

**Supplemental information**

**Organic geochemistry and mineralogy suggest  
anthropogenic impact in speleothem chemistry  
from volcanic show caves of the Galapagos**

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# *Organic geochemistry and mineralogy suggest anthropogenic impact in speleothem chemistry from volcanic show caves of the Galapagos*

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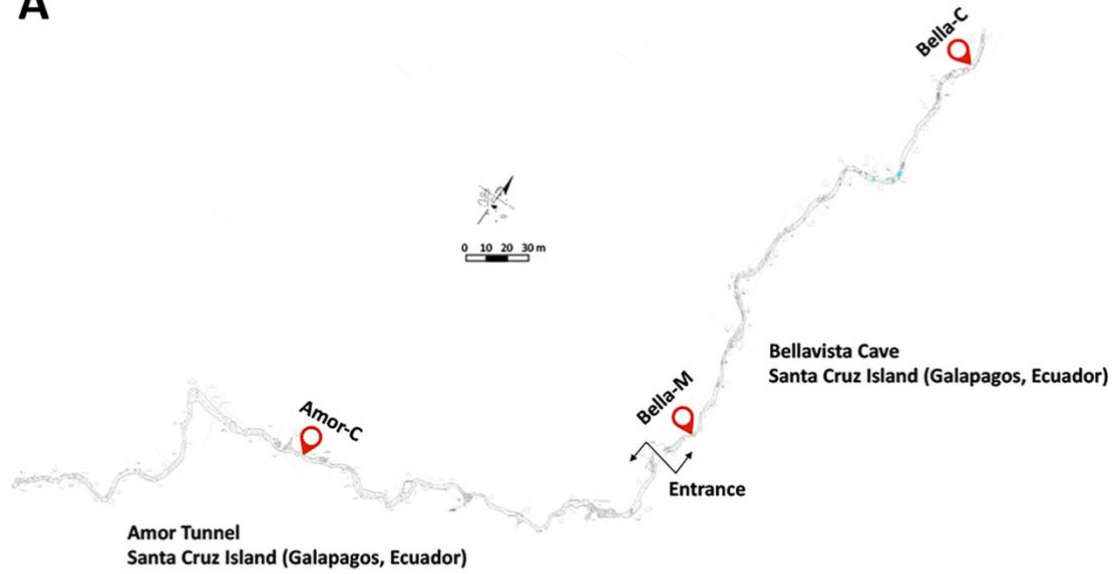
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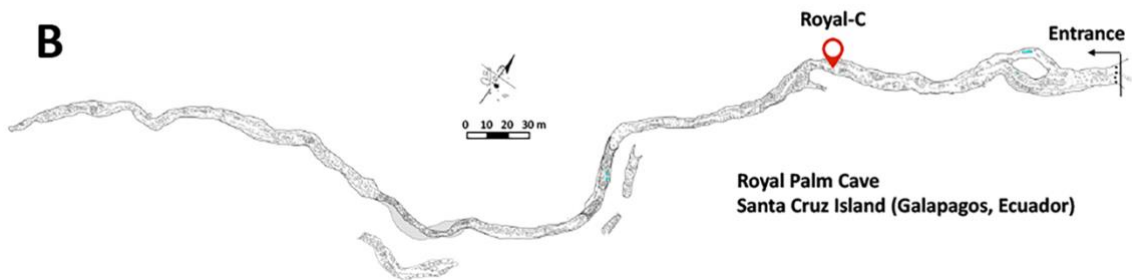
## Supplemental information

### Supplemental Figures

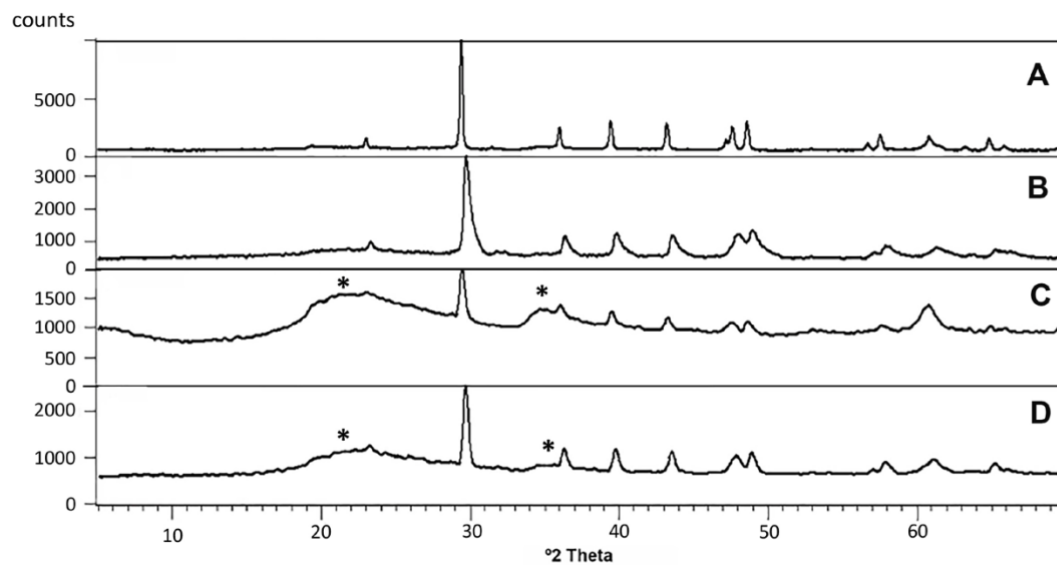
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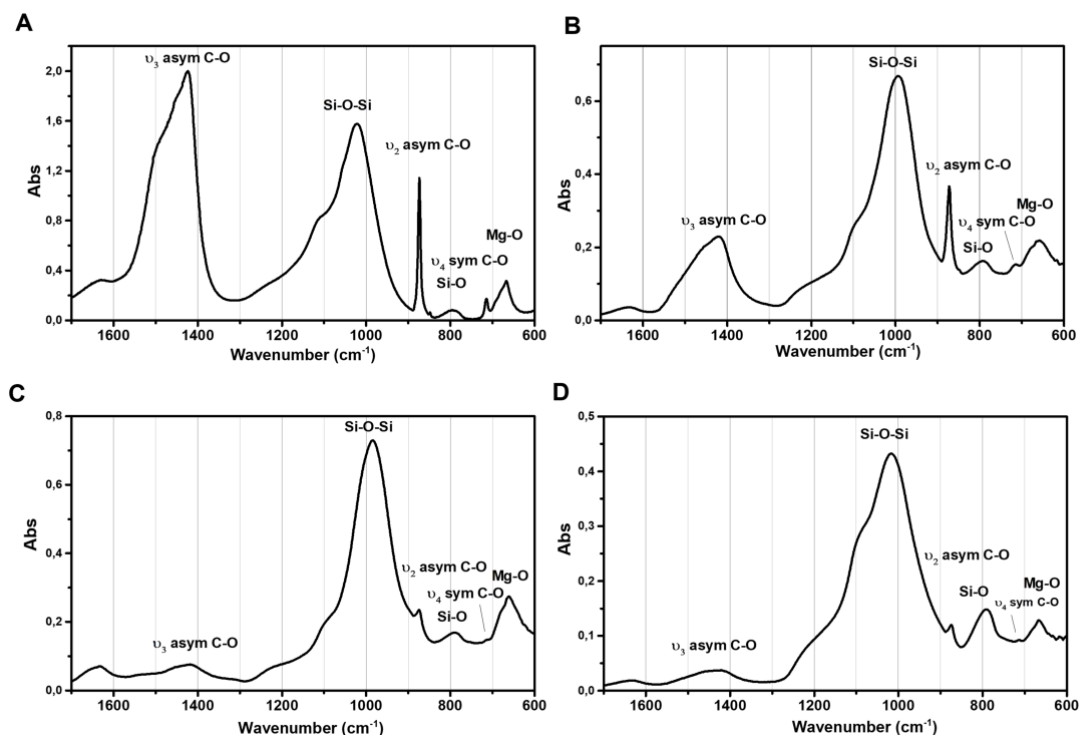
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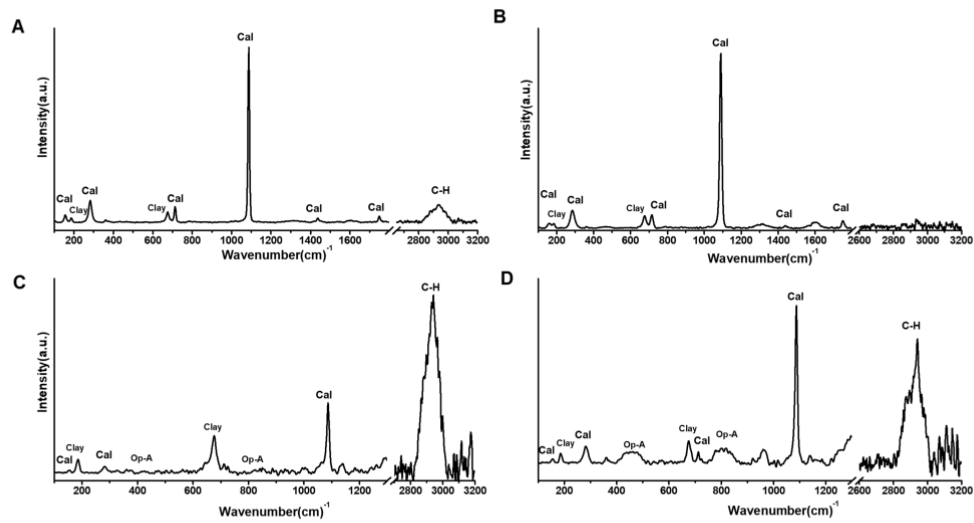
**Figure S1.** Topographical maps of the two lava tubes studied from Santa Cruz Island (Galapagos, Ecuador) with indication of the sampling points: (A) Bellavista Cave and Amor Tunnel section; (B) Royal Palm Cave. Related to STAR Methods.



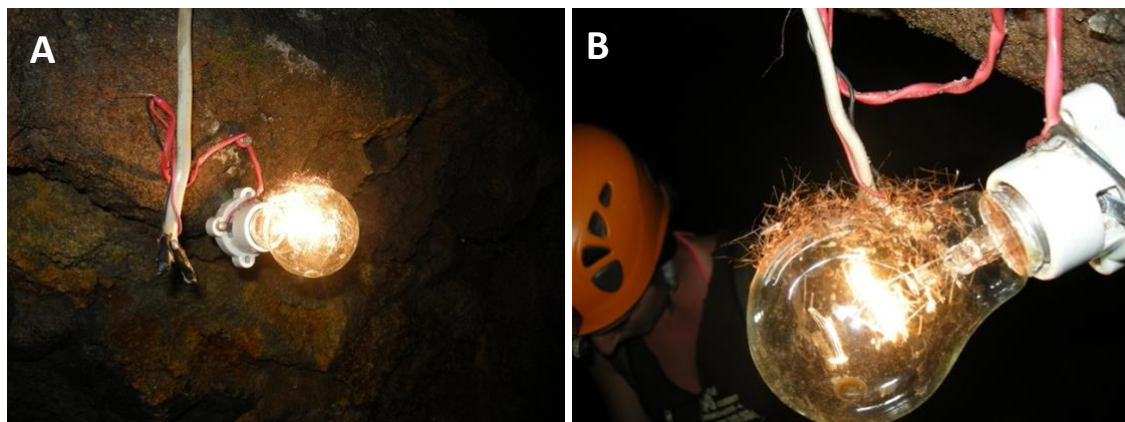
**Figure S2.** X-Ray diffraction patterns of the studied speleothems from lava tubes of Santa Cruz Island (Galapagos, Ecuador): (A) Bella-M (moonmilk); (B) Bella-C (coralloids); (C) Amor-C (coralloids); (D) Royal-C (coralloids); \* – amorphous compound. Related to Figures 1 – 4.



**Figure S3.** Infrared spectra of the studied speleothems from lava tubes of Santa Cruz Island (Galapagos, Ecuador): (A) Bella-M (moonmilk); (B) Bella-C (coralloids); (C) Amor-C (coralloids); (D) Royal-C (coralloids), showing the characteristic IR spectra of calcite, opal-A and magnesium oxide. Related to Figures 1 – 4.



**Figure S4.** Raman spectra of the studied speleothems from lava tubes of Santa Cruz Island (Galapagos, Ecuador): (A) Bella-M (moonmilk); (B) Bella-C (coralloids); (C) Amor-C (coralloids); (D) Royal-C (coralloids). Cal = calcite; Clay = montmorillonite, Op-A = opal-A. Related to Figures 1 – 4.



**Figure S5.** Royal Palm Cave lighting system. A) Electrical system installation; and B) Dead insects on the lamp. Related to Figure 6.

## Supplementary Tables

**Table S1.** Interpretation of band positions in FTIR and Raman spectrum of the speleothems. Related to Figures 1 – 4.

IR (cm <sup>-1</sup> )	Assignment	Possible mineral phase	Speleothem	Ref.	Raman (cm <sup>-1</sup> )	Assignment	Possible mineral phase	Speleothem	Ref.
660-667	Mg-O	Sepiolite	Bella-M, Bella- C, Amor-C, Royal-C	Miller et al. 2014	154-157	Lattice mode calcite	Calcite	Bella-M, Bella- C, Amor-C, Royal-C	Parker et al. 2010
711-716	O-C-O bending (in-plane deformation)	Calcite	Bella-M, Bella- C, Amor-C, Royal-C	Miller et al. 2018	186-188	Lattice mode clay	Clay mineral (montmorillonite)	Bella-M, Bella- C, Amor-C, Royal-C	Wang et al. 2015
791-797	Si-O s-stretch	Opal A	Bella-M, Bella- C, Amor-C, Royal-C	Miller et al. 2014; Sodo et al. 2016	282-286	Lattice mode calcite	Calcite	Bella-M, Bella- C, Amor-C, Royal-C	Parker et al. 2010
870-875	O-C-O bending (out-plane deformation)	Calcite	Bella-M, Bella- C, Amor-C, Royal-C	Miller et al. 2018	674-678	Si-O-Si vibrations	Clay mineral (trioctahedral mineral)	Bella-M, Bella- C, Amor-C, Royal C	Wang et al. 2015
983-1100	Si-O a-stretch (SiO <sub>4</sub> )	Opal A	Bella-M, Bella- C, Amor-C, Royal-C	Miller et al. 2014; Sodo et al. 2016	713-715	Sym. in-plane bending C-O	Calcite	Bella-M, Bella- C,	Parker et al. 2010
1420-1430	C-O a-stretch	Calcite	Bella-M, Bella- C, Amor-C, Royal-C	Miller et al. 2018	800	Si-O-Si vibrations	Opal-A	Amor-C, Royal-C	Dovbeshko et al. 2004, Sodo et al. 2016
					960	Silanol group (Si-OH)	Opal-A	Amor-C, Royal-C	Sodo et al. 2016
					1086-1089	C-O s-stretch	Calcite	Bella-M, Bella- C, Amor-C, Royal-C	Parker et al. 2010
					1318-1435	C-O a-stretch	Calcite	Bella-M, Bella- C,	Parker et al. 2010
					1602-1748	C-O a-stretch	Calcite	Bella-M, Bella- C,	Parker et al. 2010
					2934-2940	C-H vibrations	Organic compounds	Bella-M, Amor6, Royal-C	Howell et al. 1999

**Table S2.** List of compounds identified by Py-GC/MS in speleothem samples. Related to Figure 6.

Family	RT (min)	Name of compound	Bella M %	Bella C %	Amor C %	Royal C %
<b>Alkyl hallogen</b>	8.6684	Alkyl hallogen	-	-	-	+
	9.2939	Alkyl hallogen	-	-	-	+
	10.0207	Alkyl hallogen	-	-	-	+
	10.5678	Alkyl hallogen	-	-	-	+
	10.9051	Alkyl hallogen	-	-	-	+
<b>Aromatic</b>	3.0540	Toluene	++	++	-	-
	3.6307	<i>o</i> -Xylene	-	++	-	-
	3.6935	1,2-Dihydrocatechol	-	-	+	-
	3.7782	Styrene	++	++	+	-
	4.2587	Benzene, 1-ethyl-2methyl	-	-	-	++
	4.4923	Benzene, 1,2,3-trimethyl	+	++	-	+
	5.2083	Benzenamine, 2-methoxy-	-	-	++	-
	5.4155	<i>o</i> -Cymene	+	+	-	-
	5.5271	Benzene, 1,2,4,5-tetramethyl-	++	++	-	++
	5.7315	Benzene, 1-methyl-2-(2-propenyl)	-	+	-	-
	5.8371	<i>p</i> -cymene	++	++	-	++
6.1950	3,4-Dimethylcumene	++	-	-	-	
7.0036	Benzene, pentamethyl	++	+	-	+	
<b>Condensed compound</b>	6.1994	Naphthalene	-	++	-	-
	6.8773	Naphthalene, 1,2-dihydro-6-methyl-	-	+	-	-
	7.2069	Naphthalene, 1-methyl-	-	+	+	+
	7.3765	Naphthalene, 2-methyl-	+	+	-	+
	8.3494	Naphthalene, 1,3-dimethyl-	-	++	-	+
	9.2886	Naphthalene, 2,3,6-trimethyl	-	++	+	-
	10.6747	Chamazulene	-	+	-	-
<b>Lipid</b>	2.0115	Propanal, 2-methyl	+	+++	++	-
	2.0189	2-Pentene, 4-methyl	-	-	-	+
	2.3276	Acetic acid	-	-	++	-
	2.4434	Butanal, 3-methyl	++	+++	+++	-
	2.4457	Cyclopentene, 4-methyl-	-	-	-	++
	2.5845	2-Propanone, 1-hydroxyl	-	-	+	-
	2.6075	Cyclopentane, 1,2-dimethyl	+	-	-	-
	2.6855	3-Hexyne, 2-methyl	-	+++	-	+++
	2.9467	Cyclopropene, 3,3-diethyl	++	+++	-	+++
	3.1727	4-Octene	+	++	-	+++
	3.2849	Heptane, 2,4-dimethyl-	-	++	-	-
	3.4630	Cyclopentane, butyl	-	-	-	+++
	3.7341	Cyclohexane, 1,2,3-trimethyl	-	-	-	+++
	3.8599	Cyclopentene, 1-(1-methylethyl)	+	-	-	-
	3.9994	5-Decene-	-	-	-	+
	4.1617	Nonane, 2-methyl	-	-	-	+
	4.1619	Hexane, 3-ethyl-3-methyl	-	+	-	-
	4.2572	<i>trans</i> -3-Decene	-	-	-	++
	4.2638	Heptane, 2,6-dimethyl-	+	-	-	-
	4.3737	1-Decene	+	-	+	-
	4.4049	Decane	-	+	-	+
	4.5806	Decane, 4-methyl	+	+	-	-
	4.5845	Octane, 3,3-dimethyl	-	-	-	+
	4.8709	Decane, 3,8-dimethyl-	+++	-	-	+++
	4.8533	<i>L</i> -Linalool	-	-	+	-
	4.8711	Heptane, 2,5,5-trimethyl	-	+++	-	-
	5.0333	Borneol	-	-	++	-
	5.1369	2-Dodecene	+	++	-	+++
	5.2221	Decane, 3,7-dimethyl-	+	-	-	-
	5.9848	4-Dodecene	+	-	-	-
	6.0467	Dodecane	-	-	+	+++
	6.6338	Dodecane, 4,6-dimethyl-	+++	++	-	++
	6.7975	Dodecane, 2,6,11-trimethyl-	+++	+	-	-
6.8808	1-Tridecene	-	-	+	-	
6.9460	Tridecane	-	-	+	-	
7.2927	Nonane, 3-methyl-5-propyl	+	-	-	-	
7.4663	3-Methyl-1-(tetrahydropyrrolo(1,2-c)oxazol-3-ylidene)-butan-2-one	-	-	+	-	
7.5285	Eicosene, 10-methyl	-	-	-	+	
7.7856	1-Tetradecene	-	-	+	-	
7.8576	Tetradecane	++	+	+	+	
8.4295	Undecane, 4,7-dimethyl	+++	-	-	-	
8.5448	Pentadecane, 2,6,10-trimethyl	+	-	-	-	
8.6720	Heptadecane, 2,6,10,15-tetramethyl	++	-	-	-	

*Continued*

<i>Family</i>	<i>RT (min)</i>	<i>Name of compound</i>	<i>%</i>	<i>%</i>	<i>%</i>	<i>%</i>
<b>Lipid</b>	8.7531	Pentadecane	+++	+	-	+++
	9.1373	Branched Alkane	++	+	-	-
	9.1349	Branched Alkane	-	-	-	+
	9.2991	Branched Alkane	++	-	-	-
	9.6067	Hexadecane	++	-	++	+
	9.6892	Branched Alkane	++	-	-	-
	9.9453	Branched Alkane	++	-	-	-
	10.0253	Branched Alkane	++	-	+	-
	10.1251	Branched Alkane	+	-	-	-
	10.2815	Branched Alkane	++	-	-	-
	10.3596	Branched Alkane	+	-	-	-
	10.4322	Heptadecane	+++	-	++	+
	10.5715	Branched Alkane	+++	-	-	-
	10.7400	Branched Alkane	+	-	-	-
	10.9084	Branched Alkane	+++	-	-	-
	11.0872	Branched Alkane	+	-	-	-
	11.2243	Octadecane	++	-	-	-
	11.6447	Branched Alkane	++	-	++	+
	11.9512	Branched Alkane	++	-	-	-
	12.1569	Branched Alkane	+	-	-	-
	12.2490	Branched Alkane	++	-	-	-
	12.5068	Branched Alkane	+	-	-	-
	12.5868	Nonadecene	+	-	+	-
<b>Nitrogen compound</b>	2.1141	Pentanenitrile	-	-	+	-
	2.8169	Butanenitrile, 3-methyl	-	-	++	-
	2.8218	1-Allylazetidine	+	-	-	-
	3.1028	Acetamide	-	-	+++	-
	3.4083	2-Cyanohe-3-ene	-	-	+++	-
	4.6999	Benzamine, <i>N</i> -ethyl	-	-	+	-
	5.3533	2-Pentenenitrile, 4,4-dimethyl	-	-	+	-
	5.6637	Benzyl nitrile	+	-	+	-
	6.3511	Diisopropylaminoacetonitrile	-	-	+	-
	6.5697	Benzenepropanenitrile	-	-	+	-
	7.3669	Cyclohexanamine, <i>N</i> -cyclohexyl- <i>N</i> -methyl	-	-	+	-
	8.4045	<i>N</i> -(3-Amino-2-hydroxy-phenyl)-acetamide	-	-	++	-
12.0544	Hexadecanenitrile	-	-	+	-	
<b>Peptide</b>	2.9442	1H-Pyrrole	-	-	++	-
	3.4065	1,3-Diazine	++	-	-	-
	3.4184	1H-Pyrrole, 3-methyl	-	+++	-	-
	3.5894	Pyridine, 4-methyl-	-	-	+	-
	3.9308	1H-Pyrrole, 1-ethyl	-	++	++	-
	4.0099	Pyridine, 2,5-dimethyl	+	-	-	-
	4.0676	3-Cyclohexene-1-carboxaldehyde, 1-methyl-	+	-	-	-
	4.1248	3-Pyridinol, 2-nitro	+	-	-	-
	4.1281	2-Pyridinecarboxylic acid, 6-methyl	-	-	+	-
	4.5692	1H-Pyrrole, 2,3,5-trimethyl-	-	-	++	-
	5.4210	2,5-Pyrrolidinedione	-	-	+	-
	5.5001	1H-Pyrrole, 3-ethyl-2,4,5-trimethyl-	-	-	+	-
	5.7318	1H-Indene, 2,3-dihydro-4-methyl	-	-	-	+
	5.8382	1H-Indene, 3-methyl	-	-	+	-
	6.2127	5- <i>sec</i> -Butyluracil	-	-	+	-
	6.7823	5-Hydroxy-indan-2-one	-	-	+	-
	7.1082	Indole	-	-	+	-
	7.6272	Quinoline, 4-methyl	-	-	+	-
	7.9615	Tryptamine	-	+	-	-
	7.9726	1H-Indole, 7-methyl-	+	-	++	-
	8.0549	Diketopyperazine	-	+	-	-
	8.5019	2-(Methoxycarbonyl)-2-methyl-3-( <i>N</i> -pyrrolidino)(2H)azirine	-	-	+	-
	8.6886	Pyridine, 4-phenyl-	-	-	++	-
8.8508	1H-Indole, 1,2-dimethyl	-	-	+	-	
9.6159	Diketopyperazine	-	+	-	-	
10.0278	Diketopyperazine	-	+	-	-	
10.8699	<i>N</i> -(Dimethylthiophosphinyl)-3-aminopyridine	-	-	+	-	
<b>Polysaccharide</b>	2.2024	Furan, 2-methyl-	++	+++	+	+++
	2.6882	Furan, 2,5-dimethyl-	+	-	+	-
	3.2520	Furfural	-	-	++	-
	4.2768	2-Cyclopenten-1-one, 3-methyl	-	-	++	-

\* + = Low relative abundance; ++ = medium relative abundance; +++ = high relative abundance; and - = null