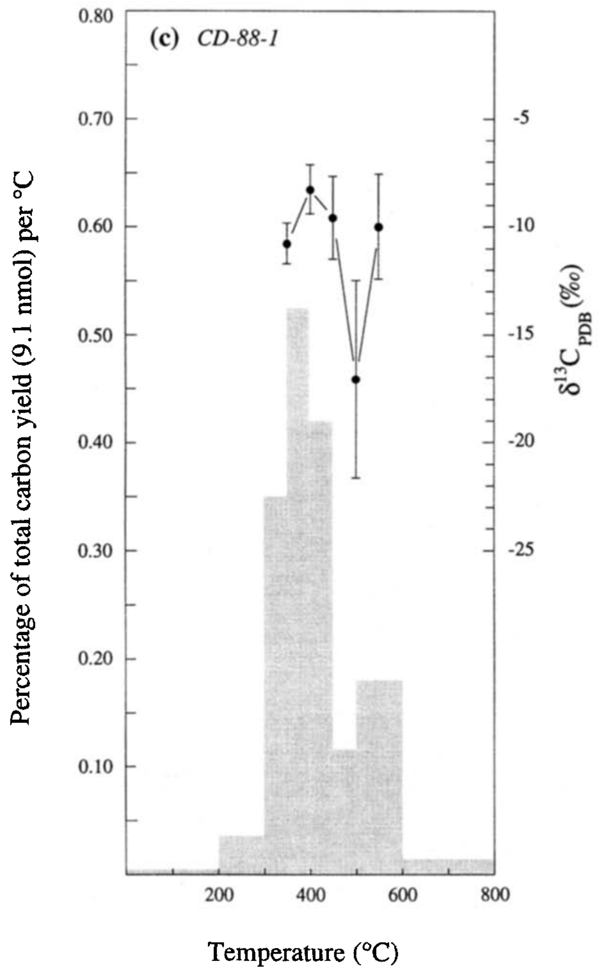

Fig. 2. (Continued)

A testament to the potential effectiveness of the stepped heating technique when conducted in the absence of a Pt combustion catalyst is shown in Fig. 3a. In this example, using dual-inlet mass spectrometry for $\delta^{13}C$ analysis, the three isotopic data points corresponding to fluid inclusion release are very consistent, with a range of less than 0.1‰. On the basis of the simple, two-component model suggested above, the blank carbon yield required to produce a shift of 0.1‰ (negative) in the fluid inclusion $\delta^{13}C$ measurement is ~2.9 nmol for the 300–400°C step. The same model indicates that the CO_2 blank contribution to the initial (ambient to 300°C) step was ~11.9 nmol. As an indication of the error in fluid inclusion $\delta^{13}C$ measurement that would be incurred by single-step heating (ambient to 600°C) of this example, incorporation of the data for the lowest temperature release results in a shift of −0.25‰ in the weighted mean $\delta^{13}C$ value.

A potential complication occurs when authigenic or interstitial carbonate is associated with the sample. The temperature range over which thermal decomposition of carbonate ion occurs is mineral specific (Milodowski and Morgan, 1980), but in many cases overlaps with that used for stepped heating extraction of fluid inclusion volatiles. Evidence suggesting that the decomposition of carbonate ion was contributing to the peak CO_2 release, despite acid pretreatment of the quartz sample grains, is exemplified by sample CF-77-39A, shown in Fig. 3b and Table 1. Here, the isotopic profile at 500–700°C indicates mixing between fluid inclusion CO_2 of $\delta^{13}C$-7.5‰ and that derived from the onset of carbonate decomposition ($\delta^{13}C \sim 0$‰).

Depending on the lithology associated with the quartz samples, H_2S was occasionally present as a contaminant in the CO_2 isolated for isotopic analysis. This was indicated by ion beam currents corresponding to m/z 32, 33, and 34, together with unstable 45/44 and 46/44 ratios and more positive $\delta^{13}C$ values than given by the pure CO_2 component. The H_2S was probably derived primarily from the reduction of finely-disseminated, interstitial sulphide grains, rather than being a significant component of the palaeofluid, as it was only detectable for heating steps >500°C. To obtain the lowest possible CO_2 blanks, however, no CuO (450°C) oxidation of H_2S to SO_2 was incorporated, although that would permit cryogenic separation of the sulphur-bearing compound from CO_2. In a small number of examples, including HEM-80-47 as shown in Table 1, this necessitated using data from only those heating steps at which the extraction temperature was ≤500°C.

5. DISCUSSION

5.1. The Magnitude and Sources of the Carbon Blank during Stepped Heating

Jackson et al. (1988a,b) suggested that $\delta^{13}C$ isotopic profiles from their stepped heating experiments indicated mixing between an indigenous (fluid inclusion) source of isotopically homogeneous composition (the value of which was generally assumed to correspond to the maximum $\delta^{13}C$ value measured) and an extraneous (contaminant) carbon component, characterised by $\delta^{13}C \approx -25$‰. Jackson et al. (1988a,b) also suggested that, for in vacuo heating steps after the 400°C combustion, the CO_2 system blank was typically <1.7 nmol per step, for temperatures up to 1200°C, which is low enough to be ignored. In more recent studies using the same procedure (Harris et al., 1993; Mattey et al., 1994), it was reported that CO_2 blank yields were typically 1.7–4.1 nmol, with $\delta^{13}C \approx -25$‰, and that errors introduced by not background-correcting the $\delta^{13}C$ results may be as high as ±2‰ for samples containing < ~700 nmol g^{-1}. The quoted system blank yields, however, refer to measurements made on an empty extraction chamber (Mattey et al., 1989; Table 1). Stepped heating of inclusion-free quartz grains showed that the associated CO_2 blank yield was substantially greater (Jackson, 1990; Miller, 1994), the enhancement being presumably caused by contaminant matter adsorbed onto the quartz.

From data reported by Jackson et al. (1988a,b) for an example of quartz associated with incipient charnockite formation in southern India, mass balance considerations involving a homogenous fluid inclusion component of $\delta^{13}C = -6.2$‰ (the peak value obtained) mixing with a blank of $\delta^{13}C = -25$‰ show that the isotopic profile reported by those authors (Jackson et al., 1988a, Fig. 2; Jackson et al., 1988b, Table 1) is consistent with the CO_2 blank yield per

Table 1. $\delta^{13}C$ data and associated carbonaceous yields from stepped heating (in vacuo throughout) or crushing of hydrothermal quartz samples. Released gases were not exposed to heated Pt during fluid extraction. nm indicates not measured, usually because of insufficient quantity of gas. Entries in *italics* refer to isotopic analysis by static vacuum mass spectrometry. Instrumental precision shown for $\delta^{13}C$ values refers to $\pm 1\sigma$.

Sample	Quartz mass (mg)	Extraction method	Extraction temperature (°C)	CO_2		CH_4	
				yield (nmol)	$\delta^{13}C_{PDB}$ (‰)	yield (nmol)	$\delta^{13}C_{PDB}$ (‰)
HEM-80-1	1112.7	Stepped heating	300	21	nm		
			400	195	−11.0		
			450	302	−9.5		
			500	298	−9.6		
			550	283	−9.8		
			600	167	−10.4		
			650	95	−11.3		
			700	52	−14.5		
			300–600			43	−36.7
	282.8	Crushing	—	57	−9.6		
	20.326	*Stepped heating*	*200*	*0.21*	*nm*		
			250	*0.08*	*nm*		
			300	*0.35*	*nm*		
			350	*1.99*	*−11.6 ± 0.93*		
			400	*3.82*	*−13.5 ± 1.32*		
			435	*2.82*	*−11.9 ± 0.95*		
			470	*2.69*	*−9.8 ± 1.02*		
			500	*2.61*	*−9.1 ± 1.00*		
			550	*3.60*	*−13.5 ± 0.96*		
			575	*1.83*	*−12.3 ± 0.94*		
			605	*0.48*	*nm*		
CD-88-1	892.7	Heating	300–600	275	−7.4	27	nm
	12.625	*Stepped heating*	*200*	*0.03*	*nm*		
			300	*0.35*	*nm*		
			350	*1.68*	*−10.8 ± 0.94*		
			400	*2.50*	*−8.3 ± 1.15*		
			450	*2.01*	*−9.6 ± 1.90*		
			500	*0.56*	*−17.1 ± 4.57*		
			600	*1.72*	*−10.0 ± 2.42*		
			800	*0.26*	*nm*		
			1000	*0.42*	*nm*		
BQ[§]	23.730	*Stepped heating*	*200*	*<0.02*	*nm*		
			300	*<0.02*	*nm*		
			600	*0.28*	*nm*		
			800	*0.30*	*nm*		
			1000	*0.24*	*nm*		
			1200	*0.35*	*nm*		
HEM-80-47	862.5	Stepped heating	300–400	134	−10.5		
			500	343	−8.32		
			600	368	nm*		
			300–600			23	nm
	444.2	Crushing	—	66	−8.3		
XHS-02	1012.0	Stepped heating	300	39	−9.7		
			400	649	−3.07		
			500	292	−3.0		
			600	250	−3.0		
			700	15	nm		
CF-77-39A	989.8	Stepped heating	300	147	−16.0		
			400	641	−7.54		
			500	347	−7.27		
			600	201	−5.7		
			300–600			208	−54.5
CF-77-79B	1207.3	Heating	300–600	2540	−11.35	58	−47.5
	1254.7	Heating	300–600	2640	−11.36	60	−47.0

* Indicates H_2S present as a contaminant.

[§] BQ was a single grain of gem-quality, "inclusion-free" quartz, used as an indication of the associated procedural blank.

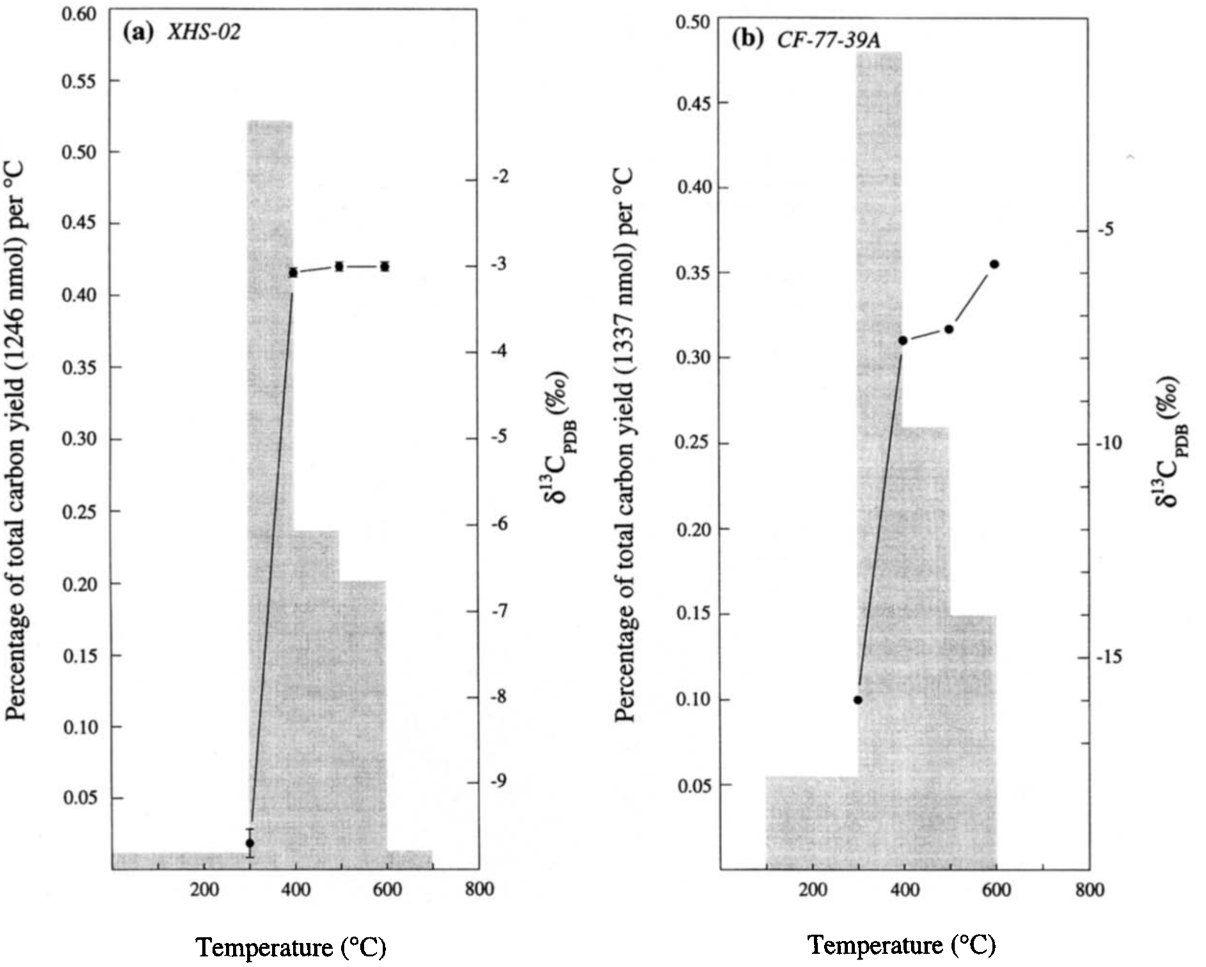

Fig. 3. Stepped heating release profiles of CO_2 from hydrothermal quartz; released gases not exposed to heated Pt: (a) An example of the consistency of isotopic data obtainable under optimal conditions (minimal effect of blank); (b) Evidence for mixing of fluid inclusion CO_2 with a component derived from thermal decomposition of interstitial or authigenic carbonate.

step being up to fifteen times higher than the value of typically <1.67 nmol originally claimed.

During all stepped heating experiments reported by Jackson et al. (1988a,b), the released gas was exposed to Pt foil at ~1000°C (an integral feature of the extraction line described by Swart et al., 1983), in the belief that any methane present (from, e.g., the pyrolysis of trace organic contaminants or, indeed, derived from fluid inclusions) would not be oxidised under these circumstances in the absence of supplied oxygen (Jackson, 1990) and would not, therefore, contribute to isotopic measurements of CO_2. Boyd et al. (1988), however, showed that oxidation of CH_4 to CO occurs rapidly in the presence of Pt foil at 1150°C and was probably mediated by oxygen adsorbed onto the Pt. Boyd et al. (1988) also showed that CuO at 450°C does not give rise to methane oxidation, whereas CO is rapidly converted to CO_2 under these conditions. This latter finding is in accord with experimental procedures used by Sakai et al. (1976), who used CuO at 425°C to purify methane from carbon monoxide. As the Pt foil in the preparation line used for the present study was regularly exposed to oxygen (during stepped combustion experiments), it is improbable that the metal surface ever became depleted in this gas.

In view of the findings illustrated in Fig. 1, it seems probable that oxidation of the pyrolysis products of surficial, microbiological matter (and traces of fluid inclusion methane?) by the heated Pt foil was giving rise to a significantly higher CO_2 blank yield than was recognized in earlier studies. Methane, together with a lesser quantity of alkanes of higher molecular weight, is a significant product of the low-temperature (<600°C) pyrolysis of biological matter (Evans and Felbeck, 1983); whether the major oxidation product in the presence of Pt foil at ~1000°C is CO or CO_2 depends on the initial partial pressure of methane and on the respective rate constants for the two consecutive, first-order oxidation reactions (e.g., Frost and Pearson, 1961). It, therefore, seems reasonable to postulate that, at relatively low partial pressures of methane in the extraction chamber and in the absence of supplied oxygen, complete oxidation of methane to CO_2 will be effected by an adsorbed oxygen layer on the heated Pt foil, resulting in a $\delta^{13}C$ shift of CO_2 to lower values. For relatively high partial pressures of methane in the system, CO is the predominant oxidation product; this reservoir of ^{13}C-depleted carbon does not then contribute to the measured δ^{13}C result. Another possibility (R. Becker, pers. commun.) is that the hot Pt foil catalyst may promote carbon isotopic exchange between inclusion-derived CO_2 and coexisting CO from methane oxidation, on the timescale of a heating increment. If this is the case, then even for relatively high methane partial pressures initially, and incomplete oxidation of this component, it might be possible for the "contaminant" carbon to contribute to the measured δ^{13}C value of fluid inclusion CO_2.

If the Pt foil catalyst at ~1000°C contained adsorbed oxygen, the question arises as to whether the formation of nitrogen oxides may have occurred on the Pt surface during stepped heating. Although Pt foil at ~1150°C catalyses the decomposition of nitrogen oxides (e.g., Boyd et al., 1988), the partial pressures of nitrogen oxides under these conditions may not be negligible. Nitrous oxide, in particular, would not be removed from CO_2 during the cryogenic purification procedure and would, if present, strongly influence the isotopic data. Nitrogen is a palaeofluid component in all samples from southwestern England and Carrock Fell reported herein, with abundances in the range ~75–450 nmol g^{-1} with respect to the quartz host (Miller, 1994). However, thermodynamic considerations indicate that, under equilibrium conditions, the yield of nitrous oxide would be several orders of magnitude less than that of NO and NO_2 over a wide range of O_2/N_2 initial ratios (Miller, 1994) and should, therefore, not be detectable.

For determination of the isotopic composition of fluid inclusion CO_2, our recommended procedure is, therefore, to perform stepwise heating in vacuo and to dispense with the Pt foil catalyst, or leave it unheated. No combustion step is necessary, although the importance of discarding any volatiles released at ≤300°C (or higher temperature, if no significant loss of inclusion fluid is thereby incurred) is evident from Figs. 2 and 3. CO_2 released at these low temperatures was attributed primarily to thermal degradation of surficial organic matter.

This approach is obviously inapplicable to samples which release significant quantities of inclusion fluid at temperatures below 300°C. CO_2-rich inclusions from some high pressure metamorphic environments are in this category (e.g., Hollister and Burruss, 1976). In such cases, however, the abundance of inclusion CO_2 is such that crushing of the mineral host may generally be used to release sufficient gas for isotopic analysis.

Controversy regarding the origin of the ^{13}C-depleted contaminant component, particularly from, e.g., samples of basaltic glass, might be resolved in principle by the application of high-sensitivity ^{14}C measurements, using accelerator mass spectrometry. If the low-temperature carbonaceous component is indeed due to surficial contamination by modern, microbiological matter, it should be possible to distinguish it from carbonaceous material deposited in situ, on the basis of the associated age. The present requirement for > ~50 μmol C for a ^{14}C measurement, however, presents a major limitation.

For a given value of analytical precision of δ^{13}C measurement of a CO_2 sample gas aliquot, the influence of the CO_2 system blank on the accuracy of this measurement is dependent on both the magnitude of the blank component and on the difference between the δ^{13}C values of sample and blank. For samples with a δ^{13}C value close to that of the blank, a lower sample-to-blank ratio may be tolerated than would otherwise be the case. For the effect of the system blank to be less than the analytical precision of isotopic analysis, the following relationship must be satisfied, where the left-hand side of the inequality refers to the sample-to-blank carbon yield ratio:

$$\frac{C_{\text{sample}}}{C_{\text{blank}}} > \frac{|\delta^{13}C_{\text{sample}} - \delta^{13}C_{\text{blank}}|}{\sigma} - 1 \quad (1)$$

This is illustrated in Fig. 4. The principal difficulty inherent in the stepwise heating approach to the carbon stable isotopic analysis of fluid inclusions is thus to establish whether the maximum sample-to-blank carbon yield ratio obtained during incremental heating is large enough to ensure that the associated blank contribution to the measured δ^{13}C value is less than the analytical precision of the isotopic measurement.

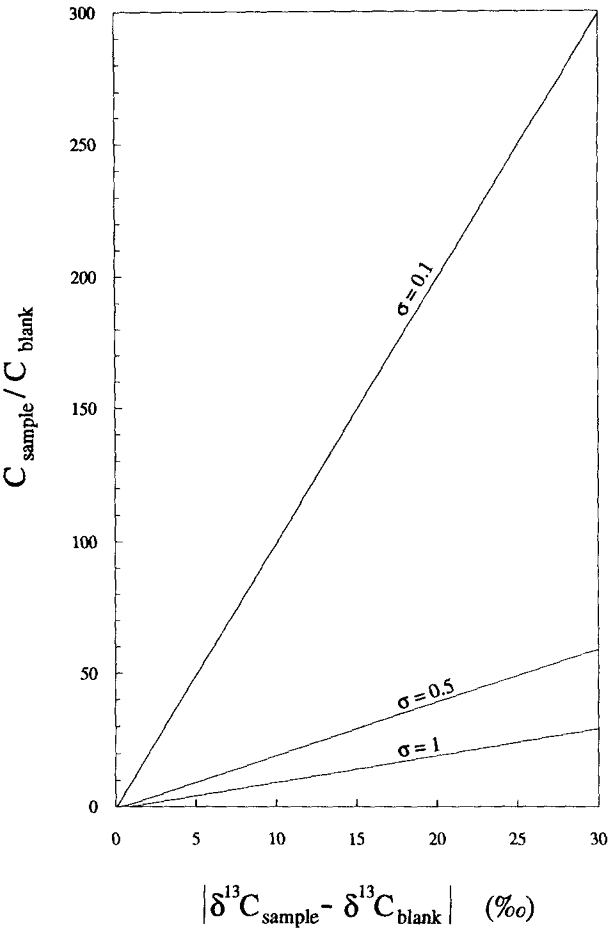

Fig. 4. The variation of minimum sample-to-blank carbon abundance ratio, as a function of the difference in δ^{13}C value between sample gas and attendant blank, such that the blank contribution to the δ^{13}C measurement is less than the associated analytical precision, for the latter fixed at 0.1, 0.5 or 1‰.

5.2. Release of Fluid from Vesicles by Crushing the Quartz Host

Mechanical crushing of the host grains offers the advantage that gas release from sources other than the fluid inclusions will be minimised, at the expense of a relatively low yield. The latter may preclude the extraction of sufficient gas for isotopic analysis by dual-inlet mass spectrometry (e.g., Nadeau et al., 1990). Furthermore, extended crushing/grinding creates a large increase in surface area, which may cause significant gas adsorption (Wahler, 1956; Piperov and Penchev, 1973). Barker and Torkelson (1975) reported that CO_2 is particularly prone to adsorption onto powdered quartz produced during this process. Kazahaya and Matsuo (1985), however, found that CO_2 was readily desorbed from fine-grained quartz at 200–280°C and, moreover, detected no carbon isotopic fractionation for the overall extraction process. The results of the present study also confirm that, where sufficient CO_2 is released for isotopic analysis ($> \sim 50$ nmol, for the dual-inlet instrument used), mechanical crushing of the host quartz yields fluid inclusion CO_2 characterised by the same $\delta^{13}C$ value as that obtained by stepped heating.

5.3. Extension to Other Carbonaceous Palaeofluid Components: CO and CH_4

Whereas the speciation of carbon in fluids of lower crustal or upper mantle origin is usually dominated by CO_2, the presence of CO in fluid inclusions in mantle xenoliths has been reported (Bergman and Dubessy, 1984; Sugisaki and Mimura, 1994). Indeed, it has been suggested (Sugisaki and Mimura, 1994) that CO is a ubiquitous component of inclusions in mantle xenoliths whereas, with the notable exception of A-type granites, it is absent from most other rock types. In principle, the extraction and isolation of fluid inclusion CO for isotopic analysis may be achieved as for methane, described above, but with the incorporation of an additional stage whereby the CO $\pm$ CH_4 ($\pm N_2$ $\pm$ Ar) gas fraction is exposed to CuO at 425–450°C (Sakai et al., 1976; Boyd et al., 1988) or even 300°C (Boyd, 1988), to selectively oxidise the CO.

Methane, often coexisting with CO_2, is a significant component of inclusion fluids in rocks from many geological settings. These include both low- and high-grade metamorphic environments (e.g., Kreulen and Schuiling, 1982; Van Den Kerkhof et al., 1991; Mullis et al., 1994), igneous intrusions (e.g., Larsen et al., 1992), and associated hydrothermal mineralisation (e.g., Miller, 1994); also oceanic gabbros (Kelley, 1996). Methane in crustal fluids is considered to be derived primarily from either thermal maturation of biogenic matter, or abiogenic synthesis at $> \sim 300$°C (Welhan, 1987; Schoell, 1988; Sherwood Lollar et al., 1993). The isotopic characteristics are a valuable diagnostic to methane source identification (Schoell, 1988).

With regard to experimental procedures, Table 1 shows that the total quantity of methane (together with any trace of CO) released during in vacuo stepped heating of sample HEM-80-1 over the temperature range 300–600°C, and in the absence of heated Pt, was relatively minor, corresponding to a CO_2/CH_4 molar ratio of ~ 29. As this methane fraction was characterised by a $\delta^{13}C$ value of −36.7‰, its effect, if fully oxidised and mixed with the "indigenous" CO_2, would be to lower the $\delta^{13}C$ value of the latter by only ~0.9‰. This is surprising, in view of the findings depicted in Fig. 1. In particular, it would seem reasonable to assume that the carbonaceous volatiles responsible for significantly lowering the $\delta^{13}C$ value of CO_2 extracted in the presence of heated Pt foil would simply be transferred (unoxidised) to the 5Å molecular sieve used to subsequently trap any coexisting methane component, if the Pt foil was not heated. In turn, this would lead to a "masking" of the yield and $\delta^{13}C$ value of any inclusion-derived methane component. We cannot at present offer an explanation for this observation. However, as we obtain $\delta^{13}C$ reproducibility to within 0.5‰ on 60 nmol of methane that we ascribe to fluid inclusion origin (sample CF-77-79B, Table 1), and with a value substantially different to that derived from surficial organic contaminants, we believe that we are not simply recording the isotopic composition of a procedural blank in cases where the total methane yield is a few tens of nanomoles.

A systematic investigation of the source and magnitude of the methane and CO blank yields associated with stepped heating extraction from fluid inclusions was not undertaken during the present investigation, where the primary objective was to develop extraction procedures appropriate to accurate isotopic analysis of small (ultimately, sub-nanomole) quantities of CO_2.

5.4. Effects of Graphite, Disseminated in the Host Matrix or Present in the Inclusions

Stepped combustion of NBS-21 graphite in excess of pure oxygen gives a maximum CO_2 yield at 700–800°C, negligible release below 600°C, and complete combustion by 900°C (Grady, 1982; Wright and Pillinger, 1989). Equilibrium thermodynamic modelling (Fig. 5) of the oxidation of graphite by silica (anhydrous conditions) indicates that carbon monoxide would be essentially the only carbonaceous reaction product. The results of similar modelling of graphite oxidation by excess water vapour, relevant to a consideration of hydrothermal samples, are also shown in Fig. 5 and indicate the predominance of CO at temperatures above ~80C°C. In practice, reaction kinetics may preclude the attainment of an equilibrium composition, particularly at lower temperatures, in which case the formation of carbonaceous volatiles (and especially those other than CO) would be negligible. What is suggested by this analysis, therefore, is that any graphite present either in the host mineral matrix, or indeed in the fluid inclusions, should not contribute to the fluid inclusion CO_2 yield obtained by the stepped heating procedure recommended in the present work. Further experimental data are needed to confirm or refute this assertion.

5.5. Does Isotopic Exchange between CO_2 and CH_4 Occur during Stepped Heating?

The possibility of carbon isotopic exchange between coexisting CO_2 and CH_4 is still a matter of some controversy. Experimental evidence indicates that, if such exchange occurs at all, it proceeds exceedingly slowly, even at tempera-

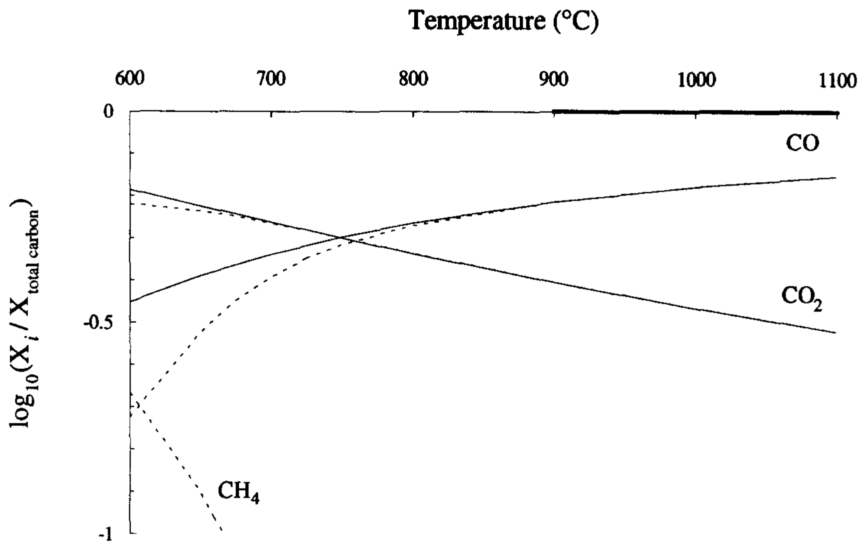

Fig. 5. Equilibrium composition, as a function of temperature, of carbon-bearing compounds resulting from reaction between graphite and excess water (1:100 molar ratio) at 10^{-7} MPa (solid line) and 0.1 MPa (dashed line), modelled on the basis of ideal gas conditions using the computational routine of Gordon and McBride (1971). Unreacted graphite is absent. The bold line indicates, for comparison, the CO value resulting from reaction between graphite and silica, for the same reactant molar ratio and at 10^{-7} MPa total pressure. This reactant mixture is essentially stable at 0.1 MPa pressure, over the temperature range shown. X_i is the mole fraction of component i.

tures >500°C (Sackett and Chung, 1979; Harting and Maass, 1980; Giggenbach, 1982, 1987; Hulston, 1986) and is unlikely to occur at all below ~320°C (Sheppard, 1981; Lyon and Hulston, 1984). During the timescale of a typical stepped heating extraction, it can therefore be assumed that effectively no ^{13}C exchange occurs between these compounds.

5.6. Future Trends

An ultra-high sensitivity static vacuum mass spectrometer for carbon stable isotope measurements has been described by Prosser et al. (1990). Subsequent refinements to that instrument and the associated gas preparation and handling system (Yates et al., 1992) have resulted in a level of performance whereby attendant analytical precision is worse than ~ ±1‰ only for <80 pmol of CO$_2$. These developments offer potential benefits to ultratrace isotopic analysis of fluid inclusion carbonaceous components. In particular, the isotopic characterisation of coexisting reduced and oxidised carbon in fluid inclusions may now be feasible for significantly lower abundances of these components that has hitherto been possible, subject to minor modifications to the gas handling system so as to permit the separation and isolation of extracted CO$_2$ and CH$_4$. From data given in Yates et al. (1992), a typical carbon procedural (combustion) blank yield over the temperature range 300–600°C (as used for palaeofluid release) is ~250 pmol. A significant proportion of this, however, probably derives from the use of a Pt "envelope" used to contain the loaded sample; this would not be required in the case of mineral grain samples used for fluid inclusion analysis. On this basis, it would appear that a lower limit of ~5 nmol CH$_4$ is required to produce a minimum sample-to-blank ratio of ~20. Vesicle opening by crushing, rather than heating, may provide a means of lowering the system blank even further, if precautions are taken to avoid metal-to-metal contact, which itself may give rise to methane formation (Andrawes and Gibson, 1979). Further investigations are, therefore, required to fully benefit from the degree of mass spectrometer sensitivity currently available.

6. CONCLUSIONS

The present work supports the view that surficial contamination by organic matter of presumed microbiological origin is a ubiquitous problem with regard to the thermal extraction, for stable isotope ratio analysis, of CO$_2$ from fluid inclusions in rocks and minerals. The findings show, however, that previous stepped heating procedures designed to eliminate this component by combustion at 400°C in the presence of supplied oxygen and a Pt foil catalyst at ~1000°C, followed by in vacuo stepped heating in the presence of the heated Pt foil, potentially results in inaccurate δ^{13}C measurements in the case of small (< ~1 μmol) samples of CO$_2$. The problem stems from the presence of the heated Pt foil, which appears to retain adsorbed oxygen and catalyse the oxidation of methane (and possibly carbon monoxide, if present) during stepped heating. These components derive from the pyrolysis of organic contaminant matter and, in some instances, from the fluid inclusions.

Heating in vacuo at 300°C is shown to be effective in removing surficial contaminants by pyrolysis. Subsequent stepped heating in vacuo, in the absence of heated Pt foil, results in a significantly reduced yield of CO$_2$ from extraneous sources, thereby permitting the extraction, isolation, and δ^{13}C characterisation of nanomole quantities of fluid inclusion CO$_2$ with an accuracy of isotopic measurement limited ultimately by the attendant analytical precision. Except in cases where the presence of interstitial carbonates was inferred from the stepped heating isotopic profile, excellent agreement was obtained between the $\delta^{13}C$ value of CO_2 extracted by either stepped heating or crushing of the host mineral. Ultimately, the principal difficulty with the stepped heating method is to ensure that the fluid inclusion CO_2 yield is large enough to ensure that the contribution from extraneous sources to the measured $\delta^{13}C$ value is less than the analytical precision of the isotopic measurement. To enhance the sample-to-blank ratio to an acceptable level, it is generally advantageous to minimise the number of heating increments over the temperature range in which the inclusion fluid is extracted. A limitation of the stepped heating approach is that it is restricted to samples which do not lose significant quantities of fluid during the temperature step (300°C minimum) used for removal of surficial contamination.

Further progress, including the extension of such methods to the isolation and isotopic analysis at the nanomole level of other carbonaceous fluid components, ultimately relies on rigorous control of the associated blanks.

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