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Chapopote Asphalt Volcano May Have Been Generated by Supercritical Water

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Asphalt volcanoes and lava-like flows of solidified asphalt on the seafloor (Figure 1) were first discovered and described by *MacDonald et al.* [2004]. The flows covered more than one square kilometer of a dissected salt dome at abyssal depths (~3000 m) in the southern Gulf of Mexico. "Chapopote" (93°26'W, 21°54'N) was one of two asphalt volcanoes they discovered. MacDonald et al. determined that the apparently fresh asphalt must initially have flowed in a hot state, and subsequently chilled, contracted, and solidified, much in the same way as normal lava does on the surface of the Earth.

The two asphalt-volcanoes discovered occur at the apex of salt domes that pierce through the seafloor. These "piercement salt domes," known as the Campeche Knolls, are pertinent features of the deep Campeche Sedimentary Basin, which has a sediment thickness of about 10 km. According to conventional theory [*Vendeville and Jackson*, 1992], piercement salt domes represent "salt diapirs" that have risen up, due partly to density contrasts between salt and clay/sand from the "mother salt" located between 7 and 10 km below seafloor. A salt diapir is a vertical body of sub-surface salt, which is most often circular in cross section, is one to several kilometers in diameter, and can be 8–10 km high.

A close examination of the asphalt material by scanning electron microscopy and energy dispersive spectroscopy indicates that the material contains a myriad of varying sized, non-connected, isolated pores (0.1–0.5 mm). The largest pores contain pore-lining coats of chloride, sulfate, alumosilicate, and possibly carbonate minerals.

The earth-like, amorphous, and fine-crystalline structure of these pore-lining minerals suggests that they are authigenic precipitates, most likely deposited during cooling and solidification of the asphalt. Carbonate minerals also form macroscopic cement intermixed with the asphalt matrix [*MacDonald et al.*, 2004].

The observation of the precipitates raises questions concerning their mineralogical composition and crystalline structure, the temperature and origin of the source fluids (brines), and the role, if any, of microbes.

Supercritical Water – A 'Magic' Substance

Natural seepage of liquid oil also occurs from the Chapopote salt dome/asphalt volcano and from several of the other Campeche Knolls [*MacDonald et al.*, 2004]. Because "asphalt volcanism" was previously unknown and because there is no apparent strong heat source near the seafloor (the ambient water temperature is 4°C), *MacDonald et al.* [2004] were tentatively unable to provide a geologically sound formation model for the asphalt volcanoes.

A possibility is that hot hydrothermal fluids originating at the crust/sediment interface at about 13 km depth below sea level are able to transport molten asphalt inside the piercement salt structures, which may act as vertical "thermally insulated" conduits.

A recent model designed to explain how terrestrial mud volcanoes erupt similarly suggests that hot water may form near the base of very deep sedimentary columns [*Hovland*, 2005]. Thus, in the Caspian Basin of Azerbaijan the sediments are about 20 km deep [*Feyzullayev et al.*, 2001]. If the pore water temperature at this depth rises above 400°C, the water can no longer boil because of the high ambient pressure. Instead, it attains another phase; it becomes "supercritical water" [*Bellissent-Funel*, 2001]. This water phase is neither vapor nor liquid, but something in between.

Considering that supercritical water has a density of only one-third of liquid water (i.e., 0.3 g/cm^3: grams per cubic centimeter), it may represent the driving mechanism for some, if not all, mud volcanoes [*Hovland*, 2005]. Supercritical water forms at temperature and pressure conditions above 374°C (405°C for seawater) and 221 bars (300 bars for seawater) [*Tester et al.*, 1993; *Bellissent-Funel*, 2001]. This means that seawater will become supercritical when heated to beyond 405°C at water depths beyond 2800 m (equivalent to a pressure of 300 bars). The depth of 2800 m may therefore be called "the potential critical point" depth of the ocean.

Supercritical water also has other important properties, which include being very highly compressible, being highly corrosive, and having a very low viscosity. The water behaves as a non-polar rather than a polar fluid [*Bellissent-Funel*, 2001; *Tester et al.*, 1993; *M. Hovland et al.*, Salt formation by supercritical seawater and submerged boiling, submitted to Marine and Petroleum Geology, 2005, hereinafter referred to as submitted manuscript, 2005]. This means that when seawater or saline pore waters become supercritical, their salts precipitate as solid, small amorphous particles, by a process

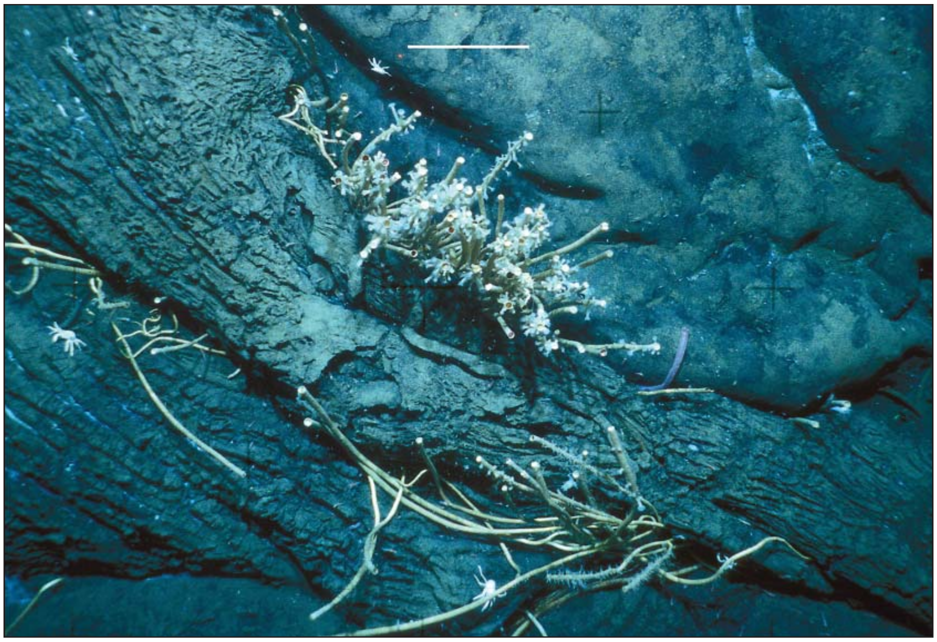

Fig. 1. Folds in the freshest Chapopote asphalt material, lined with tubeworms and white films (probably bacterial mats). Note the similarity to flow structures in terrestrial lava flows.

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observed in the laboratory by *Tester et al.* [1993] and termed "shock crystallization." Because these particles were amorphous rather than crystal-formed, the term "autoprecipitation" of solid salts could also be used.

In this new explanation model, there is an analogy with mud volcanoes in that the asphalt volcanoes suspectedly form above deep basinal or crustal fault intersections, where hot (hydrothermal) water from the underlying crust intrudes into the overlying sediments. Thus, the supercritical water would likely form and transport materials, including dissolved hydrocarbons and salt slurries vertically upward inside the piercement salt structures.

A possible but unlikely mode of formation, based on conventional salt tectonic theory, would need to be as follows: A salt diapir that slowly rises upward through the sediments and penetrates a bituminous (asphalt) reservoir and transports some of this material up to the surface. The necessary heat for making the asphalt flow must come from within the salt structure, but there is no existing (conventional) model that accounts for such heat. Upon cooling and biodegradation on the seafloor, the asphalt then becomes stiff and friable.

A Novel Model

Rather than discuss this option further, an attractive alternative model elegantly explains (1) how molten asphalt can be transported over great vertical distance without cooling too much, (2) the closely observed association with salt piercement structures, and (3) why similar structures have not been observed in shallower water.

The model relies on the concept that some salt- and/or mud-cored piercement structures in deep sedimentary basins actually contain warm, deep-rooted vertical conduits, which are able to transport "hydrothermal-like" fluids to the surface [*M. Hovland et al.,* submitted manuscript, 2005]. These fluids include brines, supercritical water, low-chlorinity condensation water, early generated hydrocarbons, and hydrothermally associated minerals such as carbonates, sulphates, sulfides, silicates, and metals (i.e., minerals normally associated with deepwater hydrothermal vents).

Furthermore, the model is based on the fact that even if old hydrothermal systems become buried by thick sediments, they are not "turned off," as amply demonstrated by the Ocean Drilling Program (ODP) in its campaigns on sedimented ridges, such as Middle Valley and Escanaba Trough in the eastern Pacific. Supercritical water may actually still form at the base of very deep sedimentary basins founded on hot crust, such as relatively young oceanic or transitional crust.

To justify the new explanation model, the following three items are regarded as facts:

- The asphalt has arrived in a heated state (i.e., temperatures >100°C) and has been rapidly deposited onto the seafloor in a heated state.
- The asphalt has been deposited from the center of at least two of the Campeche Knolls.

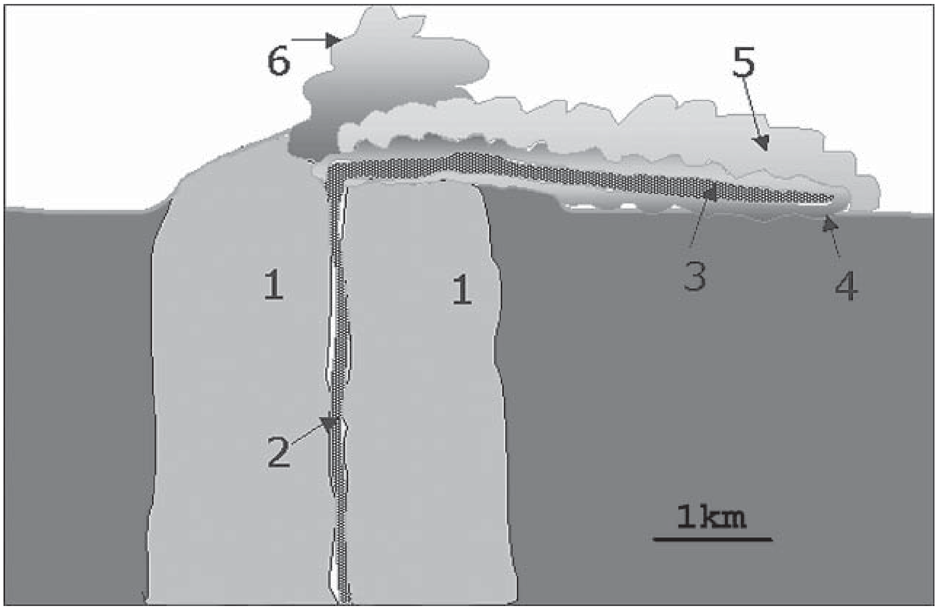

*Fig. 2. New conceptual model for the Chapopote asphalt flow event. Numerals indicate 1, the Chapopote salt-cored diapiric/hydrothermally derived structure (*M. Hovland et al., *submitted manuscript, 2005); 2, internal conduit system, transporting supercritical water and hydrothermal-like fluids (including early generated oils and bitumens) and particles to the surface; 3, the mantle of the "bituminous lava flow," which probably partly contains supercritical water and hot brines, insulated from ambient temperatures by sheaths of solidified bitumen and asphalt; 4, the solidified outer sheath of the asphalt flow, which acts as an effective heat insulator; 5, plume of volatiles originating from the rapidly devolitizing warm bitumen and asphalts; and 6, plume of condensed materials including light hydrocarbon oils and gases, and particulate matter.*

- The water depth during emplacement was over 2800 m.

The new explanation model relies on supercritical water being transported vertically upward through a suspected internal conduit within the Chapopote salt structure, from near the base of the sedimentary column, at perhaps 13 km total depth. The asphalt deposition occurs either over a prolonged period, or during a freak (periodic?) eruption event, whereby a large volume of bituminous material is transported up to the surface (Figure 2).

The sequential mode of formation is as follows:

1. Supercritical water (T > 405°C) forms at the root of the Chapopote structure, probably immediately above or within a major basement fault intersection.
2. Because of the low density of supercritical water, mass transport will go upward through the Chapopote central conduit (system), which was probably established synsedimentarily and which has been more or less active throughout its existence.
3. Organic material including bitumens are transported upward together with other "hydrothermal-like" substances as a hot, partly dissolved, and partly liquefied particulate mass (slurry).
4. Because of adiabatic and conductive cooling (adiabatic cooling is cooling by depressurization (expansion), according to Boyle's Law), some of the transported fluids will cool and condense out as oil, bitumen, crystals, and particles.
5. Even so, an internal core of slurry will remain at supercritical water temperatures (>405°C), insulated against conductive cooling by sheaths of salts and condensed bitumen.
6. At the very summit of the Chapopote structure, the slurry flows out onto the seafloor, expands, cools, and rapidly devolitizes (Figure 2).
7. However, because the outer skin of the devolitizing and condensing bituminous material thermally insulates the core of the flowing material, there is still an intact hot, gassy, and volatile-rich mantle. The "bituminous lava flow" now resembles a fast flowing proper lava flow, where the inner hot stream is insulated by solidified lava.
8. Upon further cooling and devolitization, however, the whole flow eventually "freezes" (solidifies).
9. Finally, it cools, degasses, deflates, and shrinks, and its outer surface becomes hard.

Because this model presumes that supercritical water is part of the system, it is unlikely that such flows will have occurred from the four shallowest of the mapped Campeche Knolls [*MacDonald et al.*, 2004], since these are shallower than the potential critical point. However, these structures should also have deeper cores consisting of asphalt or bitumen.

Although this new explanation model may seem far-fetched, it is based on sound reasoning and obeys well-documented physical, thermodynamic, chemical, and geologic facts and properties. The authors hope that supercritical water is considered and recognized as an important active entity in sedimentary geological processes.

The two discovered asphalt volcanoes, including the better studied Chapopote [*MacDonald et al.,* 2004], are the first ever such structures to be found at the apex of a salt diapir and are therefore unique. Further fieldwork (including mapping and sampling) on the unique asphalt volcanoes is important in order to shed light on poorly understood piercement structures that seem to be relatively common in deep sedimentary basins.

References

Bellissent-Funel, M.-C. (2001), Structure of supercritical water, *J. Mol. Liq., 90,* 313–322.

Feyzullayev, A. A., I. S. Guliyev, and M. F. Tagiyev (2001), Source potential of the Mesozoic-Cenozoic rocks in the South Caspian Basin and their role in forming the oil accumulations in the Lower Pliocene reservoirs, *Pet. Geosci., 7,* 409–417.

Hovland, M. (2005), *Is there a close link between salt diapirs and mud volcanoes?,* paper presented at the International Workshop on Methane in Sediments and Water Column of the Black Sea, Res. Cent. Ocean Margins, Univ. of Bremen, Sevastopol, Ukraine, 17–22 May.

MacDonald, I. R., et al. (2004), Asphalt volcanism and chemosynthetic life in the Campeche Knolls, Gulf of Mexico, *Science, 304,* 999–1002.

Tester, J., H. R. Holgate, F. J. Armellini, P. A. Webley, W. R. Killilea, G. T. Hong, and H. E. Berner (1993), Supercritical water oxidation technology, in Emerging Technologies in Hazardous Waste Management III, Am. Chem. Soc. Symp. Ser., vol. 518, pp. 35–76, Oxford Univ. Press, New York.

Vendeville, B. C., and M. P. A. Jackson (1992), The rise of diapirs during thin-skinned extension, Mar. Pet. Geol., 9, 331–354.

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Repeat Hydrography Cruises Reveal Chemical Changes in the North Atlantic

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The U.S. contribution to a large international effort to document long-term trends in carbon storage and transport in the global oceans by reoccupying selected hydrographic sections on decadal timescales began with three North Atlantic cruises in 2003. The initial results from these reoccupation cruises have shown significant long-term changes in oxygen, carbon dioxide (CO_2), and several other measurable parameters since the last global survey, which occurred in 1993.

The ocean has a memory of the climate system and is second only to the Sun in affecting variability in the seasons and long-term climate change. The ocean stores an estimated 1000 times more heat than the atmosphere, and 50 times more carbon. Additionally, the key to possible abrupt climate change may lie in deep-ocean circulation.

Accordingly, the U.S. Climate Variability and Predictability (CLIVAR)/CO_2 Repeat Hydrography component of the Global Earth Observing System of Systems (GEOSS) sustained ocean observing system for climate consists of a systematic reoccupation of select hydrographic sections in order to quantify decadal changes in the storage and transport of heat, freshwater, and CO_2. The CLIVAR/CO_2 Repeat Hydrography program builds upon earlier programs (e.g., the World Ocean Circulation Experiment (WOCE)/Joint Global Ocean Flux Survey (JGOFS) during the 1990s) that have shown where atmospheric constituents are stored in the oceans and have provided full water column data sets against which future changes can be measured. [*Sabine et al.,* 2004a].

This program should provide significant information about how changing biochemical processes may affect carbon distributions and sinks on decadal timescales. The program is also designed to assess changes in the ocean's biogeochemical cycle in response to natural and/or human-induced activity. For instance, global warming-induced changes in the ocean's transport of heat and freshwater, which could affect the circulation by decreasing or shutting down the thermohaline overturning, can be followed through long-term measurements.

In addition, the program will provide reference data for the sensor calibration (e.g., www.argo.ucsd.edu) and support for continuing model development that could lead to improved forecasting skill for oceans and global climate.

Historical Background

Studies over the last two decades have increased the understanding of many aspects of the carbon cycle in the oceans. However, it is still uncertain how to interpret the sum of these studies for all of the oceans. For example, *Bates et al.* [2002] suggested that a lack of strong wintertime mixing in the subtropical mode waters of the North Atlantic Ocean during the positive phase of the North Atlantic Oscillation (NAO) may help to explain why subsurface dissolved inorganic carbon (DIC) concentrations increased almost twice as fast in the early 1990s as surface concentrations near Bermuda.

Moreover, *Gruber et al.* [2002] conducted modeling studies that indicated that the NAO could account for an interannual variability of about ±0.3 petagram carbon (Pg C) yr^{1} in the North Atlantic carbon sink. Similarly, *Emerson et al.* [2001] and *Ono et al.* [2001] reported on increases in apparent oxygen utilization (AOU) in the upper thermocline of the eastern and western North Pacific Ocean, respectively, which they attributed to recent decadal changes in circulation.

The following year, *Keller et al.* [2002] examined a larger area of the Pacific and also found AOU changes. However, they suggested that compensating changes in the opposite direction may be found deeper in the water column.

These studies examined different regions, depth zones, and time periods using differing approaches, making it difficult to assess if the

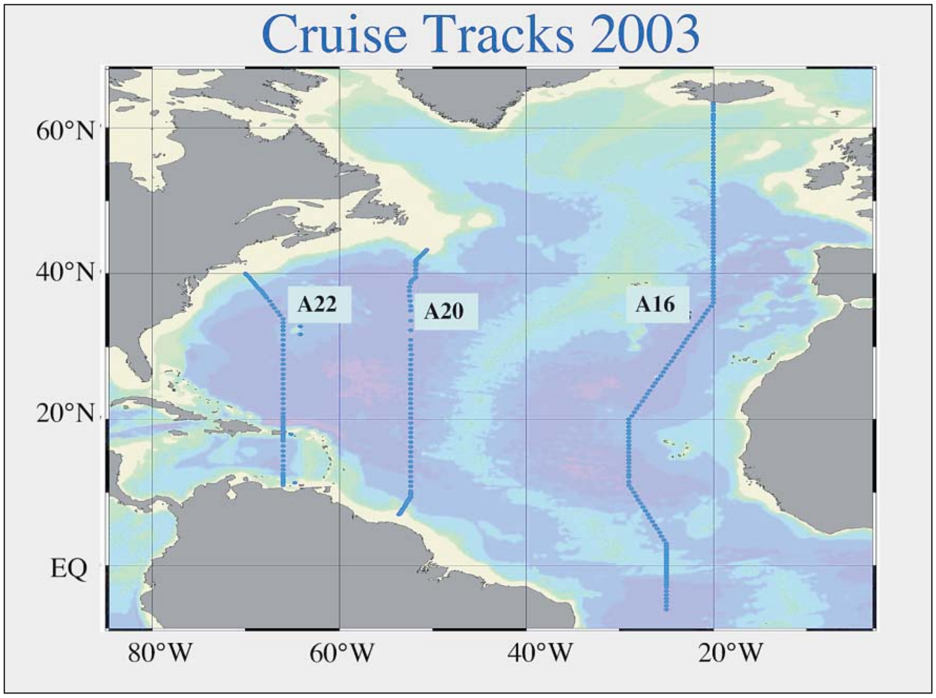

Fig. 1. Map of CLIVAR/CO_2 Repeat Hydrography Program hydrographic sections in the North Atlantic during 2003. The U.S. A16N (along 20°W), A20 (along 52°W), and A22 (along 66°W) cruises are designated with solid blue dots.

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