Constraining the Geochemical Fingerprints of Gases from the UK Carboniferous Coal Measures at the Glasgow Geoenergy Observatories Field Site, Scotland

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Usage of thermal energy contained in abandoned, flooded, coal mines has the potential to contribute to low carbon heating or cooling supply and assist in meeting net-zero carbon emission targets. However, hazardous ground gases, such as CH_4 and CO_2, can be found naturally in superficial deposits, coal bearing strata and abandoned mines. Determining the presence, magnitude, and origin of subsurface gases, and how their geochemical fingerprints evolve within the shallow subsurface is vital to developing an understanding of how to manage the risk posed by ground gases in geoenergy technology development. Here, we present the first CH_4 and CO_2 concentration-depth profiles and stable isotope ($\delta^{13}C_{CH4}$, $\delta^{13}C_{CO2}$, and δD_{CH4}) profiles obtained from UK mine workings, through analysis of headspace gas samples degassed from cores and chippings collected during construction of the Glasgow Observatory. These are used to investigate the variability of gas fingerprints with depth within unmined Carboniferous coal measures and Glasgow coal mine workings. Stable isotope compositions of CH_4 ($\delta^{13}C_{CH4}$ = −73.4‰ to −14.3‰; $\delta^{13}C_{CO2}$ = −29‰ to −6.1‰; δD_{CH4} = −277‰ to −88‰) provide evidence of a biogenic source, with carbonate reduction being the primary pathway of CH_4 production. Gas samples collected at depths of 63–79 m exhibit enrichments in $13C_{CH4}$ and ^2H, indicating the oxidative consumption of CH_4. This correlates with their proximity to the Glasgow Ell mine workings, which will have increased exposure to O_2 from the atmosphere as a result of mining activities. CO_2 gas is more abundant than CH_4 throughout the succession in all three boreholes, exhibiting high $\delta^{13}C_{CO2}$ values relative to the CH_4 present. Gases from unmined bedrock exhibit the highest $\delta^{13}C_{CO2}$ values, with samples from near-surface superficial deposits having the lowest $\delta^{13}C_{CO2}$ values. $\delta^{13}C_{CO2}$ values become progressively lower at shallower depths (above 90 m), which can be explained by the increasing influence of shallow groundwaters containing a mixture of dissolved marine carbonate minerals (~0‰) and soil gas CO_2 (−26‰) as depth decreases. Our findings provide an insight into the variability of mine derived gases

within 200 m of the surface, providing an important 'time-zero' record of the site, which is required in the design of monitoring approaches.

Keywords: geochemistry, geothermal, mine water, environmental monitoring, geoenergy

INTRODUCTION

The use of thermal energy contained within groundwater in abandoned, flooded, coal mines has considerable potential to contribute to the provision of low carbon heating or cooling to assist in meeting global net-zero carbon emission targets (Adams et al., 2019; Stephenson et al., 2019; Monaghan et al., 2022a). A quarter of UK homes and businesses lie above former coalfields, providing a highly permeable network of buried mine workings flooded with water at above-ambient temperatures (Adams et al., 2019; Monaghan et al., 2022b). However, there are a multitude of manageable, but significant techno-societal risks associated with the utilisation of the heat from minewaters, related to both the direct site operation and the environment surrounding it, such as resource sustainability and efficiency, reservoir quality, operation maintenance, ground motion, ground gases and environmental change (University of Strathclyde, and BGS, 2019; NERC, University of Strathclyde and BGS, 2019; Monaghan et al., 2022a).

In order to address these issues, there is a clear need for applied research on minewater heat utilisation, to provide an open evidence base to enable knowledge transfer to assist with social acceptance, constraining the economic models and reducing development, operational and post closure risk of a mine water heat site (NERC et al., 2019; Stephenson et al., 2019). In conjunction with a growing number of underground laboratories worldwide, the UK Geoenergy Observatory in Glasgow ("Glasgow Observatory") is a unique facility for investigating shallow, low-temperature mine water thermal energy resources in abandoned and flooded workings at depths of around 50−85 m. This site provides a vital record of the "time-zero" baseline conditions prior to activities commencing at the site and a record of any environmental changes induced by operations to extract or reinject heat into the mine workings.

Coal derived gas is an important energy resource and a potential source of greenhouse gas, as the majority of coal and coal bearing strata contain significant quantities of gases (Hall et al., 2005; CL-AIRE, 2021). These gases pose a significant potential hazard as they are either potentially explosive in critical concentrations when mixed with air, or are toxic to life at elevated (from ambient) concentrations. Gases found in a mine are typically mixtures of atmospheric air, inert gases, water vapour and one or more of the following: O_2, CO, CO_2, CH_4, H_2S, H_2 and NO_x (Hall et al., 2005; CL-AIRE, 2021). Whilst these pose no threat provided they stay in the mine, they can migrate through voids and strata and be emitted at the surface above the mine. Release of this gas as a result of minewater heat extraction would pose both an unwelcome climate feedb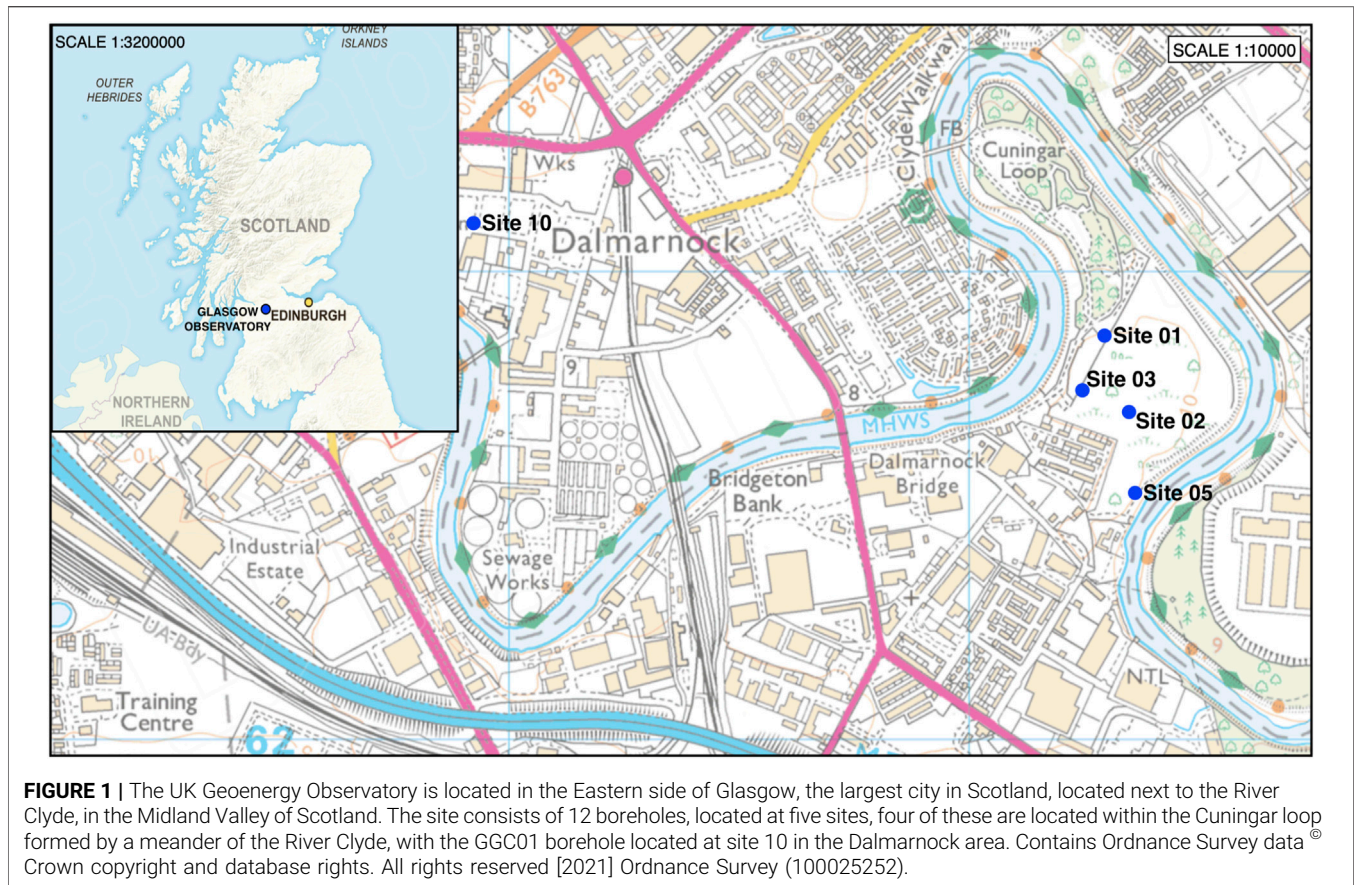ack of greenhouse gases, and a potential hazard to the local population, as exemplified by recent demolition of a public housing estate in the Scottish town of Gorebridge due to mine gas ingress (Ramsey et al., 2017).

Whilst CH_4 associated with coal is predominantly considered as being produced thermogenically due to the burial and thermal maturation of coals, a number of studies have shown that bacterial coal bed CH_4 can be produced from microbial activity within lower maturity coals under anoxic conditions (Krüger et al., 2008; Strąpoć et al., 2011; Guo et al., 2012; Gründger et al., 2015). Traditionally, hydrocarbon abundances ($C_1/(C_2+C_3)$) and stable isotopes ($\delta^{13}C_{CH4}$, $\delta^{13}C_{CO2}$, and δD_{CH4}) of CH_4 and other associated hydrocarbon gases are used to distinguish between thermogenic and bacterial CH_4 sources (Schoell, 1980; Whiticar, 1999; Osborn et al., 2011; Stuart, 2012; Jackson et al., 2013; Györe et al., 2018). Hydrocarbon ratios of 10^3 to 10^5, $\delta^{13}C_{CH4}$ of < −55‰; and δ^2H_{CH4} < −150‰ are characteristic of bacterial CH_4 (Schoell, 1980); with thermogenic CH_4 gas typically containing ratios of <100, with $\delta^{13}C_{CH4}$ values −45‰ to −110‰ and δ^2H_{CH4} > −255‰, respectively (Stuart, 2012; LeDoux et al., 2016). However, several processes can alter the hydrocarbon abundance and stable isotope signature of CH_4 and can result in the misidentification of the gas source. Processes include the mixing of different sources of CH_4; or microbial oxidation, which can enrich bacterial CH_4 in ^{13}C and ^2H to that of thermogenic sources (Barker and Fritz, 1981; Whiticar, 1999; Molofsky et al., 2013; LeDoux et al., 2016).

Here, we outline how sampling and analysis of gases from drilling at the Glasgow Observatory during its construction has enabled the determination of the presence, source and volume of coal and mine derived gases (CO_2 and CH_4) in the subsurface at the site. We use the geochemical tools outlined above to determine the source of the gases encountered and to provide a unique insight into the variation of gas signatures with depth and mining activities within flooded coal mines.

SETTING OF THE UK GEOENERGY OBSERVATORY IN GLASGOW, SCOTLAND

The Glasgow Observatory has been developed to investigate the potential energy resource available and variability of low temperature geothermal energy from shallow mine workings (Monaghan et al., 2019). The Observatory is located on the west side of the Central Coalfield of the Midland Valley of Scotland, in the east of the city of Glasgow within the Cuningar Loop (Monaghan et al., 2019) in an area where prolific coal mining activity has occurred. Due to historic coal mining and extensive industrial activity, the site contains significant made ground of waste building material, which overlies Quaternary

FIGURE 1 | The UK Geoenergy Observatory is located in the Eastern side of Glasgow, the largest city in Scotland, located next to the River Clyde, in the Midland Valley of Scotland. The site consists of 12 boreholes, located at five sites, four of these are located within the Cuningar loop formed by a meander of the River Clyde, with the GGC01 borehole located at site 10 in the Dalmarnock area. Contains Ordnance Survey data © Crown copyright and database rights. All rights reserved [2021] Ordnance Survey (100025252).

glacial and post glacial deposits that are up to 25 m thick (Monaghan et al., 2019). These superficial deposits overlie the Scottish Coal Measures Group, a group of fluvio-deltaic Carboniferous sedimentary rocks that contain cyclical sequences of mudstone, siltstone, sandstone, and coals that were deposited during repeated marine regressions and transgressions in the Westphalian period (Cameron and Stephenson, 1985; Monaghan et al., 2019). The Glasgow Observatory's infrastructure consists of 12 boreholes: a 200 m seismic monitoring borehole (GGC01), drilled and installed on site during a 3-month period from November 2018 to January 2019; and 11 shallow (max 90 m depth) mine characterisation and monitoring boreholes, drilled and installed from May 2019 to January 2020. Superficial deposits and the bedrock encountered by all boreholes at the Cuningar Loop site were drilled by reverse circulation rotary drilling to ensure good sample recovery (Monaghan et al., 2022b). The 11 monitoring boreholes are situated in the Cuningar loop of the River Clyde, on four sub-sites (GGERFS01, GGERFS02, GGERFS03, GGERFS05); with the seismic monitoring borehole located on sub-site GGERFS10, >1.5 km east in the area of Dalmarnock (**Figure 1**). Strata at site GGERFS10 was unmined, and a continuous 199 m long core was recovered from drilling. All other 11 monitoring boreholes on site encountered shallow mine workings, and rock chipping samples were obtained during drilling.

Hydrogeologically, the glacio-fluvial superficial deposits found on the site are thought to form part of a linear shallow aquifer system, which is up to 2–3 km wide, located beneath Glasgow (Ó Dochartaigh et al., 2019). The superficial aquifer is thought to be highly heterogeneous and complex, due to the heterogeneity of the deposits, and the effect of urban influences (Ó Dochartaigh et al., 2019). The Carboniferous bedrock on the GGERFS site typically forms complex, layered aquifer systems that are dominated primarily by fracture flow (Ó Dochartaigh et al., 2019). Mining of such deposits has resulted in significant changes in the natural groundwater flow paths and hydrogeological conditions (Ó Dochartaigh et al., 2019). The presence of mine voids, workings and other waste materials frequently results in significant change (often increases) in transmissivity within the aquifer, resulting in previously unconnected groundwater bodies to be linked (Ó Dochartaigh et al., 2019; Younger and Robins, 2002).

MATERIALS AND METHODS

Samples were collected from three boreholes on site: GGA05, located at site GGERFS02; GGA08, located at site GGERFS03; both of which are mine characterisation and monitoring boreholes, and GGC01; the 200 m deep seismic monitoring
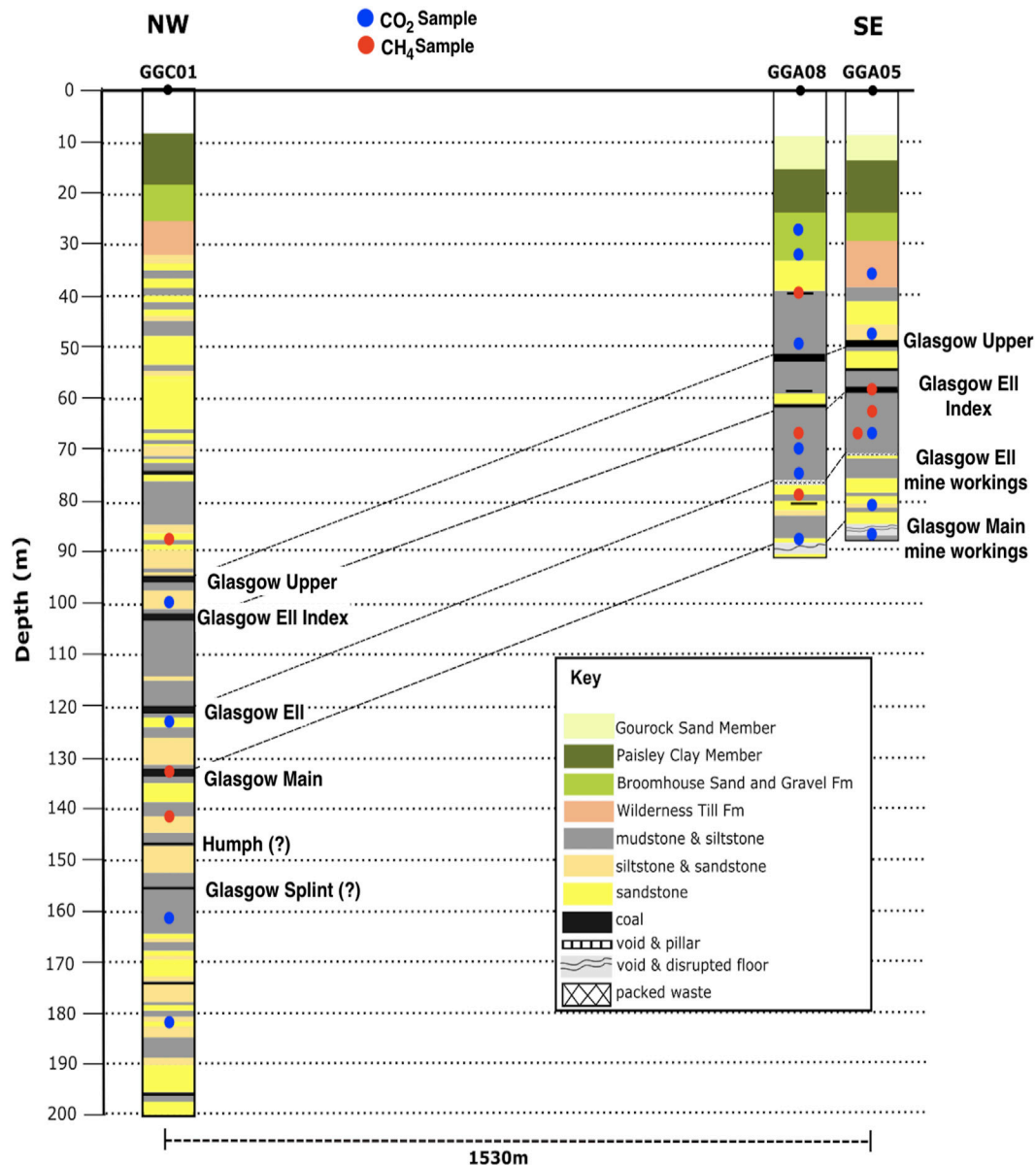
FIGURE 2 | Composite logs of GGC01, GGA05, and GGA08 boreholes, and the depths of the core and cutting samples that were obtained for stable isotope analysis. The borehole logs indicate the major coal seams (Glasgow Upper, Glasgow Ell Index, Glasgow Ell, Glasgow Main), with Glasgow Ell and Glasgow Main coal seams have been mined in the shallow GGA05 and GGA08 boreholes. These seams can be correlated to unmined coal seams in GGC01.

borehole located in Dalmarnock. (Full borehole data obtained from Monaghan et al. (2021), British Geological Survey (2020a), and British Geological Survey (2020b).

Rock samples consisting of two 50 mm quarter sections of core were obtained approximately every 10 m depth during drilling of the GGC01 seismic monitoring borehole and drill cutting samples from GGA05 and GGA08 boreholes were collected over 3 m depth intervals (**Figure 2**). The collection of core and cutting samples at 10 and 3 m intervals within the subsurface allowed for additional resolution in the complexity of the gas signatures on site, which would not have been

obtained from standard borehole samples. These core and cutting samples were then stored in gas tight isojars prior to analysis of the exsolved gases. Duplicate sampling from the seismic monitoring borehole allowed two different isojar storage methods to be tested; with one set of samples stored in de-ionised water that had 1 mL (20 drops) of Benzalkonium (Zephiran) Chloride biocide added to the Isojar, and the other purged with N_2 gas. Preliminary analysis of the samples from the seismic monitoring borehole clearly indicated that storage in de-ionised water resulted in higher concentrations of the exsolved gases,
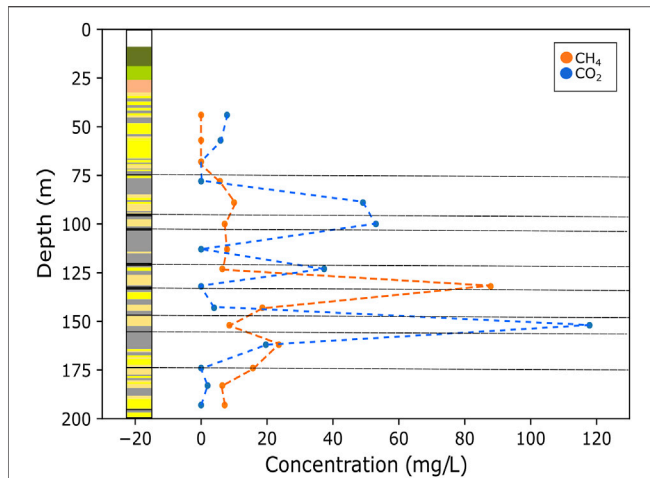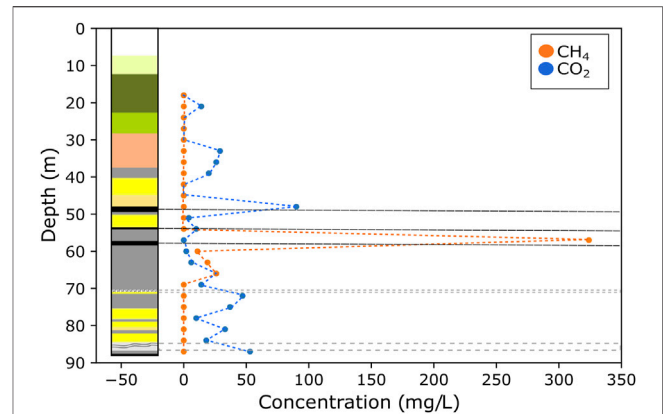
FIGURE 3 | Stratigraphic log of BH GGC01 and CH_4 and CO_2 concentrations with depth (black dashed lines indicate coal seams). The figure highlights that increased concentrations of CH_4 gas correlate to areas immediately surrounding the unmined coal seams in the subsurface. The highest CO_2 concentrations occurred in samples with lowest CH_4 concentrations, or where CH_4 was absent.

FIGURE 4 | Stratigraphic log of BH GGA05 and CH_4 and CO_2 concentrations with depth (black dashed lines indicate coal seams and grey dashed boxes indicate coal mine workings). CH_4 was solely detected at 57−67 m depth in a cluster of samples, in the succession directly above the Glasgow Ell mine workings. The CO_2 gas did not show the same trend, and was present throughout the stratigraphic succession.
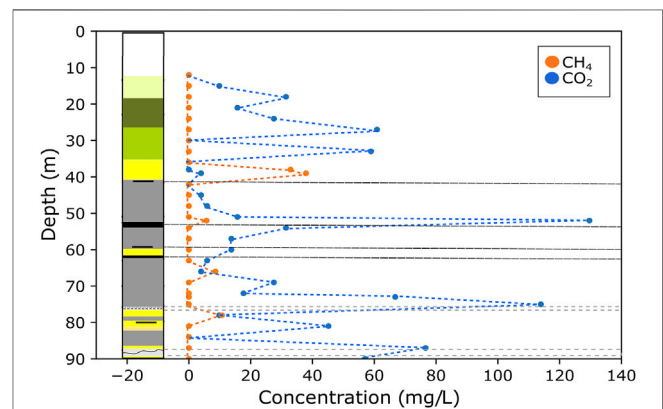
FIGURE 5 | Stratigraphic log of BH GGA08 and CH_4 and CO_2 concentrations with depth black dashed lines indicate coal seams and grey dashed boxes indicate coal mine workings). CH_4 was identified at four stratigraphic depths; all of which correspond to areas of coal seams or mine workings. Conversely, CO_2 was present throughout the entire stratigraphic sequence, and generally present in higher concentrations than CH_4.

indicating better sample preservation, hence the subsequent obtained cutting samples were solely stored in de-ionised water, with added Benzalkonium (Zephiran) Chloride biocide. The full suite of GC data for all core and cutting samples from both preservation methods is provided in **Supplementary Tables S1, S2**. All samples were then stored at standard temperature (25°C) and pressure (1atm) for a 2-month period, to allow the samples to equilibrate with the headspace prior to gas analysis conducted at the Scottish Universities Environmental Research Centre (SUERC).

50 µL of the gas headspace was collected from the isojars in a 100 µL syringe and injected manually into the septa port of a Perkin-Elmer AutoSystem XL gas chromatograph (GC), *via* a 30 m long and 0.53 mm internal diameter Sigma-Aldrich Carboxen 1010 PLOT column using helium carrier gas. The GC was also equipped with a flame ionization detector to measure light hydrocarbons and was calibrated with appropriate gas mixtures produced by CalGaz Ltd. Concentration data is recorded as mg/L in the gas phase, as determined from % components, with the full GC data provided in **Supplementary Tables S1, S2**.

Samples that exhibited CO_2 and CH_4 concentrations above 1.5% by volume were then selected for stable isotope analysis. Stable isotope determinations were conducted on the gas combustion line at SUERC. The extraction inlet was attached directly to the sealed isojars; with a pressure gradient applied to draw gas through the line. CO_2 was separated from volatile hydrocarbons using a procedure modified from Kusakabe (2005). A liquid N_2 cooled isopentane trap (−160°C) was applied to collect CO_2 and water before an acetone slush bath was used (~-78°C) to retain water and vaporise CO_2. The CO_2 was then collected separately in a liquid N_2 cooled cold finger. The CH_4 samples

were combusted over a CuO catalyst at 900°C into CO_2 and water, which were collected in a liquid N_2 cooled cold finger. A pressure gradient drawing gases through the furnace was maintained by the cold finger trapping combustion products. After combustion, the cold finger was heated with an acetone slush bath (~−78°C) to retain water and vaporise CO_2. This CO_2 was collected separately in a separate liquid N_2 cooled cold finger. Both the original and combusted CO_2 were analysed on a VG SIRA II dual-inlet IRMS, calibrated to internal standards (Dunbar et al., 2016), with measured values relative to V-PDB standards. The cold finger containing the collected water was connected to a manifold, heated to vapour, and reduced to H_2 over a nickel catalyst at 800°C. H_2 was analysed in a separate

TABLE 1 | Measured C-H-O isotope values of CH_4 and CO_2 collected from GGERF site from boreholes GGC01, GGA05, and GGA08.

Borehole	Site	Sample depths (m)	SSK core sample no.	$\delta^{13}C_{CH4}$	δD_{CH4}	$\delta^{13}C_{CO2}$	$\delta^{18}O_{CO2\ (SMOW)}$
GGC01	GGERFS10	88	105480	−71.6	−249		
GGC01	GGERFS10	88	105481	−73.4	−251		
GGC01	GGERFS10	100	105492			−6.1	26.5
GGC01	GGERFS10	123	105520			−8.5	33.2
GGC01	GGERFS10	132	105528	−68.3	−240		
GGC01	GGERFS10	132	105529	−68.3	−252		
GGC01	GGERFS10	143	105544	−64.0	−242		
GGC01	GGERFS10	143	105545	−64.0	−277		
GGC01	GGERFS10	161	105569			−7.8	30.5
GGC01	GGERFS10	183	105592			−12.7	28.8
GGA05	GGERFS02	36−37	105658			−22.49	33.2
GGA05	GGERFS02	48−49	105668			−11.06	35.09
GGA05	GGERFS02	57−58	105674	−70.0	−182.4		
GGA05	GGERFS02	63−64	105676	−32.2	−122.0		
GGA05	GGERFS02	66−67	105677	−14.3	17.3	−11.6	33.5
GGA05	GGERFS02	81−82	105686			−10.0	33.58
GGA05	GGERFS02	87−88	105693			−29.03	13.6
GGA08	GGERFS03	27−28	105654			−25.46	25.38
GGA08	GGERFS03	33−34	105656			−21.06	34.22
GGA08	GGERFS03	38−39	105701	−74.1	−259		
GGA08	GGERFS03	39−40	105703	−70.5	−207.9		
GGA08	GGERFS03	52−53	106032			−18.3	33.2
GGA08	GGERFS03	66−67	105610	−19.7	−94.7		
GGA08	GGERFS03	69−70	105611			−15.24	28.25
GGA08	GGERFS03	75−76	105614			−12.93	34.75
GGA08	GGERFS03	78−79	106041	−19.8	−87.8		
GGA08	GGERFS03	87−88	106044			−11.43	34.82

Delta Optima Plus dual-inlet IRMS, and calibrated to internal standards (Donnelly et al., 2001). $\delta^{13}C$ values are reported relative to V-PDB international standard and δD values are quoted relative to V-SMOW (Craig, 1957; Gonfiantini, 1984; Coplen, 1995) with known uncertainties of 0.3% ($\delta^{13}C$) and 3% (δD).

RESULTS

CH_4 and CO_2 Gas Concentrations From Core and Cutting Samples

Gas concentration data for all core and cutting samples are provided in **Supplementary Tables S1, S2**. Exsolved gas headspace analysis of core samples from the unmined GGC01 borehole determined the presence of both CH_4 and CO_2 gas from depths below 77 m. CH_4 gas concentrations for GGC01 range from 6 to 88 mg/L (mean = 17 mg/L, Std. dev = 23 mg/L), with samples with increased concentrations correlating to areas immediately surrounding unmined coal seams (Glasgow Main coal, and potentially the Humph coal and Glasgow Splint coals) (**Figure 3**). CO_2 concentrations in GGC01 occur in samples where CH_4 concentrations are lowest or absent, and range from 2 to 118 mg/L (mean = 33 mg/L, Std. dev = 37 mg/L) (**Figure 3**).

For mined boreholes GGA05 and GGA08, considerably less instances of elevated CH_4 concentrations were found to be present throughout the succession. It is noted that the majority of samples have CH_4 levels below detection limits,

which compliments groundwater concentration data (Palumbo-Roe et al., 2021) (**Figures 4, 5**). In GGA08, CH_4 gas was identified at four stratigraphic depths, and correlates with unmined coal seams (a minor coal unit at 38−40 m depth, and the Glasgow Upper coal seam at 52−53 m depth), and the area directly below the Glasgow Ell coal mine workings (78−79 m depth). In GGA05, CH_4 gas was solely detected at 57−67 m depth in a cluster of samples in the area directly above the collapsed Glasgow Ell mine workings (**Figure 4**). CH_4 concentrations for GGA05 and GGA08 boreholes ranged from 6 to 324 mg/L mean = 53 mg/L, Std. dev = 102 mg/L), with the highest CH_4 concentration correlating to the unmined Glasgow Ell index coal seam in GGA05. These values are higher than *in-situ* groundwater CH_4 concentrations recorded, e.g., Glasgow Main (174−185 μg/L) and Glasgow Upper (117−145 μg/L) (Palumbo-Roe et al., 2021).

However, CO_2 gas was present throughout the succession of both GGA05 and GGA08 boreholes, with concentrations ranging from 4 to 130 mg/L (mean = 31 mg/L, Std. dev = 30 mg/L) (**Figures 4, 5**), and corresponds well with measured groundwater concentrations of 105−256 mg/L (Palumbo-Roe et al., 2021). In both GGA05 and GGA08, the highest CO_2 gas concentrations occurred at the unmined Glasgow Upper coal seam, and at both the Glasgow Ell and Glasgow Main mine workings.

CH_4 and CO_2 Stable Isotope Values

Core samples from the unmined GGC01 borehole exhibit a narrow $\delta^{13}C_{CH4}$ range of −73.4‰ to −64‰, which is characteristic of a biogenic CH_4 source (Schoell, 1980;
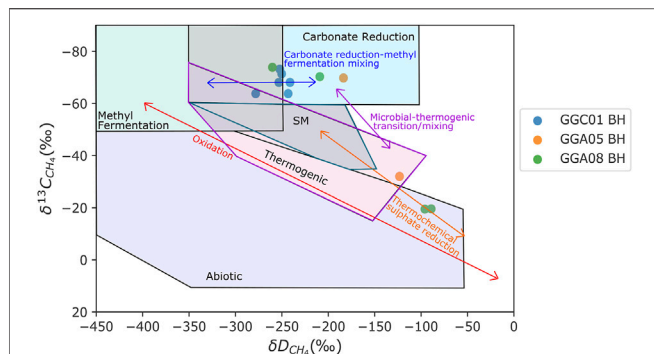
FIGURE 6 | Plot of δD_{CH_4} and $\delta^{13}C_{CH_4}$ stable isotopic analyses of CH_4 gas exsolved from core and cutting samples from GGC01, GGA05, and GGA08 boreholes. (Secondary CH_4 (SM) boundary indicated in green and thermogenic CH_4 boundary indicated in purple). Processes that affect the isotopic and molecular composition are highlighted (oxidation and thermochemical sulphate reduction). Mixing of microbial gases produced through carbonate reduction and methyl fermentation is indicated by the blue mixing arrow, with mixing of thermogenic and microbial methane indicated by the purple mixing arrow. The majority of samples plot within the biogenic CH_4 zone, with a potential mixing of both carbonate reduction and methyl type fermentation sources. Enriched samples plotting outside of biogenic origin fields are a result of CH_4 oxidation. The classification areas of biogenic and thermogenic CH_4 sources are adapted from Whiticar (1999), and the plot is adapted from Milkov and Etiope (2018).
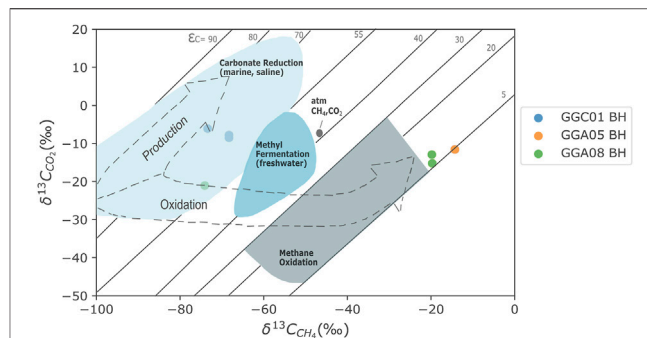
FIGURE 7 | Isotope combination plot of $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{CO_2}$ data from GGC01, GGA05, and GGA08 boreholes; with isotope fractionation lines and partitioning trajectories as a result of CH_4 formation and oxidation processes. The majority of samples exhibit greater ^{12}C enrichment with an isotopic fractionation indicative of CH_4 production by carbonate reduction. The three enriched samples that plot around 5% isotope fractionation indicate CH_4 oxidation, as ^{12}C is preferentially removed resulting in a decrease in isotopic fractionation between $^{13}C_{CH_4}$ relative to $^{13}C_{CO_2}$. Isotope plot adapted from Whiticar (1999).

Whiticar et al., 1999; Osborn et al., 2011; Stolper et al., 2018). Associated deuterium values for GGC01 also fall within a narrow range of δD_{CH_4}, with values of −277‰ to −240‰, and compliment the biogenic origin implied by $\delta^{13}C_{CH_4}$ values. The shallow mined GGA05 and GGA08 boreholes have $\delta^{13}C_{CH_4}$ values that range from −70‰ to −14.3‰, and −74.1‰ to −19.7‰, respectively. GGA05 and GGA08 δD_{CH_4} values also exhibit a large range; with values of −182‰ to 17.3‰, and −259‰ to −88‰. However, as evidenced in **Table 1**, there are four samples from GGA05 and GGA08 that are enriched in $^{13}C_{CH_4}$ and $^2H_{CH_4}$, which account for the large range in $\delta^{13}C_{CH_4}$ and δD_{CH_4} values. Excluding these samples, GGA05 and GGA08 have $\delta^{13}C_{CH_4}$ values of −74.1‰ to −70‰ and δD_{CH_4} values of −259‰ to −182‰ corresponding with the biogenic CH_4 signatures observed in GGC01.

Carbon isotope compositions for CO_2 range from −12.7‰ to −6.1‰ for GGC01; −29‰ to −10‰ for GGA05; and −25.5‰ to −11.4‰ for GGA08. Such values align with previously reported values of coal bed globally ($\delta^{13}C_{CO_2}$ = −27‰ to +19‰) (Rice, 1993). The carbon isotope values of Dissolved Inorganic Carbon ($\delta^{13}C_{DIC}$) of produced waters were obtained during pumping tests conducted by the BGS for the shallow mine monitoring boreholes. Analysis of these samples found that $\delta^{13}C_{DIC}$ in the groundwaters range from −12.8‰ to −7.1‰, with an average value of −10.9‰ (Palumbo-Roe et al., 2021). For the Midland Valley of Scotland, these results fall within the upper range of values previously recorded for coal measures (Palumbo-Roe et al., 2021).

DISCUSSION

Subsurface CH_4 Sources at the Glasgow Observatory

Figure 6 shows the genetic $\delta^{13}C_{CH_4}$ and δD_{CH_4} diagram by Milkov and Etiope (2018) for GGC01, GGA05, and GGA08 highlighting evidence for two distinct CH_4 signatures. The majority of samples show evidence for the production of CH_4 by carbonate reduction, with the indication of the addition of minor amounts of CH_4 produced through methyl-type fermentation. Through plotting isotopic values of CH_4 and CO_2 from the same stratigraphic unit (**Figure 7**), it is evident that the majority of samples exhibit a greater ^{13}C enrichment, with an isotopic fractionation >55% for $^{13}C_{CH_4}$ relative to $^{13}C_{CO_2}$. This is indicative of CH_4 production primarily by carbonate reduction (Whiticar, 1999). The $^{13}C_{CH_4}$ and $^2H_{CH_4}$ enriched samples appear to plot in the thermogenic CH_4 origin field of **Figure 6**. However, previous studies have consistently shown that during CH_4 oxidation, ^{12}C is preferentially removed resulting in a marked decrease in isotopic fractionation between CH_4 and CO_2, and during advanced stages, this fractionation can range between 5%–25% (Barker and Fritz, 1981; Whiticar, 1999). **Figure 7** highlights the difference $\Delta13C_{CO_2-CH_4}$ is close to 5‰, and follows the evolution pathway for CH_4 oxidation. Hence, this data implies that bacterial CH_4 is originally generated from high organic content sedimentary units and coals under anoxic conditions primarily *via* the carbonate reduction pathway (Krüger et al., 2008; Guo et al., 2012; Gründger et al., 2015). Subsequently, at 63–79 m depth at the GGERF site, the oxidative consumption of bacterial coal bed CH_4 occurs resulting in a distinctly enriched ^{13}C and ^2H CH_4 signature.
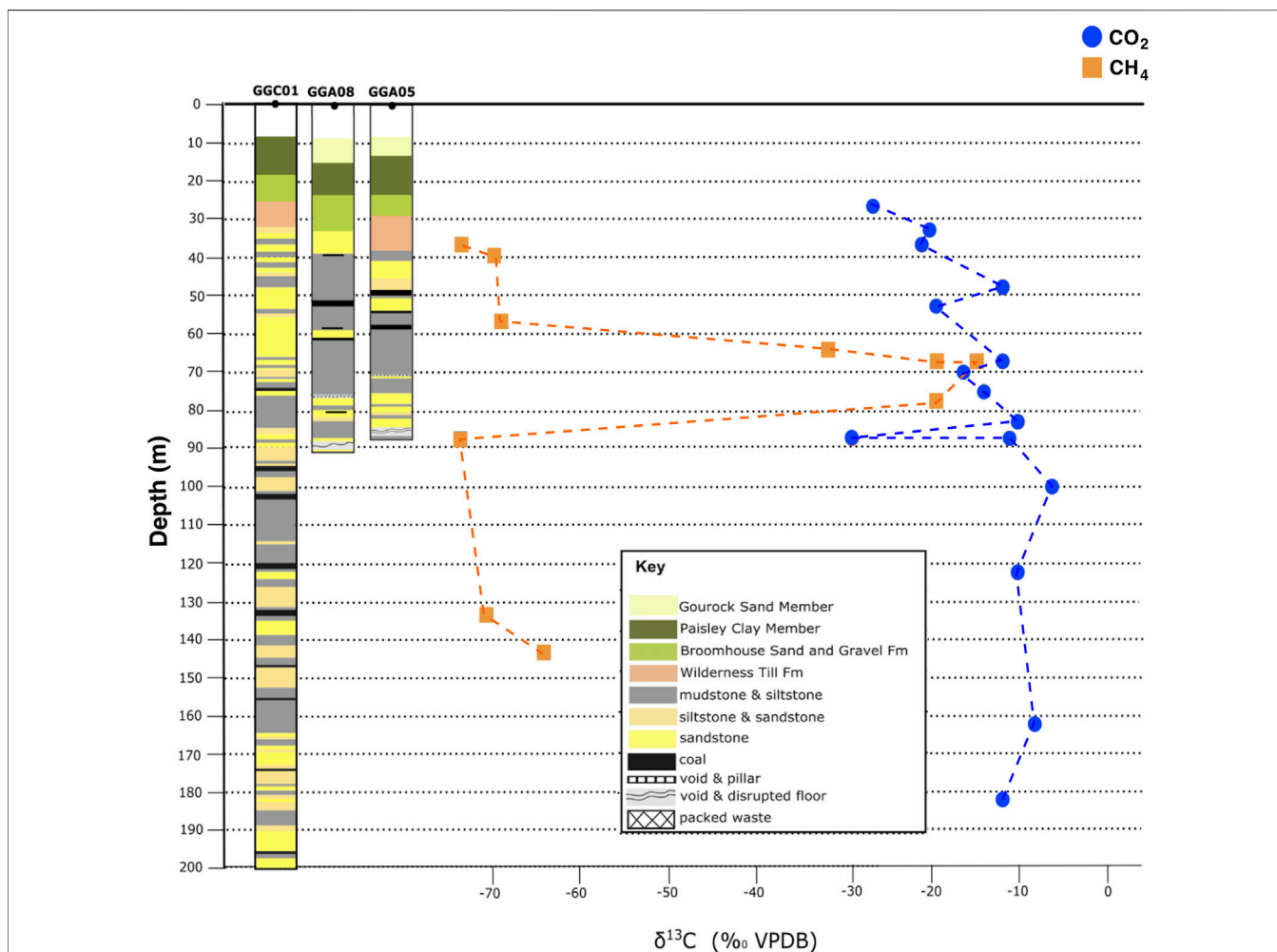
CO_2 Signatures

Sources of CO_2 gas within coal beds are dependent on the burial and uplift history of the stratigraphic units, and may also

FIGURE 8 | Isotopic depth plots of CH_4 and CO_2 $\delta^{13}C$ values from GGC01, GGA05, and GGA08 boreholes; with the corresponding stratigraphy. CH_4 stable isotopes have no clear correlation with depth, with a consistent biogenic signature present, and a distinct zone of enriched CH_4 in the area surrounding the Glasgow Ell mine workings. CO_2 gas exhibits a consistent depleted $^{13}C_{CO2}$ signature with shallower depth, highlighting the increasing influence of shallow groundwater within the subsurface.

contain CO_2 contributions from other sources such as dissolved atmospheric and soil gas, magmatic or mantle degassing, microbial degradation of organic substrates, and the thermal maturation of kerogen (Dai et al., 1996; Golding et al., 2013). In relation to interpreting $\delta^{13}C_{CO2}$ and $\alpha^{13}C_{CO2-CH4}$ values, there are a number of non-methanogenic processes that can affect gas signatures and therefore shift $\alpha^{13}C_{CO2-CH4}$ from the "true" methanogenic fractionation value (Flores et al., 2008; Golding et al., 2013; Baublys et al., 2015; Vinson et al., 2017; Chen et al., 2023). Such processes include the mixing of biogenic and thermogenic gases, methane oxidation resulting in the conversion of CH_4 to CO_2, bacterial processes which produce CO_2 such as sulfate reduction, and interaction with formation waters resulting in gas losses (Whiticar et al., 1986; Golding et al., 2013; Vinson et al., 2017). The mixing of biogenic and thermogenic gases can lower the $\alpha^{13}C_{CO2-CH4}$ value, as thermogenic gas typically has a more enriched $\delta^{13}C_{CH4}$ and depleted $\delta^{13}C_{CO2}$ signature than biogenic gas (Whiticar et al.,

1986; Vinson et al., 2017). Methane oxidation affects the $\alpha^{13}C_{CO2-CH4}$ values as the residual un-oxidated methane has a more enriched $\delta^{13}C_{CH4}$ signature and therefore lowers the apparent $\alpha^{13}C_{CO2-CH4}$ value (Whiticar, 1999; Vinson et al., 2017; Chen et al., 2023). Bacterial processes such as sulfate reduction can consume CH_4 and produce CO_2, with little fractionation on the carbon values, resulting in the lowering of the $\alpha^{13}C_{CO2-CH4}$ value (Vinson et al., 2017). Finally, CH_4 and CO_2 can be lost through dissolution and advection as groundwater flows through the coal bed formation. Therefore, a semi-open system where CH_4 and CO_2 are not fully retained results in the $\alpha^{13}C_{CO2-CH4}$ value being affected (Golding et al., 2013; Vinson et al., 2017).

Microbial coal bed gases tend to have carbon and hydrogen fractionation factors [$\alpha^{13}C_{CO2-CH4}= (1,000 + \delta^{13}C_{CO2})/(1,000 + \delta^{13}C_{CH4})$] close to expected $\alpha^{13}C_{CO2-CH4}$ values for the carbonate reduction pathway (1.06−1.09) (Golding et al., 2013; Vinson et al., 2017; Chen et al., 2023). $^{13}C_{CO2}$ and

$^{13}C_{CH4}$ values from close stratigraphic horizons, highlighted in **Figure 7**, indicate a consistent $\alpha^{13}C_{CO2-CH4}$ value of 1.06 for all GGC01 samples, and for some shallow samples from GGA05 and GGA08, indicating a characteristic CO_2 reduction pathway for methanogenesis. However, several GGA05 and GGA08 samples from 66 to 79 m depth have much lower $\alpha^{13}C_{CO2-CH4}$ values (1.003–1.007), evidencing the potential for non-methanogenic processes altering the "true" methanogenic fractionation factor. The dissolution of microbial CO_2 results in enriched $\delta^{13}C_{DIC}$ values of 8‰ relative to the gas phase CO_2 (Clark and Fritz, 1997). With pumping test data (Palumbo-Roe et al., 2021) establishing measured $\delta^{13}C_{DIC}$ values of −12.8‰ to −7.1‰ within groundwater contained in the mineworkings, a general enrichment of 8‰ can be observed between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CO2}$ values (For example: superficial deposits $\delta^{13}C_{DIC}$ = −12.8‰ to −10.9‰ and $\delta^{13}C_{CO2}$ = −25.5‰ to −21‰; Glasgow Upper $\delta^{13}C_{DIC}$ = −11.2‰ to −10.9‰ and $\delta^{13}C_{CO2}$ = −18.3‰; Glasgow Main $\delta^{13}C_{DIC=}$−10.8‰ and $\delta^{13}C_{CO2}$ = −19.8‰). The additional enrichment of $\delta^{13}C_{DIC}$ observed in the samples may be explained by interaction with carbonates *via* precipitation and dissolution reactions, the source of which may potentially derive from sulphuric acid produced through pyrite oxidation within the former coal mine workings (Palumbo-Roe et al., 2021). As such, the varying $\delta^{13}C_{CO2}$ signatures within the site highlight a potential for a combination of non-methanogenic processes such as methane oxidation and dissolution occurring, highlighting the complications of using isotopic identification techniques.

Stable Isotope Profiles With Depth

The stable isotope profiles with depth are plotted for CH_4 and CO_2 in **Figure 8**, illustrating that there is no clear correlation of the CH_4 stable isotope ratios with depth. There is a consistent biogenic $\delta^{13}C_{CH4}$ signature of −75‰ to −64‰, with a distinct zone of markedly heavier CH_4 occurring between a depth of 63 and 79 m, corresponding to enriched $\delta^{13}C_{CH4}$ values of −32.2‰ and −14.3‰. At Borehole GGA05, the heavily oxidised signatures occur within 5–9 m above the collapsed Glasgow Ell coal mine workings, in both clay and silt sedimentary units that contain thin coal seams and have high organic content. The enriched $^{13}C_{CH4}$ signatures for GGA08 are found in clay, silt, and sand sedimentary units, with moderate organic content within 3–9 m of the same Glasgow Ell workings. In both GGA05 and GGA08 boreholes, enriched $^{13}C_{CH4}$ and $^2H_{CH4}$ signatures are observed at 66–67 m depths, hence it is unlikely this enriched signature is the result of air ingress into isojars during sample storage.

A consistent signature was observed in the CO_2 from these samples, with CO_2 gas signatures showing a progressive depletion in $^{13}C_{CO2}$ at shallower depths [from ~−10‰ at 180 m depth to −23‰ in the shallowest sample (36 m depth)] (**Figure 8**). Values recorded from the superficial deposits are the most depleted in $^{13}C_{CO2}$, with the unmined bedrock samples from GGC01 being the most enriched in ^{13}C, with the exception of a distinct depleted CO_2 sample (−29‰)

occurring at ~90 m depth, in the area of the Glasgow Main mine-workings.

Lessons for the Monitoring of Minewater Geothermal Sites

In establishing the environmental baseline of the site, ground gas baseline surveys were also undertaken at the Glasgow Observatory, in order to determine if potential mine gases or gas originating from overlying made ground could be detected in the near surface environment (Monaghan et al., 2022a). Through these surveys, CO_2 and CH_4 flux at the soil-atmosphere interface, ground gas concentrations of CO_2, CH_4, H_2, H_2S, O_2, a proxy for N_2, and a limited number of carbon stable isotope samples were measured (see Monaghan et al., 2022b for full sampling methodology).

Ground gas CH_4 concentrations were comparable to atmospheric gas (<3 ppm by volume) and CH_4 flux was typically below detection limits (Monaghan et al., 2022a), which corresponds well to our measured CH_4 concentration data, with the majority of samples having CH_4 levels below detection limits, and the highest CH_4 concentration levels recorded in the areas of unmined coal seams, or the Glasgow Ell mine workings. CO_2 flux measured above the site was consistent with uncontaminated rural (Ward et al., 2019) and other UK sites previously surveyed. However, there were instances of moderate ground gas concentrations (10%–20% by volume) in isolated points across surveys (Monaghan et al., 2022b). From limited carbon stable isotope ratios, $\delta^{13}C$ values typically range from −23.59‰ to −26.31‰ and compare well to our shallowest GGA05 and GGA08 samples, as $\delta^{13}C_{CO2}$ values get progressively lower to a value of −23.0‰, as soil gas CO_2 has an increasing influence through shallow groundwaters. This also highlights gas concentrations and signatures are highly variable and closely linked to stratigraphic horizon in the shallow subsurface, as it is evident that mine gas signatures from the workings does not impact ground gas (Monaghan et al., 2022a). From stoichiometric CO_2: O_2 relationships, ground gas appears to be a mixture of natural origin of photosynthetic production, and of microbial oxidation of CH_4 to CO_2 (Monaghan et al., 2022b).

The comparison of ground gas data with core and cutting gas measurements is critical for the monitoring of geothermal and other geoenergy activities, as it allows for the sensitive measuring and tracking of key hazardous gases that may arise from subsurface use (Monaghan et al., 2022a). Our results show that the CO_2 contained in the subsurface below 100 m depth is geochemically distinct from that of the shallow subsurface (0–90 m depth), meaning that an increase of CO_2 levels at the near-surface originating from deeper mine workings below 100 m from any potential perturbation of the system may be detectable using $\delta^{13}C$ measurements. However, further work is required to ascertain the detection limit, and if gas migration processes would significantly change the $\delta^{13}C$ signature of the migrating CO_2.

CONCLUSION

We identify the presence of both CH_4 and CO_2 in the gases exsolved from core and cutting samples taken from boreholes GGC01, GGA05, and GGA08 at the Glasgow Observatory site. Our results show that there is no correlation between gas concentration and depth, as both CH_4 and CO_2 gas concentration values are highly variable and are closely linked to individual stratigraphic horizons. We find evidence that CH_4 present in the site's Carboniferous coal measures is of biogenic origin, produced primarily through the carbonate reduction pathway, with a potential mixing of CH_4 from methyl-type fermentation. Enriched ^{13}C and ^2H CH_4 signatures are found within 63–79 m depth in GGA05 and GGA08 boreholes, and provide evidence of CH_4 oxidation in proximity to the Glasgow Ell coal mine workings. CO_2 gas is more abundant throughout the succession in all three boreholes and has an enriched $^{13}C_{CO_2}$ signature relative to the CH_4 present. The observed CO_2 gas signature becomes progressively depleted in $^{13}C_{CO_2}$ at shallower depths above 90 m, with the trend being attributed to the increasing influence of groundwater containing a mixture of dissolved marine carbonate minerals and soil gas CO_2 at shallower depths. Comparing our results to determined ground gas signatures, there is no evidence of ground gas currently being impacted by gas migration from the Glasgow Observatory mine workings.

The findings presented here provide an insight into the variability of mine derived gases, and highlight the presence of distinct gas signatures that are linked to stratigraphic horizon. The gas baseline signature of the shallow subsurface of the Glasgow Observatory can be integrated into larger environmental datasets (Monaghan et al., 2022b) in order to generate a "time zero" records of the site, which are key in informing fit-for-purpose monitoring operations and developing efficient geothermal infrastructures. By characterising the shallow subsurface through depth-dependent isotopic gas fingerprints in the mined succession and comparing to distinctive ground gas isotopic compositions; there is potential to use such signatures to evaluate any potential change in the shallow subsurface environment once pumping, heat abstraction, and re-injection commence.

DATA AVAILABILITY STATEMENT

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found in the article/ **Supplementary Material**.

AUTHOR CONTRIBUTIONS

RC, GJ, and SG: conceptualisation, investigation, writing, and visualisation; AB conceptualisation, investigation and reviewing writing. RC: funding acquisition. All authors have read and agreed to the published version of the manuscript.

FUNDING

CONFLICT OF INTEREST

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

ACKNOWLEDGMENTS

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.escubed.org/articles/10.3389/esss.2023.10073/full#supplementary-material

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