This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier’s archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright
Biomolecular characteristics of an extensive tar layer generated during eruption of the Soufrière Hills volcano, Montserrat, West Indies

Ian D. Bull a,*, Heike Knicker b, Natacha Poirier a, Helen C. Porter a, Andrew C. Scott c, Robert S.J. Sparks d, Richard P. Evershed a

a Organic Geochemistry Unit, Bristol Biogeochemistry Research Centre, School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, UK
b Lehrstuhl für Bodenkunde, TU München, D-85350 Freising-Weihenstephan, Germany
c Department of Earth Sciences, Royal Holloway, University of London, Egham, Surrey, TW20 0EX, UK
d Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queen’s Road, Bristol BS8 1RJ, UK

A R T I C L E   I N F O

Article history:
Received 27 July 2007
Received in revised form 30 March 2008
Accepted 21 April 2008
Available online 30 April 2008

A B S T R A C T

On December 26th, 1997, a violent pyroclastic density current (PDC), resulting from an eruption of the Soufrière Hills volcano, occurred on the island of Montserrat. About 4 km² of the area devastated by the PDC was covered partially by a blackened tar layer, of about 1–4 mm depth. Organic geochemical evidence strongly supports the hypothesis that the tar layer was created from soil and associated vegetation, probably in the form of a combustion cloud generated by the PDC. Vegetation, soil and tar were investigated using solid state 13C nuclear magnetic resonance spectroscopy (NMR), reflectance microscopy and scanning electron microscopy (SEM) to provide a general overview of the organic matter (OM) composition and morphology. Parallel investigations of the lipid, carbohydrate and lignin contents using gas chromatography (GC) and GC–mass spectrometry (GC/MS) were also undertaken. Solid state 13C NMR revealed that the majority of the OM in both vegetation (70%) and soil (40%) was cellulose and hemicellulose, with the remainder comprising predominantly aromatic, N-alkyl/methoxyl and alkyl structures. Contrastingly, the two tar layers were shown to be composed of 44% and 52.5% aromatic moieties, attesting to their thermogenic origin. Analysis of solvent extractable lipids revealed an n-alkane distribution in the tar layer that correlated with those observed for the vegetation and soil, maximising at C33. Moreover, a higher relative abundance of the C22 and C32 n-alkanols was observed in the same tar layer compared with that obtained from the soil. This indicated that both vegetation and soil were major contributors of OM to the tar layer. Overall, the two tar layers were shown to contain lipids in differing states of preservation, indicating a higher temperature of formation for one of the layers, resulting from large, local temperature variation within the PDC. Analysis of total hydrolysable carbohydrates confirmed the large loss of these components in the tar layers, corroborating the information obtained from 13C NMR. This almost total loss of carbohydrates and concomitant increase in aromatised components in the tar layers is indicative of a PDC temperature >325°C. CuO oxidation afforded lignin derived products for each sample, the relative distributions of which revealed that significant oxidation had occurred in the tar layers. Further information obtained from the tar layers using reflectance spectroscopy enabled the minimum temperature of the PDC to be constrained to 325–370°C, possibly rising as high as 425°C.

1. Introduction

Montserrat is a mountainous volcanic island of ca. 100 km², located in the eastern Caribbean chain of islands...
at ca. 16°45' North and 62°10' West. There are four volcanic centres, of which the only active one is the Soufrière Hills, at over 900 m (Harford et al., 2002). The volcanic event of December 26th, 1997 occurred when the flank rocks of the edifice and dome talus on the southwestern side failed, as a result of hydrothermal weakening of the edifice rocks, generating a debris avalanche with an estimated volume of $46 \times 10^6 \text{ m}^3$ (Sparks et al., 2002). The avalanche was followed by a volcanic blast, initiated by disintegration of the pressurised lava dome. The blast generated a pyroclastic density current (PDC) that covered and devastated 10 km$^2$ of southern Montserrat (Fig. 1). A PDC is a flow consisting of a mixture of hot volcanic particles, volcanic gas and air generated by either a volcanic explosion or the collapse of a dome of lava. Such flows travel across the ground at typical speeds of tens of metres per second. Much of the area (~4 km$^2$) was covered with a black tar layer 1–4 mm thick (Fig. 1). Investigation of the layer indicated that it formed over a surface that had been already striated and grooved prior to its deposition (Sparks et al., 2002). The tar had skid marks and was buried by local proximal deposits of the PDC. Blocks protruding above the striated surface were also covered in tar which was locally eroded by a later more energetic current. Sparks et al. (2002) postulated that a cloud of heated organic material had combusted to form the tar layer nearly synchronously as the hot current inundated the area. The temperature of the ash clouds from other PDCs on Montserrat have been directly measured from temperature patches to be in the range 200 to $>300\,^\circ\text{C}$ (Cole et al., 2002). There are no such direct measurements for the PDC of December 26th, 1997, but a temperature of 138 °C was measured in the PDC deposit 4 days after the eruption (Cole et al., 2002).

Thermal transformation of OM is a topic that has attracted much interest, although the original driving force for the majority of the work was the study of petroleum generation (Peters et al., 2005a,b). Such changes take place naturally over a geological time scale, with the onset of catagenesis usually occurring around 100 °C (Killops and Killops, 2005). There are no such direct measurements for the PDC of December 26th, 1997. The temperature of 138 °C was measured in the PDC deposit 4 days after the eruption (Cole et al., 2002).

Thermal transformation of OM is a topic that has attracted much interest, although the original driving force for the majority of the work was the study of petroleum generation (Peters et al., 2005a,b). Such changes take place naturally over a geological time scale, with the onset of catagenesis usually occurring around 100 °C (Killops and Killops, 2005). Thermal alteration of soil organic matter (SOM) is outlined briefly here, with a more comprehensive review having been given by González-Pérez et al. (2004). Studies relating to rapid, thermally mediated (e.g. bush-fires, lava flows) changes in the OM of contemporary terrestrial environments are comparatively few in number. The consequences of thermal exposure for SOM depend directly upon the initial biogeochemical composition of the soil and the length of time of heating (Shindo and Urabe, 1993). Additional factors include the nature of the heat source (canopy or aboveground/underground fires) and its intensity and topography. Such exposure can result in almost total destruction to an increase of up to 30% in the OM in surficial soils due to OM input from overlying vegetation (Chandler et al., 1983). Such contributions have
also been observed by DeBano et al. (1970, 1976) who reported an increase of over six times in the amount of lipid extracted from soil under Pinus Pinea after a forest fire. This was attributed to the vaporization of hydrophobic components followed by migration to, and condensation in, the underlying cooler soil layers. Interestingly, studies using \(^{13}C\) NMR to investigate fire induced changes to OM in forest soils have observed enrichment of aliphatic (and aromatic) C structures in fire affected soils (Czimczik et al., 2003; Knicker et al., 2005a). Aboveground heating results in a thermal gradient through the upper soil layer, with temperatures reaching 200 °C at 1 mm depth dropping to ambient temperature at only 2–3 cm depth having been observed under wildfire conditions (Humphreys and Craig, 1981). Soil raised to the approximate ignition temperature of SOM (220 °C; Salgado et al., 1995) exhibits extensive loss of the more thermally labile holocellulose (comprising predominantly cellulose and hemicellulose) and ‘fulvic acid’ fractions, with a smaller loss of the lignin fraction and lipid components. Temperatures >300 °C result in further structural changes, primarily decarboxylation of soil biomacromolecules and an increase in the relative amount of aromatic structures (Almendros et al., 1990, 1992; Knicker et al., 1996). At 325 °C cellulose begins to break down, resulting in loss of the carbohydrate fraction and, with further heating to 350 °C, such losses are greater still for all biogeochemical fractions except lipids (Pyne et al., 1996; Fernandez et al., 2001). Studies of cellulose burning have shown that temperatures <300 °C result in char formation whilst temperatures >300 °C yield tarry anhydrosugars (e.g. levoglucosan) and volatile products (Simoneit, 2002). Source apportionment on the basis of volatile organic compounds present in smoke was proven to be a successful means of assessing the combustion of terrestrial OM (e.g. Simoneit et al., 1993, 1999; Nolte et al., 2001; Simoneit and Elias, 2001; Simoneit et al., 2001). However, whether the same suite of compounds is equally useful for making an assessment of residual OM, following exposure to a PDC, is not known. Certainly, the resistance of certain types of SOM such as lipids is heavily dependent on their interaction with other soil components and can result in enhanced thermal stability for mineral-associated components of up to 500 °C before volatilisation (Schulten and Leinweber, 1999). More recently, lipids (n-alkanoic acids, n-alkanes, n-alkanols, phytoestrogens and triterpenoids) have been shown to provide a useful means of identifying single or multiple inputs of plant matter to soils via thermal and biological processes (Oros et al., 2002). It is the inherent stability of lipids in the soil environment, combined with their diagnostic value for the identification of OM sources, that makes them a potential proxy for determining the origin of the residual tar layer found on Montserrat.

This investigation utilises a suite of analytical techniques including solid state \(^{13}C\) NMR, reflectance microcopy, SEM, GC and GC/MS to provide a comprehensive characterisation of the OM in the residual tar layer discovered on Montserrat. Through analysis of whole OM and its primary constituents (lipsids, carbohydrates, lignin) in both the tar and its putative sources, i.e. the local vegetation and soil, we test the hypothesis that the tar layer was formed by the combustion of these materials. Furthermore, any constraints on the temperature of the PDC that may be made on the basis of the results are evaluated.

2. Experimental procedures

2.1. Sample collection

Tar layers were collected 4 days after the eruption (i.e. 30th December 1997) from the Montserrat Volcano Observatory at two locations numbered 342 and 662 (Fig. 1). Sample 342 was obtained from a carbonised tar layer below the Boxing Day Deposits, collected from a locality above Morris’ whilst sample 662 was collected from a tar striated surface from the Morris’ area at a locality just in front of the debris avalanche. Tar layers were sampled as individual samples measuring about 5 × 5 cm in area in the top 5–8 mm of the soil section at each site. Surficial soil (~2 kg) and vegetation were obtained from an area close by, unaffected by the PDC. The vegetation comprised a representative mixture of grasses likely to have been growing around locations 342 and 662. Both soil and vegetation were homogenised separately and a sub-sample of each taken for analysis.

2.2. Lipid extraction and isolation

Lipid extraction and isolation were performed using a modification of a protocol reported previously by Bull et al. (1999). All samples were freeze dried, partially crushed with a pestle and mortar and sieved through a 2 mm grating. Soil, vegetation (grass) and the tar layers were extracted for 24 h in a Soxhlet apparatus using CH₂Cl₂/acetone (9:1 v/v) to obtain a total lipid extract (TLE). A mixture of internal standards comprising heptadecanoic acid (152 ng µl⁻¹), preg-5-en-3β-ol (220 ng µl⁻¹), hexadecylacetate (72 ng µl⁻¹) and hexadecan-2-ol (157 ng µl⁻¹) was added to each TLE. The relative concentration of each standard had been determined previously to parallel that of the compound classes typically observed in soil and vegetation samples. The amount of internal standard added to each TLE was ca. 10 µg µl⁻¹. Residual solvent was removed from the TLE under reduced pressure and the extract transferred to a vial using CH₂Cl₂/isopropanol (1:1 v/v), evaporated under a gentle stream of N₂ and stored in a freezer.

All four TLEs were separated into a neutral lipid and a free fatty acid (FFA) fraction using aminopropyl solid phase extraction cartridges (Phenomenex) pre-cleaned with 2:1 (v/v) CH₂Cl₂/isopropanol. TLEs were loaded using 2:1 (v/v) CH₂Cl₂/isopropanol (3 × 1 ml). The neutral lipid fraction was eluted with 2:1 CH₂Cl₂/isopropanol (8 ml) and the FFA fraction was eluted using 2% acetic acid in diethyl ether (v/v) CH₂Cl₂/isopropanol. The fraction was loaded using 2:1 (v/v) CH₂Cl₂/isopropanol (8 ml) and MeOH (4 ml) to give fractions nominally...
named ‘hydrocarbon’, ‘aromatic’, ‘ketone/wax ester’, ‘alcohol’ and ‘polar’, respectively. Residual solvent was removed from all fractions under a gentle stream of N₂. Additional separation of the acyclic and cyclic alcohols was achieved using urea addition of the ‘alcohol’ fraction, resulting in two fractions, one containing predominantly n-alkanols and the other sterols. This was achieved by dissolving the ‘alcohol’ fraction in acetone (0.5 ml) and hexane (1 ml), and transferring it to a culture tube. A solution of saturated urea in MeOH (1 ml) was added, with vortex mixing, followed by centrifugation at 2000 rpm for 5 min. The upper, non-adduct solution was transferred to another culture tube and the process repeated to ensure that a higher proportion of cyclic alcohols was separated from the n-alkanols. The adduct (predominantly n-alkanols) was washed with CH₂Cl₂ (1 ml); this process was assisted by use of an ultrasonic bath for 5 min. Urea was removed and organic components isolated, for both the adduct and non-adduct, by partitioning between CH₂Cl₂ (1 ml) and doubly distilled water (DDW; 2 ml) followed by centrifugation at 2000 rpm for 10 min and removal of the lower CH₂Cl₂ layer. The extraction was repeated and both CH₂Cl₂ layers were combined. Finally, the CH₂Cl₂ solution was passed through an anhydrous Na₂SO₄ column to ensure that no water was present. Residual solvent was removed from both fractions under a gentle stream of N₂. All fractions were stored in a freezer, to minimise decomposition, until required for analysis.

2.3. Carbohydrate analysis

Monosaccharides were obtained by hydrolysing the solvent extracted sample. The solvent extracted samples were hydrolysed in evacuated ‘O’ ring tap reaction tubes with PTFE screw cap closures (J. Young Scientific Glassware Ltd., Windsor, UK) in 12 M sulfuric acid (200 μl) for 1 h at room temperature. The tubes were periodically vortex mixed. Samples were then diluted to ca. 1 M sulfuric acid with DDW and heated for 2.5 h at 100 °C. The supernatants were decanted, filtered and neutralised with aqueous NH₃ solution (18 M) and an internal standard, pentaerythritol (10 mg ml⁻¹), added (10 μl).

2.4. CuO oxidation

The lignin composition of the soil, vegetation and tar layers was characterised using an alkaline CuO oxidation method adapted from Hedges and Ertel (1982). A sub-sample of the solvent extracted soil (ca. 20 mg of dried vegetable and ca. 1 mg of soil/tar layer) was held in a mini bomb with powdered CuO, ammonium iron (II) sulfate hexahydrate and 2 M NaOH, 1:0.1:0.7 w/w/v, under a N₂ atmosphere for 3 h at 170 °C. After cooling, ethyl vanillin was added as internal standard (200 μl). The supernatant was transferred for extraction, the residue washed with 1 M sodium hydroxide and the wash added to the supernatant. The combined supernatant/wash was acidified to pH 1 with 6 M HCl (ca. 6.5 ml). Oxidation products were extracted (×3) with diethyl ether from the aqueous supernatant. The extract was dried on a MgSO₄ column and the solvent removed under reduced pressure.

2.5. Derivatization

Prior to GC and GC/MS, all fractions, except the ‘hydrocarbon’ and monosaccharide fractions, were derivatized by heating aliquots with 30 μl N,O-bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane, at 70 °C for 1 h to convert alcohols and carboxylic acids to trimethylsilyl ethers and esters, respectively. Excess reagent was removed under a gentle stream of N₂ and hexane added prior to analysis. Monosaccharides were reduced to alditols by reaction with 2 ml of NaBH₄ solution (2 g in 100 ml dimethyl sulfoxide; 40 °C, 90 min). Excess NaBH₄ was destroyed by addition of 0.2 ml glacial acetic acid. The alditols were acetylated by reaction with 0.2 ml N-methylimidazole and 1 ml acetic anhydride. Excess acetic anhydride was destroyed by addition of 5 ml water and the alditol acetates were recovered by extraction with 2 ml diethyl ether. After drying over MgSO₄, the diethyl ether was evaporated under a stream of N₂ and the alditol acetates dissolved in 0.2 ml CH₂Cl₂ prior to instrumental analysis.

2.6. Instrumental analysis

2.6.1. Solid state ¹³C NMR

Solid state ¹³C NMR spectra were obtained using a Bruker DSX 200 operating at a ¹³C resonance frequency of 50.3 MHz using zirconium rotors of 7 mm outer diameter with KEL-F-caps. The cross polarization magic angle spinning (CPMAS) technique was applied during magic angle spinning of the rotor at 6.8 kHz. A ramped ¹H-pulse was used during the contact time in order to circumvent spin modulation of Hartmann-Hahn conditions (Peersen et al., 1993; Cook et al., 1996). Pulse delays were 1 s for plant material and 300 ms for soil and tar. The chemical shifts are given relative to tetramethylsilane (0 ppm) and were calibrated with glycine (176.04 ppm). The occurrence of spinning side bands was corrected for after Knicker et al. (2005a). Prior to analysis, the soil and tar layers were treated (×5) with 10% HF to concentrate the OM and remove any paramagnetic material (Knicker et al., 2005a). Quantification was made after dividing each spectrum into different chemical shift regions according to Knicker and Lüdemann (1995). The regions from 245 to 185 ppm and 185 to 160 ppm are assigned to carboxyl and carboxyl/amide C. Between 160 and 110 ppm, resonance lines of olefins and aromatic C are detected. In the spectra of unburned soil OM or plant residues, O-alkyl and N-alkyl C signals give rise to the intensities between 110 and 60 ppm and from 60 to 45 ppm. Resonances from alkyl C are expected between 45 and 0 ppm. Owing to insufficient averaging of the chemical shift anisotropy at a spinning speed of 6.8 kHz, spinning side bands (SSBs) from the aromatic C signals occurred at a frequency distance of the spinning speed at both sides of the central signal (300–245 ppm and 0 to –50 ppm). The SSBs of the carboxyl signal are attributed to the intensity of the chemical shift region between 325 and 300 ppm and between 45 and 0 ppm. Their contributions were considered by adding their intensities to that of the parent signal as described by Knicker et al. (2005a).
Most solid state $^{13}$C NMR data used in the field of organic geochemistry are acquired using the cross polarization technique where the sensitivity is increased by magnetization transfer from $^1H$ to $^{13}$C spins. The efficiency of this transfer decreases, if the distance between the $^{13}$C and the next proton exceeds three bonds and the respective $^{13}$C-intensities have been found to be underrepresented (Smernik et al., 2002). Conversely, comparison of CPMAS and Bloch Decay NMR spectra of peat charred with increasing temperature under a $N_2$ atmosphere exhibited no appreciable $^{13}$C intensity loss of the aromatic signal due to inefficient cross polarization differences until 500 °C (Freitas et al., 1999). Recent analyses have further demonstrated that for most charcoal the atomic H:C ratio is greater than 0.4, so the protonation is extensive enough to enable the generation of reliable NMR data (Knicker et al., 2005b). In contrast to the former spin counting experiments, indicating that only little carbon can be observed with the CPMAS technique (Smernik et al., 2002), new studies in which charcoal was mixed with peat in defined proportions showed comparable signals relating to pyrogenic and non-pyrogenic OM (Knicker et al., 2005b).

2.6.2. Reflectance microscopy

Soil samples were embedded in resin and polished. Polished blocks were examined in reflected light under oil using the technique of Scott and Glasspool (2005), and random reflectance measured. Reflectance ($R_0$) was measured under a Nikon Microphot microscope using Leica QWin image analysis software. Specimens were measured under Cargill immersion oil (refractive index 1.518 at 23 °C) using a 40× objective lens. Four standards were used, cubic zirconium ($R_o$ 3.188), GGG ($R_o$ 1.7486), YAG ($R_o$ 0.929) and Spinel ($R_o$ 0.393). The light source was a Nikon fibre optic LS-101 with a 546 nm filter. Depending on the number of charcoal particles present, between 25 and 100 points were measured and the mean reflectance calculated.

2.6.3. SEM

Sub-samples of all specimens were macerated in HF to release OM and sieved at 180 μm. Plant fragments were picked and embedded in resin and polished, and some specimens were mounted on stubs using disks of double sided tape. Using a Polaron Coating unit E5100, all samples were gold coated to ~50–150 nm thickness and examined using a Hitachi S-3000 scanning electron microscope.

2.6.4. GC/MS

GC was performed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with on-column injector. Chromatography was performed using a fused silica column: Varian-Chrompack CPSil-5CB (50 m × 0.32 mm i.d. × 0.12 μm film thickness; He carrier gas). The oven temperature program was: 40°C for 1 min, ramp to 200°C at 10°C min⁻¹, to 300°C at 3°C min⁻¹, hold 20 min (lipid analysis); 40°C for 1 min, ramp to 200°C at 20°C min⁻¹, to 240°C at 4°C min⁻¹, hold 10 min (lignin analysis). An SGE BPX70-70 column (25 m × 0.32 mm × 0.25 μm film thickness; H₂ carrier) was used for monosaccharide analysis and the oven programme was: 50°C for 1 min, ramp to 200°C at 20°C min⁻¹, to 240°C at 4°C min⁻¹, hold 10 min. The flame ionisation detector was maintained at 300°C. GC/MS was performed using a ThermoFinnigan TraceMS equipped with a programmable temperature vaporising (PTV) injector configured for splitless operation. The columns and the oven temperature programmes were the same as those used for GC. The ion source was maintained at 200°C and the transfer line at 300°C. The emission current was set to 150 μA and the electron energy to 70 eV. The analyser was set to scan m/z 50–850 with a scan cycle time of 0.8 s.

3. Results

3.1. Solid state $^{13}$C NMR

The spectra of the four samples are displayed in Fig. 2 and the integration results, based on the chemical shift regions for the different carbon environments (Knicker et al., 2005a), are listed in Table 1. The spectrum for the vegetation comprises two predominant peaks in the region ascribed to O-alkyl C (110–60 ppm) and is responsible for 69.3% of the total $^{13}$C intensity, with the aromatic C (12.2%; 160–110 ppm), N-alkyl/methoxyl C (7.4%; 60–45 ppm) and alkyl C (8%; 45–0 ppm) regions generating the remainder. The soil spectrum also exhibits a large signal (43% of the total) in the O-alkyl C region. However, a greater component of the total signal intensity results from carbon in other environments, namely carboxyl/amide C (8.8%; 185–160 ppm), aromatic C (15.0%), N-alkyl/methoxyl C (10.8%) and alkyl C (23.1%). In contrast, tar layer 342 is characterised by a dominant peak in the aromatic C region, accounting for 44% of the total intensity, whilst the remaining intensity is ascribed to carboxyl/amide C with 10.9%, O-alkyl C with 11.2% and a relatively large amount of alkyl C with 23.7%. This difference is even more pronounced for tar layer 662, where 52.5% of the carbon is assignable to aromatic C, leaving 7.7% to carbonyl C, 9.8% to carboxyl/amide C, 9.9% to O-alkyl C and 16.7% to alkyl C.

3.2. Reflectance microscopy

Tar layer 342 contains very small charred plant fragments, including rootlets. However, none of the material is taxonomically identifiable, although the presence of herbaceous angiosperm rootlets appears likely. Small charred angiosperm rootlets and small charred woody fragments afforded a mean reflectance value of 1.16 $R_o$ with a maximum of 1.46 $R_o$. Tar layer 662 contains occasional herbaceous angiosperm axes and roots of varying reflectance, with a mean value of 0.72 $R_o$, although the maximum reflectance recorded was 1.77 $R_o$.

3.3. SEM

Charcoaled plant fragments in both the samples showed excellent anatomy as observed using SEM (e.g. Fig. 3a) with a range of preservation, with the plant cell walls showing evidence of homogenization (e.g. Fig. 3b) that is typical of plants charred to temperatures over 325°C (Scott, 2000). Reflectance measurements supported...
the view of temperatures in excess of 325 and up to 425 °C (Scott et al., 2008).

3.4. Biomolecular composition

3.4.1. Straight chain alkanes

Fig. 4 shows partial gas chromatograms of the hydrocarbon fractions derived from Montserrat vegetation, soil, tar layer 342 and tar layer 662. The vegetation yields a monomodal distribution with n-alkanes ranging from C23 to C37, maximising about C33, with a carbon preference index (CPI) value of 5.48 (Fig. 4a). The soil distribution shows a strong correlation with the vegetation one (Pearson coefficient 0.97), with a maximum about C33 and a CPI of 4.87. There are, however, some minor differences between the peripheral homologues, with the overall distribution in the soil having a wider carbon number range from C20 to C35 (Fig. 4b). The n-alkane distribution of tar layer 342 is also dominated by C31 and C33 (Fig. 4c), correlating well with the major n-alkanes of the vegetation and soil (Pearson coefficients 0.92 and 0.94, respectively). However, tar layer 342 displays a wider, bimodal (maxima at C18 and C33) distribution ranging from C15 to C36 and with a CPI of 8.24. In addition, the branched compounds pristane and phytane are present. Tar layer 342 also exhibits two distinct ‘humps’ upon which the aforementioned components are superimposed. The distribution for tar layer 662 (Fig. 4d) predominantly shows homologues ranging from C16 to C20, with minor peaks in the range C27 to C35, resulting in a CPI of 1.53. As noted for tar layer 342, pristane and phytane are present but there is now only a single distinct ‘hump’ on which all of the compounds are superimposed.

3.4.2. Straight chain alcohols

Information relating to the n-alkanol, n-alkanoic acid, carbohydrate and lignin components is summarised in Table 2. The vegetation n-alkanols range from C17 to C34, with a limited bimodal distribution centred about C22 and a dominant C32 homologue, resulting in a CPI of 0.07. The total concentration of n-alkanols at 2.81 mg g\(^{-1}\) TOC is the highest of the four samples. The soil has a comparatively more complicated distribution ranging from C13 to C34. Again the distribution is bimodal, with the C22 and C32 components present at greatest concentration, although the difference is not nearly as pronounced, with peripheral homologues occurring at almost the same level, resulting in a slightly higher CPI of 0.09. The total concentration of soil n-alkanols, at 1.00 mg g\(^{-1}\) TOC, is about a third of the amount determined for the vegetation. Tar layer 342 has the widest distribution of the four samples, ranging from as low as C18 to C20, with minor peaks in the range C27 to C35, resulting in a CPI of 0.22. As noted for tar layer 342, pristane and phytane are present but there is now only a single distinct ‘hump’ on which all of the compounds are superimposed.

Fig. 2. Solid state \(^{13}\)C NMR spectra of: (a) vegetation, (b) soil, (c) tar layer 342 and (d) tar layer 662. Chemical shift assignments (ppm) for different carbon environments are: carbonyl 245–185, carboxyl/amide 185–160, aromatics 160–110, O-alkyl 110–60, N-alkyl/methoxyl 60–45, alkyl 45–0.
3.4.3. Straight chain alkanoic acids

The vegetation \(-\)alkanoic acids have a fairly wide monomodal distribution ranging from C9 to C28 with a clear maximum at C16. There is also a relatively high abundance of unsaturated components, predominantly C18:1 and C18:2, while components >C20 are present in very low abundance relative to the other homologues, although a CPI of 0.31 was calculated. The total \(-\)alkanoic acid concentration is surprisingly low at 0.42 mg g\(^{-1}\) TOC. In contrast, the soil distribution is more complex, with a bimodal distribution from C12 to C32 maximizing at C16 and C24. In addition to a similar occurrence of unsaturated components, \(\alpha\)-C15 and \(\beta\)-C15 acids are present, as are a series of \(\omega\)-hydroxy alkanoic acids ranging from C24 to C30. In this case, the summed concentration of all components is 6.71 mg g\(^{-1}\) TOC. Tar layer 342 \(-\)alkanoic acids range from C9 to C32, with a bimodal distribution maximizing at C16 (predominant) and C24 (much less pronounced). Of particular note is the low concentration of homologues >C18 and a near total absence of unsaturates. The \(i\)-C15 and \(\alpha\)-C15 acids are again present in low abundance, as is a C24 \(\omega\)-hydroxy acid. The total concentration of all components is 1.41 mg g\(^{-1}\) TOC. A narrower, less complicated distribution of \(-\)alkanoic acids is observed for tar layer 662, ranging from C9 to C24 and bimodal about C12 and C16; homologues >C18 are present at trace levels only. The total concentration of \(-\)alkanoic acids is 3.15 mg g\(^{-1}\) TOC, over double that of tar layer 342.

3.4.4. Hydrolysable carbohydrates

The monosaccharides liberated by acid hydrolysis of the lipid-free vegetation residue comprise five components at an appreciable level: arabinose, xylose, glucose, mannose and galactose, with the former three the major constituents (total concentration 768 mg g\(^{-1}\) TOC). The ratio of mannose to xylose is 0.03. The soil monosaccharides contain all these components, along with fucose, although galactose, glucose, arabinose and mannose are now the predominant compounds. The total concentration of monosaccharides, at 38.7 mg g\(^{-1}\) TOC, is greatly reduced vs. the vegetation and the ratio of mannose/xylose value is 1.79. Only one monosaccharide, galactose, is observed for tar layer 342, with a concentration of 0.93 mg g\(^{-1}\) TOC. Tar layer 662 affords three monosaccharides: fucose, rhamnose and glucose although, at 4.95 mg g\(^{-1}\) TOC, the total concentration of these compounds is very low.

3.4.5. Lignin oxidation products

CuO oxidation affords lignin derived products for all four samples, with total identified component yields of 25.9 mg g\(^{-1}\) TOC for the vegetation, 0.25 mg g\(^{-1}\) TOC for the soil, 0.04 mg g\(^{-1}\) TOC for tar layer 342 and 0.03 mg g\(^{-1}\) TOC for tar layer 662. Syringyl to vanillyl and cinnamyl to vanillyl ratio values for the vegetation sample are 1.0 and 0.41, respectively, and 0.7 and 0.43, respectively, for the soil; the lack of syringyl and vanillyl moieties as products from tar layers 342 and 662 makes the ratio irrelevant for these two samples. Acidic to aldehydic phenol ratio values [(ac/al)v] may also be calculated for the lignin derived oxidation products. Vanillyl products are generated from all four samples and give acidic to aldehydic phenol values of 0.19, 0.66, 5.3 and 1.5 for the vegetation, soil and tar layers.
342 and 662, respectively. An analogous ratio can also be calculated for the syringyl components for the vegetation and soil, giving values \( [(ac/al)_{a}] \) of 0.19 and 0.24, respectively.

**Fig. 4.** Partial gas chromatograms of hydrocarbon fractions from: (a) vegetation, (b) soil, (c) tar layer 342 and (d) tar layer 662.
4. Discussion

4.1. Origin of the tar layer

$^{13}$C CPMAS NMR provides valuable information concerning the relative importance of different carbon environments in each sample. The predominant signal for the vegetation, interpreted as O-alkyl carbon, may be readily attributed to cellulose and hemi-cellulose (768 mg g$^{-1}$ TOC, total hydrolysable carbohydrate), that together constitute about 70% of the organic carbon in vascular plants (Cresser et al., 1993) and contributions from other O-alkyl bearing structures/peptides (Malcolm, 1989; Preston et al., 1997). Whilst this predominance is largely maintained in the spectrum from the soil, the increase of the relative intensity in the chemical shift regions ascribed to carboxyl/amide, N-alkyl/methoxy and alkyl carbon indicates relatively rapid degradation of plant derived carbohydrate (38.7 mg g$^{-1}$ TOC, total hydrolysable carbohydrate) with a concomitant accumulation of more refractory OM. The spectrum for tar layer 342, in contrast to the vegetation and soil spectra, shows a predominant aromatic signal maximising at 128 ppm, indicative of naturally charred material (Almendros et al., 1992; Knicker et al., 1996; Simpson and Hatcher, 2004; Knicker et al., 2005a,b). The relative intensity of the O-alkyl C signal is now greatly diminished, paralleling the almost total loss of carbohydrate (0.93 mg g$^{-1}$ TOC, total hydrolysable carbohydrate). In addition, there is a more significant alkyl carbon component which correlates with the occurrence of the abundant, unresolved complex mixture (UCM) in the hydrocarbon fraction of this sample. With an integral of over 50% of the signal, aromatic carbon is even more dominant relative to other carbon environments in the spectrum for tar layer 662, attesting to the greater extent of thermal alteration undergone by the OM in this sample (cf. Simpson and Hatcher, 2004).

Charcoaled plant fragments in both samples show a range of preservation, with the cell walls, providing evidence of homogenization that is typical of plants charred to temperatures >325 °C (Scott, 2000). The plants also show evidence of increased reflectance that is typical of charcoalification (Scott and Glasspool, 2005).

The Montserrat vegetation n-alkane distribution is typical of terrigenous higher plants and correlates with those observed in many species of Gramineae (Eglinton and Hamilton, 1967; Maffei, 1996). The Montserrat soil has a similar distribution, indicating that vegetation is a major source of the SOM. The CPI values for both samples are high (5.48 and 4.87, respectively) as expected for modern, terrigenous OM (Bray and Evans, 1961). A vegetation signature may also be observed in the soil n-alkanol distribution, which has the same maximum as the vegetation sample, albeit at lower abundance relative to the peripheral homologues, as reflected in the slightly higher n-alkanol CPI of the soil sample. This preferential loss of the predominant n-alkanol(s) in plant waxes in soils has been observed before, but not explained (Bull et al., 2000). Further evidence supporting the conclusion that the sampled vegetation is the major source of the SOM may be obtained by considering the relative abundance of lignin (a structural component of vascular plants) derived cinnamyl (C), syringyl (S) and vanillyl (V) products generated from CuO oxidation. Previous work has shown that the abundance ratio of S:V may be used to derive information about plant types contributing to an organic input, where S/V = 0 indicates 100% input from gymnosperms (conifers) and S/V > 0 is indicative of an input from angiosperms (deciduous trees, grasses and flowering plants). Furthermore, C/V values may be used to infer inputs of woody vs. non-woody (grasses, leaves and needles) tissue, where C/V = 0 indicates 100% input from woody tissue and C/V > 0 is indicative of an input from non-woody tissue (Sarkinen and Ludwig, 1971; Hedges and Mann, 1979). In this case the S/V (0.7) and C/V (0.43)

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Biomolecule</th>
<th>Description</th>
<th>Concentration mg g$^{-1}$ TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetation</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{24}$, bimodal, max. C$<em>{22}$ and C$</em>{32}$, CPI 0.07</td>
<td>2.81</td>
</tr>
<tr>
<td>Soil</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{32}$, bimodal, max. C$<em>{16}$ and C$</em>{24}$, CPI 0.22</td>
<td>1.47</td>
</tr>
<tr>
<td>Tar layer 342</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{32}$, bimodal, max. C$<em>{16}$ and C$</em>{24}$, CPI 0.07</td>
<td>0.14</td>
</tr>
<tr>
<td>Tar layer 662</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{32}$, bimodal, max. C$<em>{16}$ and C$</em>{24}$, CPI 0.22</td>
<td>6.71</td>
</tr>
<tr>
<td>Vegetation</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{32}$, monomodal, large amount of C$<em>{18}$, and C$</em>{18}$; CPI 0.31</td>
<td>0.42</td>
</tr>
<tr>
<td>Soil</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{32}$, bimodal, max. C$<em>{16}$ and C$</em>{24}$; C$<em>{50}$ to C$</em>{90}$; CPI: trace unknown triterpenoid acids; CPI: n/a</td>
<td>25.9</td>
</tr>
<tr>
<td>Tar layer 342</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{32}$, bimodal, max. C$<em>{16}$ and C$</em>{24}$; C$<em>{50}$ to C$</em>{90}$; CPI: n/a</td>
<td>1.41</td>
</tr>
<tr>
<td>Tar layer 662</td>
<td>n-Alkanoic acids</td>
<td>C$<em>{18}$-C$</em>{32}$, bimodal, max. C$<em>{16}$ and C$</em>{24}$; C$<em>{50}$ to C$</em>{90}$; CPI: n/a</td>
<td>3.15</td>
</tr>
<tr>
<td>Vegetation</td>
<td>Carbohydrate</td>
<td>Fucose (2.20), arabinose (0.83), xylose (0.83), mannose (0.03), galactose (0.20), glucose (1.00); mannose:xylose 0.03</td>
<td>768</td>
</tr>
<tr>
<td>Soil</td>
<td>Carbohydrate</td>
<td>Fucose (0.33), arabinose (0.85), xylose (0.34), mannose (0.61), galactose (1.00), glucose (1.00); mannose:xylose 1.79</td>
<td>38.7</td>
</tr>
<tr>
<td>Tar layer 342</td>
<td>Carbohydrate</td>
<td>Galactose (1.00)</td>
<td>0.93</td>
</tr>
<tr>
<td>Tar layer 662</td>
<td>Carbohydrate</td>
<td>Galactose (1.00)</td>
<td>4.95</td>
</tr>
<tr>
<td>Vegetation</td>
<td>Lignin</td>
<td>Syringyl:vanillyl 1.00, cinnamyl:vanillyl 0.41, (ac/af), 0.19, (ac/af)</td>
<td>25.9</td>
</tr>
<tr>
<td>Soil</td>
<td>Lignin</td>
<td>Syringyl:vanillyl 0.70, cinnamyl:vanillyl 0.43, (ac/af), 0.66, (ac/af)</td>
<td>0.246</td>
</tr>
<tr>
<td>Tar layer 342</td>
<td>Lignin</td>
<td>(ac/af) 5.3</td>
<td>0.04</td>
</tr>
<tr>
<td>Tar layer 662</td>
<td>Lignin</td>
<td>(ac/af) 1.5</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* Values in parentheses refer to relative distribution of hydrolysable carbohydrate (by mass).
* Not measurable.
values quite clearly indicate a majority of non-woody, angiosperm derived OM in the soil (Ertel and Hedges, 1984).

The distribution of the major n-alkanes in tar layer 342 correlates remarkably well with those of the vegetation and soil, indicating that OM from one or both of these constitutes an important component of the sample. The terrigenous signal is retained, although the CPI value (8.24) is high relative to the potential sources and most likely results from some of the components with even chain length below the limit of detection. Investigation of other function-alised acyclic lipids provides additional clarification about the OM source. The tar layer 342 n-alkanols show a wide distribution, as observed for the soil. However, the C_{22} and C_{32} homologues are present in higher abundance relative to the peripheral components than in the soil, indicating that there has also been a contribution from the vegetation, although the CPI indicates a more biodegraded distribution (0.22) relative to the sources (Bray and Evans, 1961). A contribution of OM from the soil is also supported by n-alkanoic acid data for tar layer 342 by way of the co-occurrence of a cutin and/or suberin derived C_{24} homologue (Holloway, 1982; Bull et al., 2000; Nierop et al., 2006) and bacterially derived i-15:0 and a-15:0 alkanoic acid components (Kaneda, 1991) in both the soil and tar layer 342. Due to a total lack of syringyl and cinnamyl products from CuO oxidation, no S/V or C/V values could be obtained. However, the more recalcitrant vanillyl sub-units (Simonet, 2002) afforded a number of products, enabling calculation of \((ac/\text{al})\), values. The value of 5.3 for tar layer 342 is very high, indicating that this sample has been highly oxidised (Ertel and Hedges, 1984). From these data it is concluded that the organic component of tar layer 342 originates from both the vegetation and soil present at the time of the PDC event.

Compared with tar layer 342, the lipid fractions from tar layer 662 contain far less informative suites of compounds from which to deduce the origin of the OM. The hydrocarbon fraction contains no diagnostic signature that may be related back to the vegetation or soil and this is also the case for the n-alkanoic acid fraction. The occurrence of a dominant C_{22} homologue in the n-alkanol fraction could be interpreted as representative of an input from vegetation or soil. However, the predominance of a C_{32} component is not observed. This relative loss of the higher n-alkyl homologues is also observed for the n-alkanoic acid distributions for both tar layer 342 and tar layer 662. This is interpreted as thermally-mediated, destructive loss of the higher homologues, combined with a concomitant release of lower molecular weight components from biomolecules, at higher temperature. This tendency towards a selective decrease in chain length for free alkyl lipids has been observed previously, where it was noted in a study of the effect of fire on the humic and lipid fractions of a Spanish soil (Almendros et al., 1988). Interestingly, the value of 1.5 for the \((ac/\text{al})\) ratio is lower than that for tar layer 342, indicating that tar layer 662 has been oxidised to a lesser extent (Ertel and Hedges, 1984), consistent with a lower concentration of oxygen in the combustion cloud associated with the formation of tar layer 662 (Otto et al., 2006). These data clearly demonstrate that, despite the high temperatures associated with the PDC, a lipid signature, indicative of the original OM source, is still present in tar layer 342 (and possibly tar layer 662), supporting the use of lipids for investigations involving thermally altered material in the natural environment.

4.2. Formation temperature of the tar layer

The temperatures at which tar layer 342 and tar layer 662 were formed are difficult to estimate. The OM composition of the samples will reflect not only the maximum temperature to which they were exposed but also the duration of exposure, the soil moisture content, the oxygen concentration, the original OM composition and any protective or catalytic attributes conferred by mineral components associated with the OM (González-Pérez et al., 2004). The level of heterogeneity in the combustion cloud will also be a significant factor. The increase in abundance of early eluting n-alkanes and the presence of a hump resulting from a large UCM can be observed for both tar layer 342 and tar layer 662. Both features are characteristic of OM as it is thermally degraded, indicating that the organic content of the samples has been subjected to elevated temperatures (Peters et al., 2005a,b). Moreover, the hydrocarbon fraction from tar layer 662 is dominated by a monomodal UCM and low molecular weight components, with no characteristic distribution of long chain n-alkanes, thereby inferring greater thermal degradation (Tissot and Welte, 1984; Almendros et al., 1988). Previous work has shown that the OM in soils heated to high temperature (>300 °C) experiences decarboxylation of soil biopolymers (i.e. humic and fulvic acids) and an increase in the proportion of aromatic structures (Almendros et al., 1990,1992; Knicker et al., 1996). The \(^{13}\text{C}\) CPMAS NMR spectra for tar layers 342 and 662 show a huge increase in the relative proportion of aromatic carbon, indicating that both samples were formed at temperatures >300 °C and that the thermal degradation of the majority of the OM in tar layer 662 is more extensive than that of tar layer 342.

The mean reflectance value for tar layer 342 is higher (1.16) than for tar layer 662 (0.72), with the latter containing less reflecting charcoal material, possibly from further down in the tar layer. These findings are supported by the higher concentration of hydrolysable carbohydrate (presumably from intact roots) observed for tar layer 662 (4.95 mg g\(^{-1}\)\text{TOC}) vs. tar layer 342 (0.93 mg g\(^{-1}\)\text{TOC}). The huge loss of hydrolysable carbohydrate in both samples, relative to the vegetation and soil, enables further constraint on the temperature since cellulose decomposes >325 °C (Pyne et al., 1996). However, the range of reflectance values obtained for tar layer 662 is much wider than that observed for tar layer 342 and the maximum reflectance value of the former (1.77) is higher than for the latter (1.46). Constraints on the emplacement time of the PDC estimate a time of no more than a few minutes, and likely less, for both tar layer 342 and tar layer 662 (Sparks et al., 2002). When viewed together, it can be inferred from the reflectance and molecular analyses that tar layer 662 formed at a higher temperature than tar layer 342 (greater destructive loss/transformation of lipids, higher relative aromaticity of the OM and higher maximum reflectance value), but that heating was more heterogeneous than that
leading to formation of tar layer 342 (wider range of reflectance values). Using the curves constructed by Scott and Glasspool (2005, 2007) these reflectance data indicate minimum temperatures of 325–370 °C and possibly up to 425 °C. The two tar samples were collected close to the major flow axis of the current. The sample with the stronger thermal effects (tar layer 662) was further from the source than tar layer 342 (Fig. 1). Large local temperature fluctuations are to be expected in space and time in such highly turbulent and energetic currents.

5. Conclusions

This study was conducted in order to test the hypothesised origin of, and constrain the temperature of formation of, an extensive ~4 km² tar layer discovered on Montserrat following a violent PDC resulting from the volcanic event of December 26 1997. Along with reference vegetation and soil, the organic content of two tar layers was assessed using solid state ¹³C NMR, reflectance microcopy, SEM, GC and GC/MS. The primary outcomes are:

(a) Distributional and quantitative analysis of extractable lipids (similar distributions and homologue maxima in the vegetation, soil and tar) and lignin moieties (input of non-woody angiosperm derived organic matter) uphold the hypothesis that the major source of organic matter that contributed to the formation of the tar layer was a mixture of local vegetation and nearby soil.

(b) Given the similar heating times as estimated by Sparks et al. (2002), tar layer 662 formed at a higher temperature than tar layer 342, although the dispersion of heat applied to tar layer 662 was more heterogeneous than that experienced by tar layer 342, as evidenced by the wider range of reflectance values determined for tar layer 662.

(c) Solid state ¹³C NMR revealed a greatly increased aromaticity of the organic matter in the tar layer, relative to the vegetation and soil, enabling a minimum temperature of 300 °C to be estimated. By considering the large destructive loss of hydrolysable carbohydrates observed for the tar layer, this was further constrained to a minimum temperature of 325 °C. Furthermore, reflectance data obtained for the tar layer indicated a minimum temperature range of 325–370 °C, thereby corroborating the range predicted by organic geochemical means, although the highest reflectance value obtained corresponds to a possible minimum temperature of 425 °C.

It is envisaged that further constraints on the formation temperature will be possible through future laboratory studies simulating the pyrolytic transformation of the organic matter comprising Montserrat vegetation and soil.

Acknowledgements

The authors wish to thank two anonymous reviewers for constructive comments and the NERC for funding of the mass spectrometry facilities at Bristol (Contract No. R8/H112/15; www.lsmfs.co.uk). ACS acknowledges a grant from the Royal Society to study Montserrat charcoal. This aspect of the work was completed during sabbatical leave at Yale University. Royal Holloway Research Strategy Fund and the Department of Geology and Geophysics at Yale University are thanked for additional funding. ACS thanks N. Holloway for making the polished blocks, S. Gibbons for macerating the samples and P. Goggin of the Electron Microscope Unit for help with SEM. RSJS thanks colleagues at the Montserrat Volcano Observatory and The Royal Society for a Wolfson Merit Award.

Associate Editor—G.D. Abbott

References


