
Data report: bitumen extracted from hydrothermally altered sediments encountered during Expedition 331¹

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Abstract

Drilling during Integrated Ocean Drilling Program Expedition 331 encountered sediments variably altered by hydrothermal activity. Site C0013 was highly altered, Site C0014 was hydrothermally altered below ~12 meters below seafloor (mbsf), and Site C0017 evidenced little hydrothermal alteration in near-surface sediments (to 90 mbsf) and more alteration at greater depths. Bitumen from these sites was variably altered, with the most thermally altered bitumen found in sediments close to the present-day hydrothermal mound (Site C0013). Similarly, deeper samples evidence more thermal alteration than their shallower counterparts for any given site. Despite these broad patterns, these trends are not clearly observed in many instances; thus, overall patterns of thermal alteration are complicated. This complication is likely because much of the bitumen present migrated into its present position during the movement of hydrothermal fluids, although it may also indicate complex circulation of fluids in the subsurface and temperature regimes that are spatially heterogeneous. The biomarker fingerprint of most of the bitumen is consistent with the hemipelagic nature of the sediments.

Introduction

Hydrothermal activity at seafloor spreading centers is known to convert sedimentary organic matter into petroleum (Simoneit et al., 1984). Key variables that govern the type of hydrocarbons present within hydrothermally altered sediments include the type of organic matter found within host sediments, its quantity, and the temperature of pyrolysis (Simoneit, 1993). Iheya North hydrothermal field is located in the middle Okinawa Trough at 27°47.415'N, 126°53.8605'E. It is located within a subsea collapsed-caldera complex that is filled with a mixture of mass-wasted volcanoclastic sediments and hemipelagic sediments, many of which have been hydrothermally altered into hydrothermal lithologies (see the “[Expedition 331 summary](#)” chapter [Expedition 331 Scientists, 2011]). Some sediments encountered by drilling were not hydrothermally altered, and in these locations volcanic pumice and hemipelagic mud are the most frequently encountered sediment types. The main type of sedimentary organic matter expected in sediments before hydrothermal alteration would be allochthonous terrestrial (derived from the Yang-

¹Bowden, S.A., Walker, J., Ziolkowski, M., and Taylor, C., 2016. Data report: bitumen extracted from hydrothermally altered sediments encountered during Expedition 331. In Takai, K., Mottl, M.J., Nielsen, S.H., and the Expedition 331 Scientists, *Proceedings of the Integrated Ocean Drilling Program, 331*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.331.201.2016

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tze and Yellow Rivers ~1000 km east and north) and autochthonous (pelagic) marine sedimentary organic matter. Present-day maximum temperatures encountered during drilling were 300°C for Site C0013, ~180°C for Site C0014, and <80°C for Site C0017. Excepting the highest temperatures recorded, temperatures are actually relatively low with respect to the rapid pyrolysis described by Simoneit (1993) for hydrothermal activity at seafloor hydrothermal ridges, but on geological timescales they would be considered sufficient for pyrolysis to occur (Killops and Killops, 2005). The solvent extractable organic matter present at these sites, if it is indigenous, would be expected to possess a biomarker fingerprint characteristic of both higher plant and marine plankton. Bitumen would be expected to be mobile within the more permeable pumice units but less mobile in the mud units. The purpose of this report is to record the chemical composition of bitumen from hydrothermally altered sediments and determine whether it could have been generated by high-temperature pyrolysis of local sediments.

Methods and materials

Exteriors were removed from samples (mostly wedges taken from the working half of cores) prior to being dried and solvent extracted with 97:3 dichloromethane (DCM)/methanol MeOH (v/v) in a Soxhlet apparatus for 48 h. Solvent extracts were separated by column chromatography with activated (120°C overnight) silica. Aliquots of the extracts (~0.01–0.05 mg) were absorbed onto activated silica (~500 mg). After conditioning the column with 5 mL of hexane, saturated fractions were eluted with 3 mL of hexane, aromatic fractions with 3 mL of a mixture (3:1) of hexane and DCM, and the polar fraction with 3 mL of a mixture (2:1) of DCM and MeOH. The polar fraction was reduced to dryness under N₂, redissolved in a mixture of (5:1) hexane/DCM, transferred to a clean vial (this leaves asphaltic material in the original vial) and derivatized with BSTFA (*N,O*-bis [trimethylsilyl] trifluoroacetamide) to convert alkenoic acids to their silylestere.

Gas chromatography–mass spectrometry (GC-MS) was carried out on an Agilent Technologies (AT) 6890N network GC (pulsed splitless) system fitted with a 30.0 × 250.0 μm internal diameter (ID) film thickness 0.25 μm fused capillary column coated with DB-5 coupled to an AT 5975 quadrupole mass-selector detector (electron input energy 70 eV, source temperature 250°C) with helium as carrier gas. Frac-

tions were analyzed using an oven programmed temperature of 60°C (2.0 min) to 120°C at 20°C/min to 290°C at 4°C/min and held at 290°C for 23 min. The mass-spectrometer was operated in selective ionization mode (SIM) with compounds identified by relative retention times and comparisons to well-characterized samples. Concentrations of fatty acids are reported relative to an internal standard of nonadecanoic acid.

A level of thermal maturity or thermal alteration was determined using biomarker proxies and expressed as a vitrinite reflectance equivalence (%VRE). Two tools were used. For Site C0017 and surface sediments at Site C0014, the hopane %22(S) parameter was converted to %VRE using comparative diagrams published in Peters et al. (2004) and Killops and Killops (2005). At Site C0013 and for the deeper horizons at Site C0014, the conversion equations used to obtain an approximate %VRE from the methylphenanthrene index were $R_m (\%) = 0.38 + 0.61 \text{ MPI } 1$ as presented in Radke (1988) (see also Radke et al., 1980, for additional context). Given the limited mixing thermally mature and immature bitumen inferred for these settings and the general level of error involved in using the approaches described above, the level of error for measurements is approximately ±0.15% on the VRE scale. Thermal maturation was modeled using the EASYvit model described in Sweeney and Burnham (1990). Within the model, durations of heating were varied (1y to 1 My), whereas present-day downhole temperature profiles were kept constant to produce predictions of levels of thermal alteration for different depths.

Results

n-Alkanes

Representative ion chromatograms showing the *n*-alkane content of extracted bitumen are shown in Figure F1. Distinct end-members are identified. At Site C0013, located proximal to the vent and hydrothermal mound, low carbon number *n*-alkanes predominate (C₁₆–C₂₂). At Site C0017, distal from the vent and from likely sources of heating, *n*-alkanes have a biological signature in the form of an odd over even predominance—likely reflecting terrestrially derived plant-organic matter present within hemipelagic sediments (Meyers and Ishiwatari, 1993). Samples from the deeper sections of holes drilled at Site C0014 contain *n*-alkanes in which carbon numbers ranging from C₂₁ to C₃₁ are the most prominent and for which the odd over even carbon number prefer-

ence is much reduced. The shallowest samples seen at Site C0014 are similar to those seen at Site C0017 (the least hydrothermally altered).

Terpanoid biomarkers

The classic terpanoid biomarkers found in oil derive from their biological precursor via a complex series of chemical reactions that generate a number of structural intermediaries (e.g., steranes derived from sterenes that ultimately derive from sterols [Mackenzie et al., 1982]). Typically, only the fully saturated terpanes (e.g., steranes and hopanes) are found at oil window levels of thermal maturity because unsaturated counterparts are not thermally stable (Peters et al., 2004).

Both pre-oil window and oil window biomarkers are present in samples, and in a few instances both types of biomarker are observed, indicating mixing of mature and thermally immature compounds. Figure F2 compares 217 and 215 *m/z* ion chromatograms that illustrate the carbon number distribution of steranes and sterenes present at Sites C0017 and C0014. Sterols are the chemical precursors of sterenes and steranes, and despite their ubiquity in sediments the relative proportions of a particular carbon-numbered homolog can provide a fingerprint and useful paleoenvironmental information (Huang and Meinschein, 1979). The distribution of carbon numbers is similar (e.g., the C₂₈ sterane and sterene homologs are proportionally least abundant) for both steranes and sterenes; thus, some bitumen components within zones of hydrothermal alteration are correlated to adjacent thermally immature sedimentary organic matter. This correlation strongly suggests that the bitumen obtained from hydrothermally altered samples was generated from the hemipelagic muds found within the hydrothermal system and not from a source or reservoir distal from the Iheya area.

Patterns of thermal alteration, similar to that observed for *n*-alkanes, were observed for geohopanes (Fig. F3). Adjacent to the sulfide mound at Site C0013, a low proportion of thermally unstable hopane isomers is found (e.g., low proportions of 17 β ,21 β (H) and reduced 17 β ,21 α (H) hopanes relative to 17 α ,21 β (H) hopanes; see Farrimond et al., 1998). Downslope from the hydrothermal mound at Site C0014, where hypothermal alteration is present at depth but absent at the surface, subsurface samples have an absence of thermally less stable 17 β ,21 β (H) hopanes and greater abundances of 21 β (H) hopanes. However, shallower samples at Site C0014 possess both pre-oil window and thermally mature oil window biomarkers (e.g., both 17 β ,21 β (H) and reduced

17 α ,21 β (H) hopanes). Samples obtained from the drill site most distal from the hydrothermal mound (Site C0017), including samples of thermally unaltered hemipelagic mud, contain the highest proportions of 17 β ,21 β (H) hopanes (pre-oil window biomarkers).

Despite the apparent broad correlation between the level of alteration of sedimentary organic matter and different zones of hydrothermal alteration, there are clear instances where pre-oil window and oil window biomarkers are found in the same sample (Sample 331-C0013E-5H-1, 96–104 cm, contains very small amounts of 17 β ,21 β [H] hopanes). This complicates assigning a single level of thermal maturity to a sample, as in many cases samples can be shown to contain a compounds with contrasting thermal stabilities and origins.

Polynuclear aromatic hydrocarbons

Polynuclear aromatic hydrocarbons (PAHs) were detected in samples closest to the hydrothermal mound, although their abundance varies significantly and they were not readily detected in Site C0017 samples. Figure F4 presents an ion chromatogram on which the phenanthrene compounds used to estimate thermal maturity in the most thermally mature samples are identified and provide a %VRE. Because of the varied abundance of higher ring number PAHs (e.g., pyrene and other PAHs with four or more aromatic rings), these compounds are sporadically present and were not considered further.

At Site C0014, a range of thermal maturities is found, with compounds that are stable under pre-oil window or oil window conditions found in stratigraphically adjacent samples. All samples appear to be more thermally altered than can be accounted for by present-day downhole temperatures and reasonable durations of heating (e.g., >1 My). Samples exhibiting oil-window levels of thermal maturity are explained as hydrothermally generated petroleum that has migrated through the subsurface—although there is still the possibility that the bitumen is indigenous and particularly so for bitumen within the relatively impermeable hemipelagic mud. This is not the case for samples that have relatively high but nonetheless pre-oil window levels of thermal alteration. Even for these samples, the apparent level of thermal maturity is greater than can be accounted for by present-day bottom hole temperature (Fig. F5). The implication of this thermal maturity is that although present-day downhole temperatures may indicate a suitable habitat for hyperthermophilic organisms, paleotemperatures were probably much hotter in the past.

n-Alkanoic acids

n-Alkanoic acids form a quantitatively small fraction of the bitumen (parts per million) but are potentially significant because of their ability to aid solubilization of bitumen in saline fluids (Meredith et al., 2000) and also as components of biomass and the lipid content of sedimentary organic matter (Killops and Killops, 2005). The differences between the most thermally altered and least altered sites (C0013 and C0017) are shown in ion chromatograms in Figure F6. In all instances, the most abundant *n*-alkanoic acid was hexadecanoic acid with the proportion of unsaturated acids showing the most variation between samples. The concentration of *n*-alkanoic acids and the ratio of saturated to unsaturated acids are plotted against the level of thermal alteration in Figure F7. Initially the proportion of unsaturated acids drops significantly during the early stages of thermal maturation, but then it briefly rises with increased thermal maturation. This second rise in the proportion of unsaturated fatty acids is coincidental with a rise in the concentration of *n*-alkanoic acids. This sudden influx of *n*-alkanoic acids likely represents the liberation of covalently bound acids from macromolecular sedimentary organic matter during pyrolysis.

Acknowledgments

Samples and/or data used in this research were provided by the Integrated Ocean Drilling Program (IODP). Laboratory work was performed by Jack Walker and Mateusz Ziolkowski at the University of Aberdeen (Scotland) as part of their undergraduate studies.

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Initial receipt: 6 June 2013

Acceptance: 21 January 2016

Publication: 9 May 2016

MS 331-201

Figure F1. Ion chromatograms (m/z 85) illustrating the abundance of n -alkanes for selected samples, Sites C0013, C0014, and C0017. Lithostratigraphic positions of samples and their locations within the Iheya hydrothermal system drilled during Expedition 331 are shown. C_{14} = C_{14} n -alkane, Ph = phytane, VRE = vitrinite reflectance equivalent.

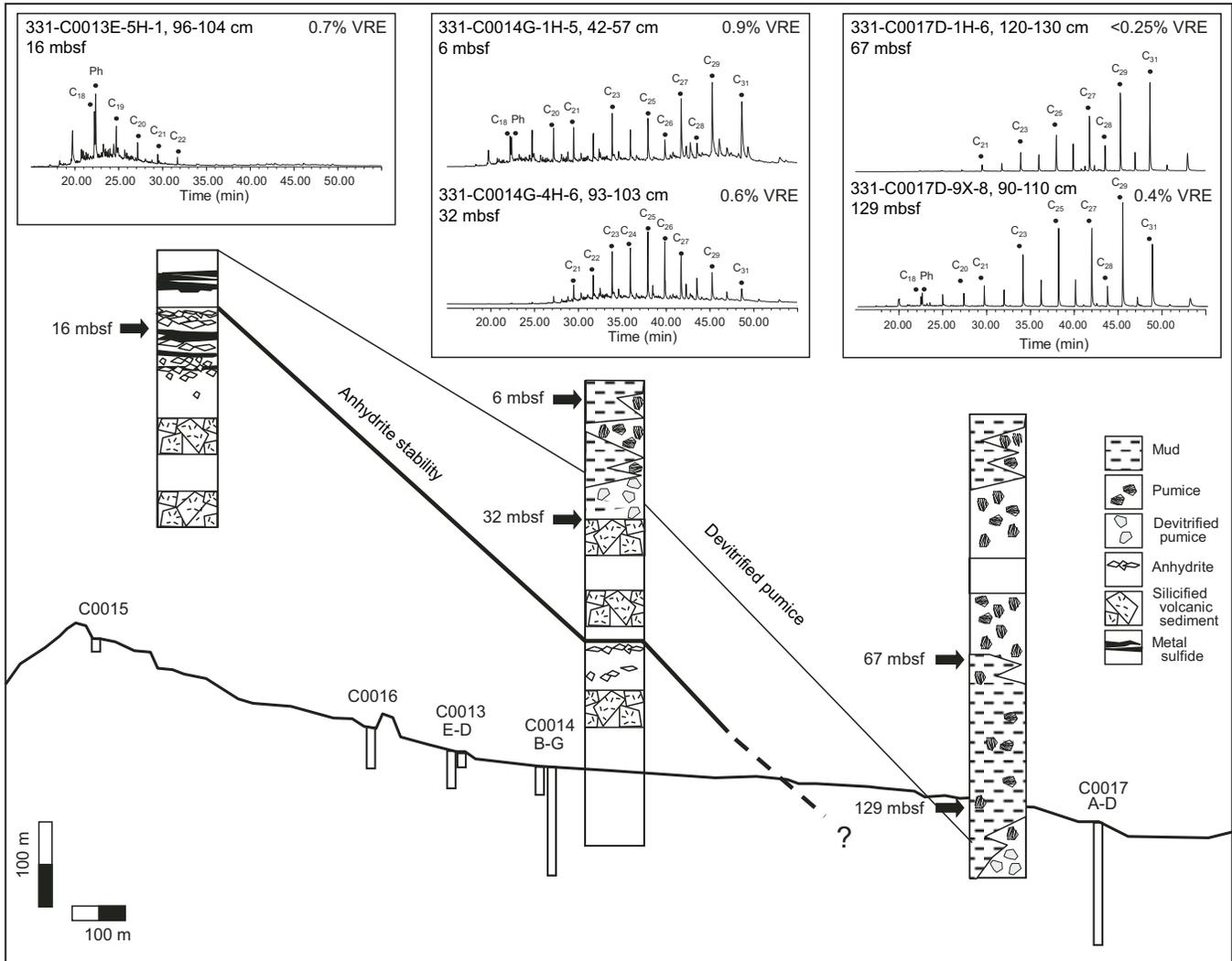


Figure F2. Ion chromatograms illustrating the similarity in carbon number distribution between the steranes (m/z 217) present in bitumen (Site C0014) and sterenes (m/z 215) from Site C0017. Carbon numbers are noted. $\Delta 4$ = ster-4-ene; $\Delta 5$ = ster-5-ene; $\alpha\alpha\alpha$ R = $5\alpha,14\alpha,17\alpha(H)20(R)$ steranes; $\alpha\alpha\alpha$ S = $5\alpha,14\alpha,17\alpha(S)$ steranes.

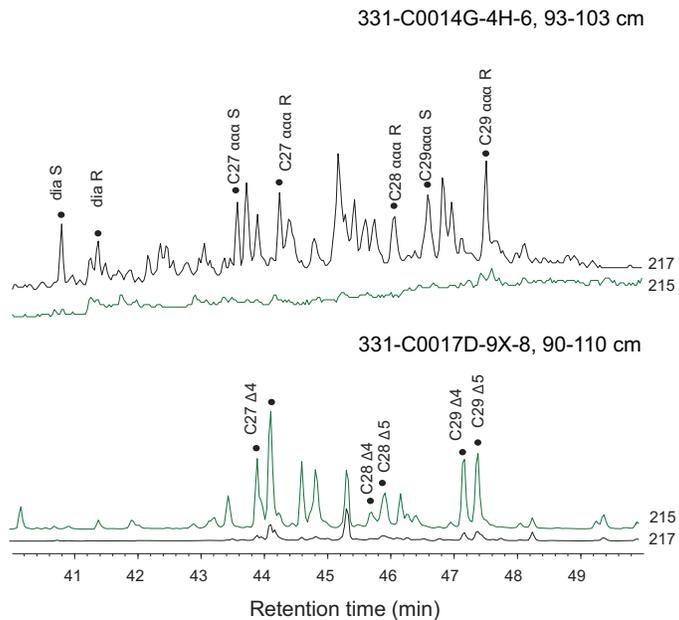


Figure F3. Ion chromatograms (m/z 191) illustrating the abundance of hopanes for selected samples, Sites C0013, C0014, and C0017. Lithostratigraphic positions of samples and their locations within the Iheya hydrothermal system drilled during Expedition 331 are shown. $\alpha\beta$ = $17\alpha,21\beta(H)$ hopane; $\beta\alpha$ = $17\beta,21\alpha(H)$; $\beta\beta$ = $17\beta,21\beta(H)$ hopane; $\Delta 13$ = hop-13-ene. Carbon numbers are noted.

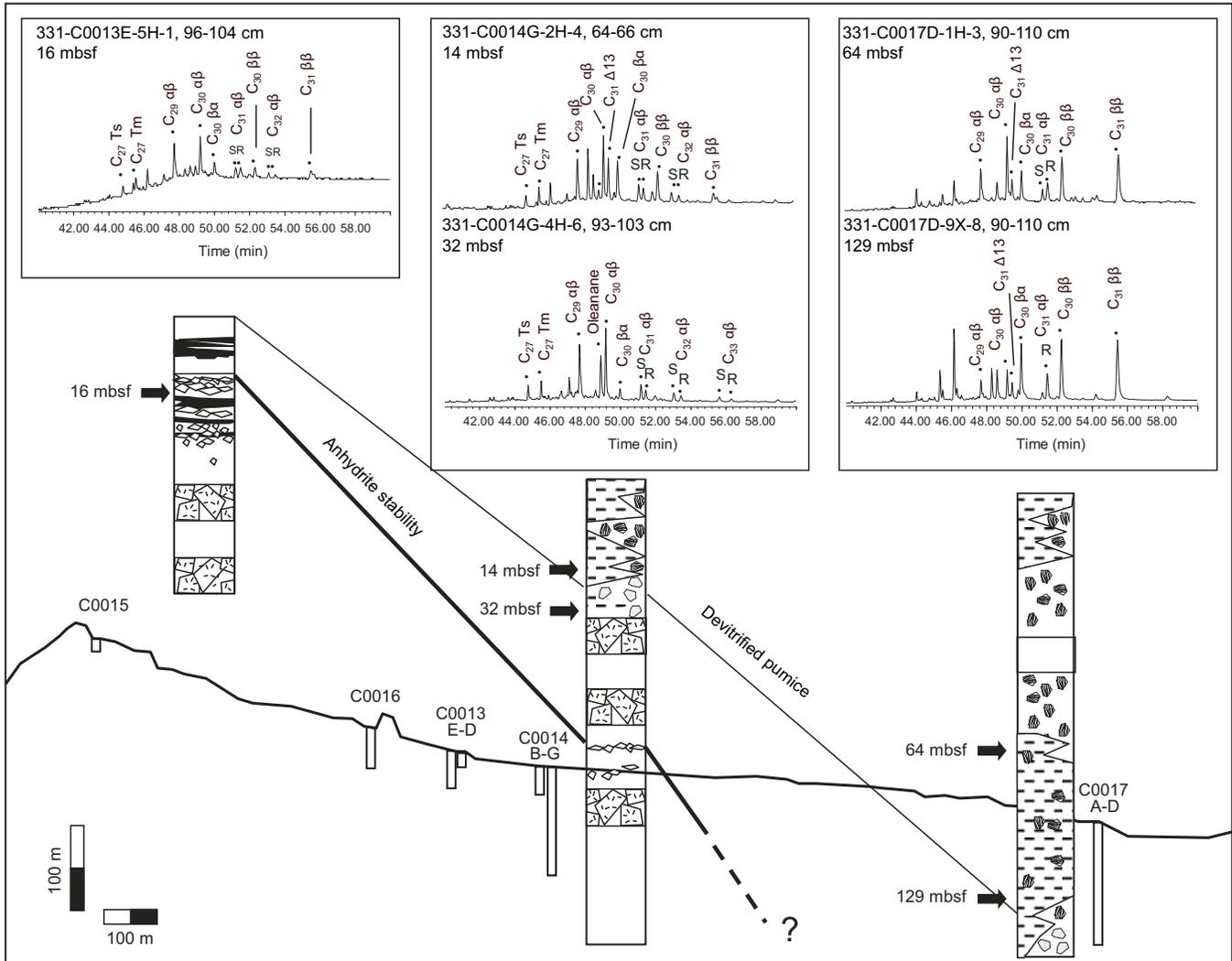


Figure F4. Summed (m/z 178, 192, 202, 216) ion chromatograms illustrating the occurrence of PAHs in two contrasting samples, Sites C0013 and C0017. P = phenanthrene, MP-2 = 2-methylphenanthrene, Fl = fluoranthene, Py = pyrene.

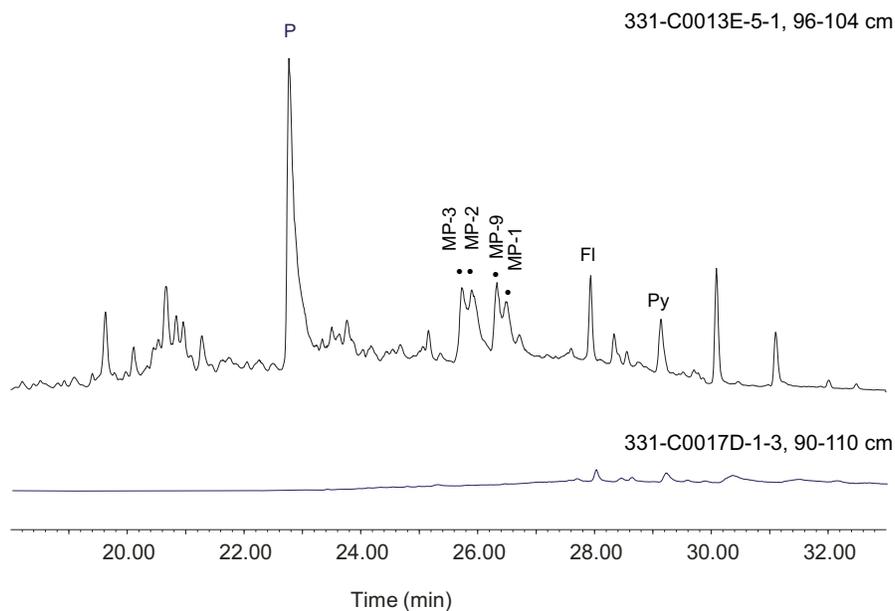


Figure F5. Plots of %VRE (vitrinite reflectance equivalent), Sites C0013 and C0014. Predictions of this parameter obtained using the EASYvit model are shown. Model utilized observed downhole temperatures and the duration of heating labeled on the graphs (1y to 1 My).

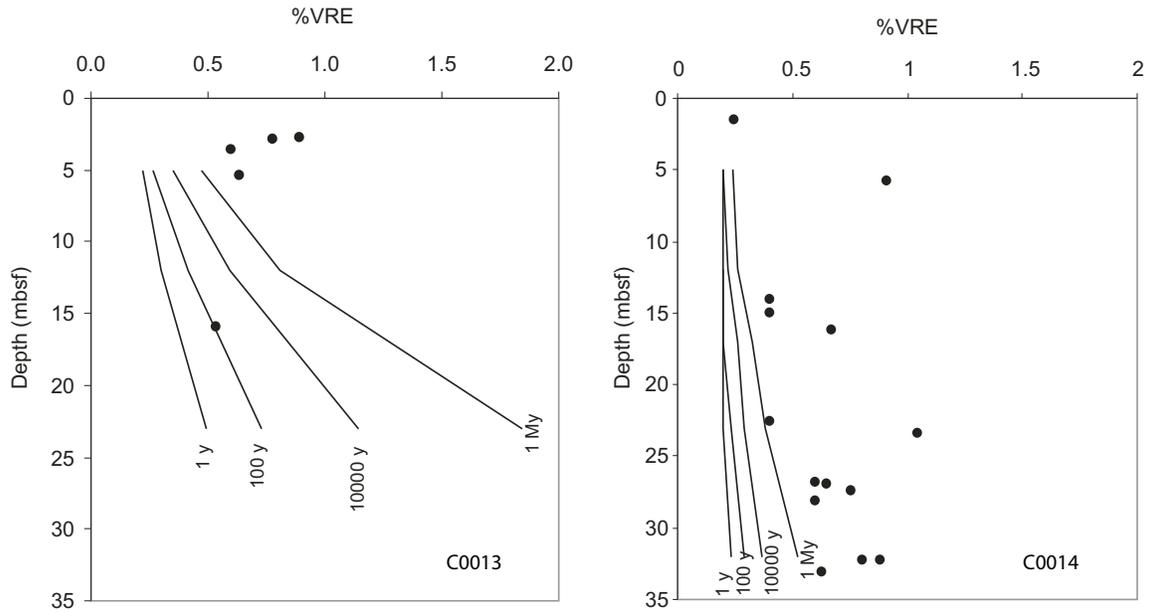


Figure F6. Ion chromatograms illustrating the abundance of *n*-alkanoic acids in two contrasting samples, Sites C0013 and C0017. The *m/z* 117 ion illustrates the abundance of *n*-alkanoic acids, whereas the *m/z* 337 and 339 ions illustrate the abundance of C₁₈ alkenoic acids. 18:1 = C₁₈ *n*-alkenoic acid.

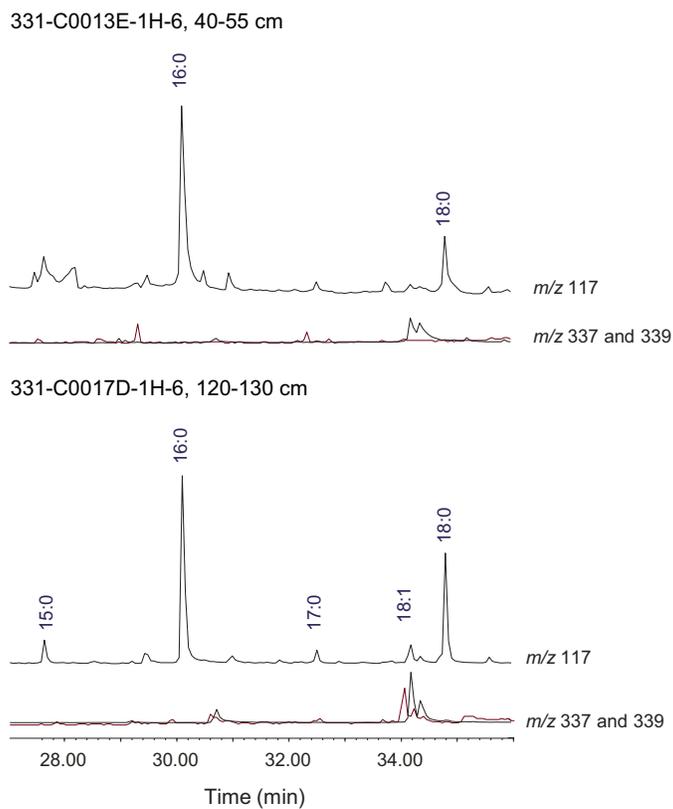


Figure F7. Plots of *n*-alkanoic acid concentration and the ratio of C₁₆ alkanolic acid to C₁₈:1 *n*-alkenoic acids against %VRE (vitrinite reflectance equivalent), Sites C0013, C0014, and C0017. EOM = extractable organic matter.

