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Accepted Manuscript

Synthesis of carbon-13 labelled carbonaceous deposits and their evaluation for potential use as surrogates to better understand the behaviour of the carbon-14-containing deposit present in irradiated PGA graphite

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1	Synthesis of carbon-13 labelled carbonaceous deposits and their
2	evaluation for potential use as surrogates to better understand the
3	behaviour of the carbon-14-containing deposit present in
4	irradiated PGA graphite.
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12	Abstract
13	The present work has used microwave plasma chemical vapour deposition to generate
14	suitable isotopically labelled carbonaceous deposits on the surface of Pile Grade A graphite
15	for use as surrogates for studying the behaviour of the deposits observed on irradiated
16	graphite extracted from UK Magnox reactors. These deposits have been shown elsewhere to
17	contain an enhanced concentration of ¹⁴ C compared to the bulk graphite. A combination of
18	Raman spectroscopy, ion beam milling with scanning electron microscopy and secondary ion
19	mass spectrometry were used to determine topography and internal morphology in the formed
20	deposits. Direct comparison was made against deposits found on irradiated graphite samples
21	trepanned from a Magnox reactor core and showed a good similarity in appearance. This
22	work suggests that the microwave plasma chemical vapour deposition technique is of value in
23	producing simulant carbon deposits, being of sufficiently representative morphology for use
24	in non-radioactive surrogate studies of post-disposal behaviour of ¹⁴ C-containing deposits on
25	some irradiated Magnox reactor graphite.
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33 **1. Introduction**

The decommissioning of the UK's first generation of gas-cooled, graphite-moderated 34 (Magnox) reactors will lead to approximately 45,000 m³ of irradiated reactor core graphite, 35 with a packaged volume of 59,000 m³, for geological disposal [1]. An important radionuclide 36 in safety assessments for the disposal of radioactive waste in a geological disposal facility 37 (GDF) is the long lived isotope 14 C (half-life 5730 years) [2]. With an approximate total 14 C 38 activity of more than 7000 TBq arising from Magnox graphite cores and the additional 39 volume of graphite waste arising from advanced gas-cooled reactors (AGR) [2], investigation 40 of the behaviour of ¹⁴C associated with such wastes after closure of a geological disposal 41 42 facility is important. Whilst reactor graphite has been extensively studied from a physiomechanical standpoint, related to core integrity, relatively little research effort has been 43 placed on understanding the behaviour of the graphite and constituent ¹⁴C in a geological 44 disposal environment. 45 Recent research [3] providing post mortem analysis of irradiated graphite from two Magnox 46 reactor cores highlighted the presence of a carbonaceous deposit on the exposed surfaces of 47 48 the graphite bricks (channel and interstitial walls) from one of the reactors that has a pronounced and markedly different morphology to the bulk graphite. The extent of this 49 50 deposit is likely to be a worst case scenario and it is anticipated that not all Magnox reactors may contain such significant deposits. However, these surface deposits have been determined 51 to have a significant ¹⁴C content compared to the bulk graphite [4] that has been created via 52 formation pathways discussed elsewhere [5]. It is not understood how these deposits will 53 behave in a GDF setting in comparison to the graphite which it coats. Specifically there is a 54 gap in the understanding of the release rate and magnitude of the labile ¹⁴C fraction, of which 55 ¹⁴C located in deposited material may contribute significantly, with this labile fraction 56 expected to achieve relatively early release in the lifetime of a GDF [6]. The pronounced 57 "cauliflower-like" morphology observed is not unique to nuclear reactors and similar 58 morphologies have been commonly reported within the scientific literature for carbon from a 59 60 range of deposition techniques unrelated to nuclear applications [7-11]. At present such deposits are of specific interest in geological disposal of graphite waste from the 61 decommissioning of Magnox reactors, as the deposited material may be present and represent 62 a significant fraction of the labile 14 C. 63 The Magnox reactors represent the first generation of gas-cooled reactors in the UK that used 64

65 carbon dioxide (CO₂) as the primary coolant and a honeycomb network of graphite bricks to

- 66 provide neutron moderation. During reactor operation significant amounts of carbon monoxide (CO) was produced from the CO₂ coolant. This CO in turn can be radiolytically 67 polymerised to form a carbonaceous deposit on free surfaces [12]. This non-graphitic carbon 68 deposit is significantly more chemically reactive to air than the underlying graphite [12, 13]. 69 70 During the lifetime of some Magnox reactors, small quantities of methane gas were injected into the coolant gas to inhibit weight loss of the graphite core due to radiolytic oxidation [14]. 71 72 Methane (CH_4) is a precursor for carbonaceous deposits that form a sacrificial layer protecting the underlying graphite from excessive weight loss [15] and reduction in 73 mechanical strength [16]. It is assumed nitrogen incorporation during deposit formation is the 74 subsequent production route for the high ¹⁴C levels observed. 75 CH₄ is also a commonly utilised feedstock gas for the production of diamond and other 76 carbon coatings by the process of chemical vapour deposition (CVD) [17]. The growth of 77 carbon materials by CVD involves the excitation of a carbon-containing precursor gas using a 78 79 thermal or plasma energy source that creates activated radicals that will bond to a suitable exposed surface. Therefore, even though differences exist in the formation of carbonaceous 80 deposits from CO and CH₄, both include the activation of carbon-containing gas creating 81 activated carbon species that will bond to surfaces. Recent work [3] showed that graphite 82 from the Oldbury Magnox power station, which had methane introduced into the coolant gas, 83 had a significant deposit on the fuel and interstitial channel walls of the graphite bricks. This 84 suggested that the deposit formed may be due to methane. A comparison of the morphology 85 and density of such deposits will help determine whether a ¹³C methane deposit can be used 86 as a simulant for the surface deposit found on irradiated graphite in further work. If ${}^{13}C$ 87 carbonaceous deposits can be used as a simulant for the deposits seen on irradiated graphite it 88 will allow easier, non-radioactive investigations of the potential release of ¹⁴C from deposits 89 on irradiated graphite in a geological disposal environment including the potential microbial 90 interaction with such material. If the deposits observed on the graphite behave differently to 91 the underlying graphite it may lead to a significantly different release rate for ¹⁴C from the 92 deposit than from the underlying graphite when contacted by groundwater some time after 93 the closure of a geological disposal facility. Microbial colonisation may also be more likely 94 on the deposit than the underlying graphite due to the increased surface area due to the 95 amorphous nature of the material. 96 The use of a ¹³C simulant allows wider access into the research of nuclear graphite, which 97
- 97 The use of a °C simulant allows wher access into the research of nuclear graphite, which
 98 contains many other radionuclides such as ⁶⁰Co, as facilities to handle radioactive materials
 99 are not required. Isotopic differences in the precursor material should not alter the chemical

nature and/or effect the chemistry of the deposited carbon material. To this end, ¹³C has 100 previously been used as a common isotopic tracer in biological systems [18] and implanted in 101 graphite [19] as a non-radioactive proxy for 14 C. In the current work we demonstrate the use 102 of microwave plasma CVD to create a carbonaceous layer on graphite substrates that exhibit 103 similar morphologies and densities to deposits observed to have formed in-service on 104 Magnox graphite moderator blocks. The non-radioactive isotope ¹³C was selected as a tracer 105 during CVD deposition such that deposit-substrate interfaces could be clearly resolved using 106 imaging mass spectrometry analysis to determine the degree of material mixing and substrate 107 108 etching.

109 The present work is part of a larger programme (C14-BIG) directed at gaining a better

understanding and predicting the release of graphite derived ¹⁴C from a GDF and the

111 influence of microbial activity under alkaline conditions expected to predominate for a

- significant time in a cement-based near field of a geological disposal facility after closure.
- 113 **2. Experimental**
- 114 2.1. Sample preparation

Pile Grade A (PGA) graphite was provided by Magnox Limited as a surplus material from the commissioning of the Wylfa nuclear power reactors, Wales. This graphite was trepanned into cores of 12 mm diameter using a stainless steel coring tool. The cores were then cut into 2 mm thick discs using a South Bay Technology Inc. Model 650 low speed diamond cutting wheel with deionised water used as coolant. This process gave a flat surface that was a



Figure 1, Schematic diagram of a single mode microwave plasma chemical vapour deposition (MPCVD) system. (A: variable power microwave controller (max. 1000 W); B: air-cooled microwave generator; C: water-cooled circulator; D: 4 port single mode TE01 microwave cavity; E: double plunge microwave tuner; F: mass-flow controllers; G: diaphragm vacuum pump; H: mass spectrometer; I: quartz tube containing a graphite disc on a porous glass sinter.)

suitable substrate for deposition. Subsequently ¹²C and ¹³C carbonaceous deposits were
 formed on the graphite surfaces using microwave plasma chemical vapour deposition

122 (MPCVD), Figure 1.

123 Coating was carried out using a computer-controlled 2.45 GHz microwave generator

124 (variable power output – maximum 1000 Watts), TE_{01} single mode cavity (Sairem

downstream plasma source WR340), double plunge microwave tuner, mass-flow controllers

126 (MFC) and a carrier (Argon) and precursor gas at a total flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. Sample

127 coatings were made at methane concentrations of 2, 10 and 20% for ${}^{12}CH_4$ and 2% for ${}^{13}CH_4$.

128 For coating, each cylindrical PGA graphite disc was placed on a glass sinter situated inside a

129 quartz tube which was aligned to position the disc within the centre of the waveguide. The

tube was then connected to the mass-flow controllers, a gas flow was established and then thesystem was placed under a low vacuum. Once a 1000 Pa system pressure had been achieved

132 the microwave generator was switched on and the microwave reflectance was reduced, as

133 much as possible, using the double plunge microwave tuner. Once the microwave reflectance

134 was tuned the CVD coating process was left to proceed for a period of 30 minutes [20].

Additionally, deposition was performed at varying pressures (1000, 5000, 10 000 Pa),

however a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ for the gas mixture did not achieve a system pressure of

137 less than 700 Pa. A lower flow rate of $20 \text{ cm}^3 \text{ min}^{-1}$ was applied at 10% ¹²CH₄ so that a

system pressure of 500 Pa could be achieved, additionally growth was performed at 10 Pa

139 system pressure at this reduced flow rate.

1-2 mm particles were also produced alongside the disc samples due to crucible size 140 141 restrictions for the Linkam catalyst stage for Raman spectroscopy. Additional PGA graphite was provided by the National Nuclear Laboratory (NNL). This graphite was sectioned into 142 143 smaller rectangular sheets using a JCB toolbox saw and then cut into smaller monoliths using an Erbauer ERB180C tile cutter (with no coolant) thus making the graphite more 144 manageable. The graphite monoliths were then put into a metal container and placed into a 145 10-ton hydraulic press, where a pressure between 5-10 tonnes of pressure was used to break 146 the graphite down into smaller pieces. The pieces were then subsequently filtered using a 3 147 compartment Fisherbrand stainless steel sieve (aperture sizes: >2 mm, 1-2 mm and <1 mm) 148

and the 1-2 mm particles were retained for subsequent microwave deposition. Both the larger

and smaller pieces were repeatedly pressed until all of the graphite was left as a mixture of

151 either particles or powder, following sieving.

152 A selection of virgin PGA samples (i.e. without deposit) and irradiated graphite specimens extracted by trepanning from a Magnox power station were also analysed for comparison, 153 exact details previously described in [4]. 154

2.2. Scanning electron microscopy/ Focused ion beam 155

A Helios NanoLab 600i combined SEM/FIB system (FEI, Oregon USA) was used to obtain 156 scanning electron micrographs. The focused ion beam (FIB) was utilised to precision mill 157 trenches to allow the thickness and morphology of the deposit to be determined with 158 159 nanometre accuracy and to allow subsequent analysis using other techniques. Electron micrographs were acquired using an accelerating voltage of 15 kV, an electron beam 160 161 current of 0.17 nA and a dwell time of 100 µs. Trenches were FIB milled with the use of a Ga⁺ ion source with an accelerating voltage of 30 kV. A Selective Carbon Mill (SCM) gas 162 was used throughout to enhance milling rates. The SCM admits small amounts of water 163 vapour directly over the milling area, promoting gasification of the milled material, 164 enhancing the etch rate and reducing redeposition. It also minimises beam damage and 165 therefore reduces the need to deposit platinum on the surface as a protective measure. 166 Initially a 20 nA beam current was used to generate coarsely defined trenches, with 167 subsequent incremental reductions in ion current to reach a final beam current of 0.9 nA for 168 surface finishing. The milled trenches had approximate dimensions of 50 µm x 56 µm x 20 169 170 μm (x, y and z respectively). The trench faces were smooth and flat, allowing for direct and high spatial resolution observation of structures and features. 171

172

2.3. Magnetic Sector-Secondary Ion Mass Spectrometry

For isotopic analysis of the samples, an in-house built magnetic sector secondary ion mass 173 spectrometer (MS-SIMS) was utilised. Full details of the system are described elsewhere 174 [21]. In summary the system comprised of a focused gallium ion gun (FEI electronically 175 variable aperture type) fitted to a Vacuum Generators model 7035 double-focusing magnetic 176 sector mass analyser with a channeltron detector. The sample was held at a 4 kV potential 177 during analysis. The equipment was controlled using PISCES software, written in-house by 178 Dayta Systems Ltd (Thornbury, UK). The system was capable of providing selected ion 179 mapping and depth profiling with sub-micron resolution. 180

MS-SIMS analyses were performed in negative ion mode for both spectral acquisition and 181

182 secondary ion imaging. Mass spectra and depth profiles were initially acquired from 4

- different areas of the 2% ¹²C and ¹³C methane deposits, detecting mass/charge (m/z) signals 183 at 12, 13, 24 and 26 Da. These ion signals are generated due to the C⁻ and C₂⁻ ions derived 184 from sputtered ¹²C and ¹³C respectively. Mass spectra were obtained by scanning through the 185 mass range 0-100 Da in 0.05 Da steps, with duration of 100 ms per step and 200 s in total. 186 187 Data acquisition was performed at a low magnification to reduce beam damage (area analysed $\sim 0.25 \text{ mm}^2$) and with a 3 nA beam current. Identification and calibration of the 188 exact m/z values for use in subsequent depth profiles and images were achieved with the use 189 of these survey spectra. 190
- 191 Depth profiles record the ion yield intensity from selected sputtered analyte ions over time

192 while rastering the ion beam over a selected area. As the deposits are suitably thick it is not

anticipated that the depth profile will sputter enough material to immediately expose the

underlying graphite. This allows the signal to be averaged over a set period of time and then

- the ratio between signals to be compared. Depth profiles were acquired for 1800 s with a
- beam current of 3 nA and area analysed of approximately $2500 \,\mu m^2$. Electronic gating was
- 197 used throughout to eliminate signal created at the margins of the etched area. Signal averages
- and ratios were calculated from 200 s to 1800 s, disregarding the first 200 s of data as this

199 was the observed transient period for the experiment.

200 The species compared were the C_2^- ions at 24 and 26 Da, rather than 12 and 13 Da, due to the

strong signals obtained from these species, and also to avoid some prominent mass

- interferences. Interference peaks are difficult to eliminate, however the use of the C_2^- peak is
- appropriate as the present work is not trying to identify trace elements but aiming to
- investigate whether the surface deposits are formed of ${}^{13}C$, to what extent ${}^{13}C$ is incorporated
- 205 into the graphite and how thick the overall deposit is.

206 Secondary ion images were recorded from the FIB milled trenches using the C_2^- ions (24 and

207 26 Da). The images were obtained by selecting the m/z ratio of the ion of interest, and then

208 raster scanning the ion beam over a defined area of the sample. The images presented in this

paper were acquired over a total area of approximately 0.0225 mm^2 . Each image was

acquired over a 60 second period using a 0.3 nA beam current to give the best possible spatial

- 211 resolution whilst still maintaining sufficient ion signal.
- 212 2.4. Catalyst stage Raman spectroscopy

A CCR1000 catalyst stage reactor system connected to a T95 system controller and LinkPad
interface (Linkam, Surrey UK) was used for the thermal oxidation of the PGA graphite 1-2

mm particles. For in situ spectral acquisition, a LabRAM HR800 confocal Raman microscope 215 (Horiba Jobin Yvon, Kyoto Japan) was used. The sample was heated up in the crucible inside 216 of the catalyst stage from room temperature up to 600 °C (at 10 °C min⁻¹), with a 50 cm³ min⁻¹ 217 ¹ flow of air. Spectra were acquired using a 532 nm laser, a 50X long-working distance 218 objective, a 300 g mm⁻¹ grating, and spectral acquisition times of 25 s every 50 °C. 219 The heating regime and the spectral acquisition parameters for automated analysis were 220 221 controlled using a built-in Linkam module script in the Horiba Labspec 6 software package. The Raman spectroscopy system was calibrated using the 520 cm⁻¹ peak from a silicon 222 crystal.Spectral analysis, during thermal oxidation in air, of virgin PGA graphite and PGA 223 graphite with ¹²C and ¹³C carbonaceous deposits was carried out to analyse the thermal 224 profile of the surface material (i.e. graphite substrate) and the "cauliflower-like" 225 carbonaceous deposit. This technique allows for analysis of the thermal oxidation 226 properties/reactivity of the different carbon materials and also surface chemical changes due 227 to thermal oxidation. 228

3. Results

230

3.1. Scanning Electron Microscopy

The deposit formed on irradiated graphite taken from Oldbury Magnox reactor has a distinct 231 and pronounced morphology, Figure 2a, compared to virgin PGA graphite, Figure 2b [3]. For 232 comparison, electron micrographs of the 2% ¹²CH₄ and 2% ¹³CH₄ deposits can be seen in 233 Figure 3, a and b respectively. The distinction between deposit and underlying graphite 234 should be noticeable due to the lack of characteristic features in the deposit that are routinely 235 seen in all PGA graphite such as shrinkage cracks and ligaments between pores [22], Figure 236 4. The deposits found on irradiated graphite have a 'cauliflower-like' appearance due to an 237 agglomeration of irregular spheres, Figure 5. After FIB milling the internal morphology of 238 the 2% 13 CH₄ and 2%, 10% and 20% 12 CH₄ deposited samples can be seen in Figure 6a, b, c 239 and d respectively. 240

The 2% ¹²C and ¹³C methane CVD deposits were observed to have a porous, 'feathery' texture that appears to be significantly less dense than the underlying graphite. For the irradiated graphite however, there was very little distinction in density or fine structure between the deposit and the underlying graphite (the deposit appears to have a lower porosity compared to virgin PGA, Figure 5). It is possible that the underlying PGA graphite in the

- 246 irradiated samples is protected from radiolytic oxidation by the carbon deposit, leading to the
- 247 deposit and underlying graphite being difficult to distinguish [15].



Figure 2,a) Focused ion beam mage of deposit found on irradiated graphite surface, from [4] and b) virgin PGA surface.



Figure 3, Scanning electron micrographs from ${}^{12}C$ (a) and ${}^{13}C$ (b) carbonaceous deposits on Pile Grade A graphite, system pressure 1000 Pa.

248

Further investigation using greater methane concentrations showed increases in the apparent density of the deposit (which was only determined visually), Figures 6 (b), (c) and (d), that are more closely comparable to the deposit found on irradiated graphite. Deposits produced at system pressures of 5000 and 10000 Pa were of different morphology, instead comprising an agglomeration of spherical deposits that were not as extensive or as thick as those grown at the lower pressure of 1000 Pa. Reducing the flow rate to 20 cm³ min ⁻¹ allowed a system pressure of 500 Pa to be achieved, however even though the surface topography of the



Figure 4, Scanning electron micrograph from cross section of an uncoated Pile Grade A graphite after FIB milling showing characteristic cracking and ligaments, shown with the arrows.



Figure 5, Focused ion beam image from cross section of channel wall trepanned sample from a Magnox reactor [3].

256	deposit was	similar to	irradiated	material a	and the ot	her caulif	lower-like d	eposits for	rmed, the

- 257 internal morphology exhibited extensive porosity and this did not appear suitable as a
- simulant, Figure 7(a). Conversely, growth at a system pressure of 1000 Pa at this reduced
- flow rate formed a deposit that was very similar to that grown at 50 cm³ min⁻¹, Figure 7(b).
- 260 The deposit formed at 1000 Pa pressure at 10% methane concentration showed the closest
- resemblance to those seen on Oldbury irradiated Magnox graphite and was deemed to be the
- 262 most suitable for use as a simulant.
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Figure 6. Scanning electron micrographs showing the ion beam milled cross sections for 2% ¹³CH₄ (a) and 2% (b), 10% (c) and 20% (d) ¹²CH₄ deposited samples, all at system pressure of 1000 Pa.



Figure 7. Scanning electron micrographs showing the ion beam milled cross sections at system pressures of 500 (a) and 1000 (b) Pa, flow rate $20 \text{ cm}^3 \text{ min}^{-1}$.

272 3.2. Secondary Ion Mass Spectrometry

Survey spectra from the 2% methane ¹²C and ¹³C deposits are shown in Figures 8 (a) and (b) 273 respectively. Signals recorded at mass/charge peaks of 13 Da ($^{13}C^{-}$ and 26 Da ($^{13}C_{2}^{-}$)) are 274 significantly greater in the ¹³C deposit compared to the ¹²C deposit, although these signals are 275 also present in the ¹²C sample due to ¹²CH⁻ and ¹²CN⁻ species respectively. The mean ratio 276 (n=4) between the peak heights at 26 Da and 24 Da for the 12 C deposit was found to be 0.14 ± 277 0.03. The mean ratio (n=4) for the ¹³C deposit was 115.3 ± 19.1 . This increase of several 278 orders of magnitude is strong evidence that the deposit is predominately ¹³C as the interfering 279 peak from ¹²CH at 13 Da is unlikely to be higher in the ¹³C sample. The errors given here are 280 likely to be due to the strong dependence of signal intensity on location and geometry of the 281 sample in the SIMS system [23]. 282



Figure 8, SIMS spectra from 2% methane ${}^{12}C$ (a) and ${}^{13}C$ (b) deposit.

- 283 The areas analysed were selected randomly and the only criteria for examination was that
- they produced sufficient SIMS signal to allow analysis. Due to the surface not having a
- uniform, flat surface there are likely to be topographic effects that will affect the signal
- recorded. This has been studied by other authors [23-25] with suggestions that the changes
- may be due to the incident angle of the beam, the height of the features and variations in the
- electric field due to topographic features that may lead to trajectory changes of the secondary
- ions [24].
- SIMS ion signal maps have been recorded for 26 Da and 24 Da for a 13 C sample, Figure 9 (a)
- and Figure 9 (b) respectively. For the 13 C deposit the mass peak signal at 26 Da is present
- primarily on the deposit with a significant reduction in signal in the underlying graphite with
- the 24 Da signal being the reverse, with a more intense signal recorded in the underlying
- graphite than in the deposit. This shows that the ${}^{13}C$ is deposited on top of the underlying
- 295 graphite. The signal at the bottom of the trench has a relatively high intensity for both 24 and
- 26 Da, and this may be due to re-deposition of sputtered material originating from the ${}^{13}C$
- 297 deposit during FIB milling of samples [26].



Figure 9, Secondary Ion signal maps for 26 Da (a) and 24 Da (b) from cross section of ¹³C carbonaceous deposit on top of Pile Grade A graphite after FIB milling.

- 298 *3.3.Catalyst stage Raman spectroscopy*
- A three-vectored graph displaying Raman shift, intensity and temperature (x, y and z axis
- 300 respectively) was used to illustrate the Raman spectra at each temperature during the thermal
- 301 oxidation experiment. The Raman spectra are displayed between 1100 1700 cm⁻¹ to allow
- the critical peaks related to both ${}^{12}C$ and ${}^{13}C$ carbonaceous materials to be compared. The ${}^{12}C$

303	peaks are the ¹² D peak at ~1350 cm ⁻¹ and the ¹² G peak at ~1575 cm ⁻¹ and the ¹³ C peaks are
304	the ¹³ D peak at ~1300 cm ⁻¹ and the ¹³ G peak at ~1525 cm ⁻¹ .

305 *3.3.1. Virgin PGA*

306 The thermal oxidation spectral profile for a virgin PGA graphite 1-2 mm particle is shown in

307 Figure 10. This spectral profile shows that there was a negligible change in the intensity of

the D and G peaks between 50 - 600 °C. This indicates that between 50 - 600 °C the surface

- 309 of the PGA graphite undergoes very minimal surface oxidation and that the PGA is mostly310 unreactive.
- 311 As the surface of the virgin PGA material remains relatively unchanged during thermal
- 312 oxidation it will readily allow for any spectral changes, due to the thermal oxidation of ${}^{12}C$
- 313 and 13 C carbonaceous deposits, to be isolated.



Figure 10, *In situ* Raman spectral analysis, during thermal oxidation, of a 1-2 mm virgin PGA graphite particle.

315

3.3.2. PGA Graphite with ¹²C and ¹³C Deposits

- The thermal oxidation spectral profiles for a 2 % 12 CH₄ and 13 CH₄ deposit on a PGA graphite particle are shown in Figures 11 and 12 respectively. Figure 11 shows that there is a noticeable decrease in the 12 D peak intensity between 400 – 600 °C. This indicates that the 12 C carbonaceous deposit begins to thermally oxidise at approximately 400 °C and appears to
- have been completely removed by 600 $^{\circ}$ C indicated by the intensity of the 12 D peak at 600
- 321 °C, showing the spectral profile of the virgin PGA graphite material.
- 322 There is a noticeable decrease in the 13 D & 13 G peak intensities between 450 600 °C in
- Figure 12, which are solely present due to the ¹³C carbonaceous deposit. This indicates that
- the 13 C carbonaceous deposit begins to thermally oxidise at approximately 450 °C and
- appears to have been completely removed by 600 $^{\circ}$ C indicated by the absence of the ¹³D &



Figure 11, *In situ* Raman spectral analysis, during thermal oxidation, of a 2% CH_4 ¹²C carbonaceous deposit on a 1-2 mm PGA graphite particle

- 13 G peaks at 600 °C, showing the spectral profile of the virgin PGA graphite material.
- 327 The intensities of the ¹²D and ¹²G peaks (PGA graphite) do not decrease but in fact increase
- relative to the decrease in the intensities of the 13 D and 13 G peaks (13 C carbonaceous

- deposit), which also illustrates that the surface of the virgin PGA material, as a base substrate,
- 330 remains relatively unchanged during thermal oxidation.
- As the Raman peaks associated with the deposits decrease between 400 600 °C it indicates
- that the carbonaceous material on the surface has a similar oxidation temperature to that of
- the carbonaceous deposits found on irradiated PGA graphite (M. P. Metcalfe, personal
- 334 communication, 11^{th} November 2013).



Figure 12, *In situ* Raman spectral analysis, during thermal oxidation, of a 2% $CH_4^{-13}C$ carbonaceous deposit on a 1-2 mm PGA graphite particle

- Figure 13 illustrates the isothermal profiles of virgin PGA graphite, irradiated PGA graphite
- deposit & a 12 C microwave simulant deposit at 450 °C, in air, over a 50 hour period. The
- 337 oxidation of virgin PGA graphite is negligible whereas the irradiated PGA graphite deposit &
- the C-12 microwave simulant deposit show significantly greater rates of oxidation and are
- 339 clearly more reactive. Initially the rates of thermal oxidation remain fairly similar for the first
- 5 hours for the irradiated PGA graphite deposit & the ¹²C microwave simulant deposit but for
- the next 45 hours the irradiated PGA graphite deposit shows a greater rate of thermal

oxidation. This deviation in rates of reactivity may be due to irradiated damage caused to the
underlying PGA graphite in the irradiated PGA graphite sample whereas the underlying PGA
graphite in the microwave simulant underwent no irradiation and started off as pristine virgin
PGA graphite. However the microwave simulant carbonaceous deposit reactivity seen in the
TGA isothermal data shows a similar reactivity to that of the carbonaceous deposit seen in
irradiated PGA graphite.



Figure 13, Thermograms from virgin PGA graphite, irradiated PGA graphite and ¹²C simulant deposit on PGA graphite examined at 450 °C, in air, over a 50 hour period.

348 **4. Discussion**

Previous examination [3] of irradiated graphite from Magnox reactors has shown that during 349 generation lifetime a carbonaceous deposit can be formed on the fuel and interstitial channel 350 walls of the graphite moderator that has a markedly different morphology to the underlying 351 PGA graphite. This work aimed to form a similar carbonaceous deposit using ¹³C precursor 352 gas to allow subsequent investigation of the behaviour of such deposits in leaching and 353 microbial studies pertinent to examining graphite degradation and ¹⁴C release in a GDF [27]. 354 Use of a simulant allows future experiments to be performed more easily than using 355 irradiated graphite due to a removal of the need to work with radioactive materials. 356 However, the use of simulants necessitates care to ensure that they are representative of the 357 properties being examined. With the use of several experimental techniques (FIB, SEM, MS-358 SIMS, Raman) this work has examined the internal morphology as well as the surface 359

360 topography of carbonaceous deposits formed using microwave plasma CVD and compared them to irradiated graphite trepanned from a Magnox power station graphite core. 361 Microwave plasma CVD has been used to form adherent carbonaceous deposits on the 362 surfaces of virgin (unirradiated) PGA graphite discs. Microwave plasma CVD is widely used 363 to grow other carbon materials with differences in growth parameters (precursor gas, 364 temperature, pressure, microwave power) leading to different allotropes being formed most 365 notably Carbon-Nanotubes (CNT) [28, 29] and diamond [30, 31]. Initially, ¹²C precursor gas, 366 using a system pressure of 1000 Pa with a flow rate of 50 cm³ min⁻¹, was used, primarily due 367 to the high cost of labelled isotopic gases, and with the use of scanning electron microscopy 368 the surface topography was found to be very similar to the 'cauliflower-like' deposits found 369 on irradiated graphite [3]. However, after sectioning with a focused ion beam it was found 370 that the internal morphology was more porous than the deposit found on irradiated graphite. 371 This is believed to be due to the growth rate, approximately 50 μ m hour⁻¹, of the deposit 372 being too rapid to allow a dense deposit to be formed. By comparison, growth rates of 373 diamond using microwave plasma CVD are usually in the region of 1 μ m hour⁻¹ [32] and 374 these form 'solid' deposits. By increasing the methane concentration in the precursor gas mix 375 an increased density in the deposit was achieved, likely due to the increased availability of 376 carbon radicals available for deposition. It should be noted that the deposits formed on 377 irradiated graphite are formed at conditions that are very difficult to replicate, pressures of 1-378 3 MPa, temperatures of approximately 400 °C and in the presence of a neutron flux [33], 379 therefore the high density of the deposits found on irradiated graphite is likely due to the high 380 381 pressure environment, whereas in microwave plasma CVD low pressures are used so that the plasma can be sustained. 382 Further experiments were carried out to investigate the parameters which can affect the 383

384 growth rate of carbonaceous deposits and to determine whether a more representative

385 carbonaceous deposit could be formed using microwave plasma CVD. Experiments carried

out at 200 W using 2, 10 & 20% CH₄ failed to generate carbonaceous deposits. However,

deposition at 400 W induced a rapid growth of carbonaceous material.

Further tests were carried out at both 5000 & 10000 Pa pressures using 10% CH₄. Deposits

were produced for both pressures; however these deposits showed a thin agglomeration of

390 carbonaceous spheres on the graphite substrate. This difference in form and thickness shows

that growth at higher pressures is not suitable in producing an analogous material for studying

irradiated material. At pressures of 500 Pa with the reduced flow rate the deposit was not

analogous of those found in irradiated material, suggesting that the most representative

deposit is formed at system pressure of 1000 Pa with a 50 cm³ min⁻¹ flow of 10% CH₄:90% Ar.

Growth using ¹³C precursor gas showed a similar topography/morphology to ¹²C deposits 396 indicating that there is no appreciable difference in the growth mechanism between the 397 398 different isotopes, thereby justifying the use of this simulant to study the behaviour of carbonaceous deposits found on irradiated graphite. The clear separation of the deposit and 399 400 underlying graphite shown by isotopic imaging using a MS-SIMS has shown that a deposit is formed, and cross-sectional images indicate that the topography and morphology are very 401 similar to the ones found on irradiated graphite. Catalyst stage Raman spectroscopy 402 combined with TGA have shown these deposits to be of a similar reactivity to those found on 403 irradiated graphite. These deposits appear to be suitable for further studies involving 404 microbial systems to examine the possible release of the deposit into the environment in a 405 geological disposal facility. Based on the thermal oxidation behaviour, the density difference 406 in the surface deposit materials between irradiated and simulant samples does not appear to 407 significantly influence observed reactivity. With the surface layers exhibiting rapid 408 degradation at much lower temperatures than the underlying graphite. 409

410 **5.** Conclusion

411 Carbonaceous ¹²C and ¹³C deposits were formed on Pile Grade A graphite using microwave
412 plasma deposition and examined using Focused Ion Beam, Scanning Electron Microscopy
413 and Magnetic Sector-Secondary Ion Mass Spectrometry. Several conclusions can be drawn:

- The surface topography of both ¹²C and ¹³C deposits formed by MPCVD are very
 similar to the 'cauliflower-like' deposits found on graphite samples trepanned from a
 Magnox reactor.
- 417 2. Deposits formed at 1000 pa system pressure with a 50 cm³ min⁻¹ flow of 10% 418 CH_4 :90% Ar showed the closest resemblance to the deposits on the irradiated 419 material.
- 3. The internal morphology of the deposit is slightly more porous than that found in
 irradiated graphite. However, variations in methane concentrations and gas pressure
 can affect the density of deposited material.

To summarise, there is a potential use of the ¹³C containing deposits synthesised in this work
to act as simulants in future studies aimed at better understanding and predicting the post-

425 disposal behaviour of irradiated graphite waste in a geological disposal environment and the 426 associated release profile of 14 C arising from the labile deposit.

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