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DETERMINING THE ORIGIN OF GASES IN NEAR-SURFACE SEDIMENTS

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Over the last 5 years, we have taken over 6,000 piston cores from continental shelf and slope sediments of the northern and southern Gulf of Mexico, western and northern Africa, South America, the Caribbean, eastern Canada, the eastern and western Mediterranean Sea, and the Caspian Sea. Coring sites were selected based on existing seismic records for each region. Cores were positioned with differential GPS navigation and coring locations were fine-tuned ship-board using a Chirp II subbottom profiler. An example of a subbottom profile, showing a core site selected over a fluid-impregnated wipeout zone in the near-surface sediments, is shown as **Figure 1**. This core contained macro quantities of oil and gas.

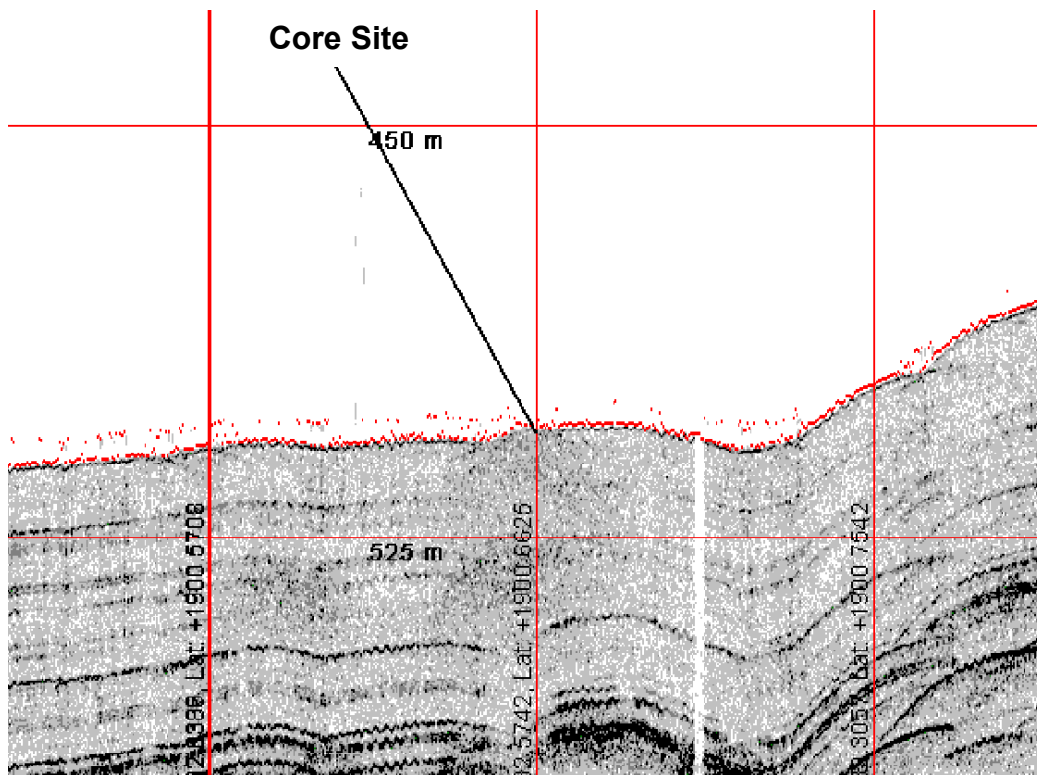


Figure 1. Example of a sub-bottom profile used for selecting a core site.

The dissolved gases were determined by acquiring 2 to 5 meter long piston cores from the seafloor, placing selected core sections of sediment into containers with clean seawater and nitrogen, partitioning the sediment gases into the container headspace by warming and agitating, and quantifying the headspace gases using gas chromatography. One (1.0) mL of headspace gas was injected onto a packed GC column for separation and then detected by thermal conductivity and flame ionization detectors in series. Measured gases include methane, ethene, ethane, propene, propane, i-butane, n-butane, i-pentane, n-pentane, neo-pentane, carbon dioxide, and nitrogen. When concentrations were sufficient, stable carbon isotopic compositions of methane, ethane, propane and other alkane gases were also measured.

The C₁-C₃ light hydrocarbon gases have been present at measurable concentrations in all sediment samples measured to date. *Background* methane concentrations dissolved in slope sediments range from 1 to 100 ppmV, whereas background concentrations of the other light hydrocarbons each typically range from 0.01 to 2.0 ppmV. In large accumulations, microbially produced (so-called *biogenic*) gases consist almost exclusively of methane, having C₁/(C₂+C₃) concentration ratios greater than 1,000 and δ¹³C_{PDB} values of methane more negative than -60 ‰. Petroleum-related (so-called *thermogenic*) hydrocarbon gases generally have C₁/(C₂+C₃) ratios smaller than 50 and δ¹³C_{PDB} values of methane more positive than -50 ‰. A simple geochemical model based on these two parameters has long been used to show that natural gas compositions can be altered due to mixing of gases from the two source end-members as well as by microbial action and migration through sediments.

Although the carbon isotopic composition of methane measured in almost all near-surface sediment samples appears to be in the biogenic gas range, the gases sometimes contain a significant thermogenic component. These seemingly biogenic isotopic compositions can be misleading when considered alone. However, the strong presence of the C₂₊ alkane gases provides compelling evidence of upward-migrating thermogenic gas in many samples because indigenous ethane, propane, the butanes, and the pentanes do not accumulate at levels higher than about 2 ppmV in such sediments. However, the absence of high levels of the C₂₊ alkane gases does not necessarily mean that thermogenically-sourced gas is not present. Also, mole fractions of the C₂₊ alkane gases from 1% to 20% in a produced gas would be indicative of a thermogenic "*wet gas*" origin for the gas, but in near-surface marine sediments the *normal background* ratios of ethane and propane are typically high enough with respect to the background methane to produce these percentages. Such mole fractions, without further indicators, are not anomalous. We have found that *the ethane/ethene ratio* in sediments is a particularly robust indicator for helping determine gas origins.

Figure 2 is a plot of the ethane/ethene ratio vs. the carbon isotope ratio of methane for the canned headspace-gas samples of a current study (*2001 Central Gulf of Mexico*). The ethane/ethene ratio is extremely definitive of the existence of a thermogenic component in a gas. It is preferred over the C₁/C₂+C₃ ratio for these purposes, because the C₁/C₂+C₃ ratio can be misleading for sediment gases at low concentrations. This figure plots individual samples of the 2001 study, as well as samples from earlier programs in the Central and Western Gulf of Mexico. Schematically represented are the general ranges of hypothetical end-members for gas of thermogenic and biogenic origins. Some mixing lines between these two end-members are also plotted. The plot illustrates that most of the gas-rich samples analyzed for the Central Gulf fall in

the “mixing zone”. The biogenic end member for this region would appear to have a carbon isotopic composition of methane of about -70 ‰. Note, however, that the gases of Western Gulf programs trend toward an isotopically lighter (-90 ‰) end-member as well as being “drier” in ethane.

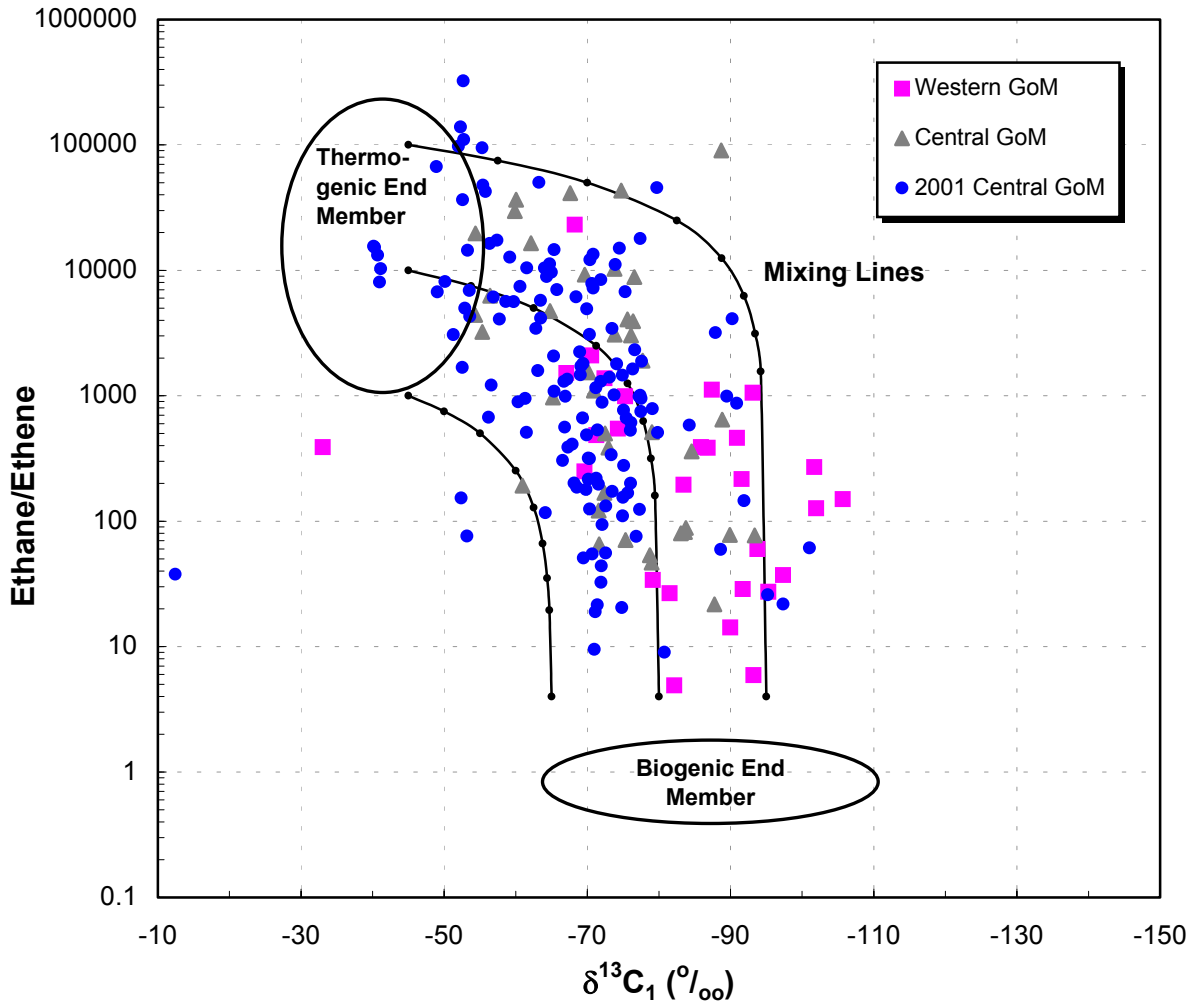


Figure 2. Ethane/ethene ratio vs. $\delta^{13}\text{C}$ of methane in near-surface sediments.

Figure 3 plots the carbon isotopic composition of ethane vs. that of propane for samples of the 2001 program. Plotted for reference as small gray dots are data from some well gases produced from the Gulf of Mexico Basin, and from other basins around the world. There is a fairly linear relationship between the isotopic composition of ethane and propane in these well gases. The samples trending toward more positive values (heavier carbon) are typically also in association with more mature oils. This plot can thus be used as a qualitative maturity diagram for thermogenic gas samples.

When a headspace gas sample is from the same core from which biological markers were determined, the point is plotted with the coding for the oil family (*e.g.*, SE2) interpreted from the

biomarkers. Some headspace gas samples were from cores that were also extracted for biomarkers, but from which no oil family could be assigned. These are coded as *extr*. Other canned samples are from cores for which we did not extract biological markers (*no extr*).

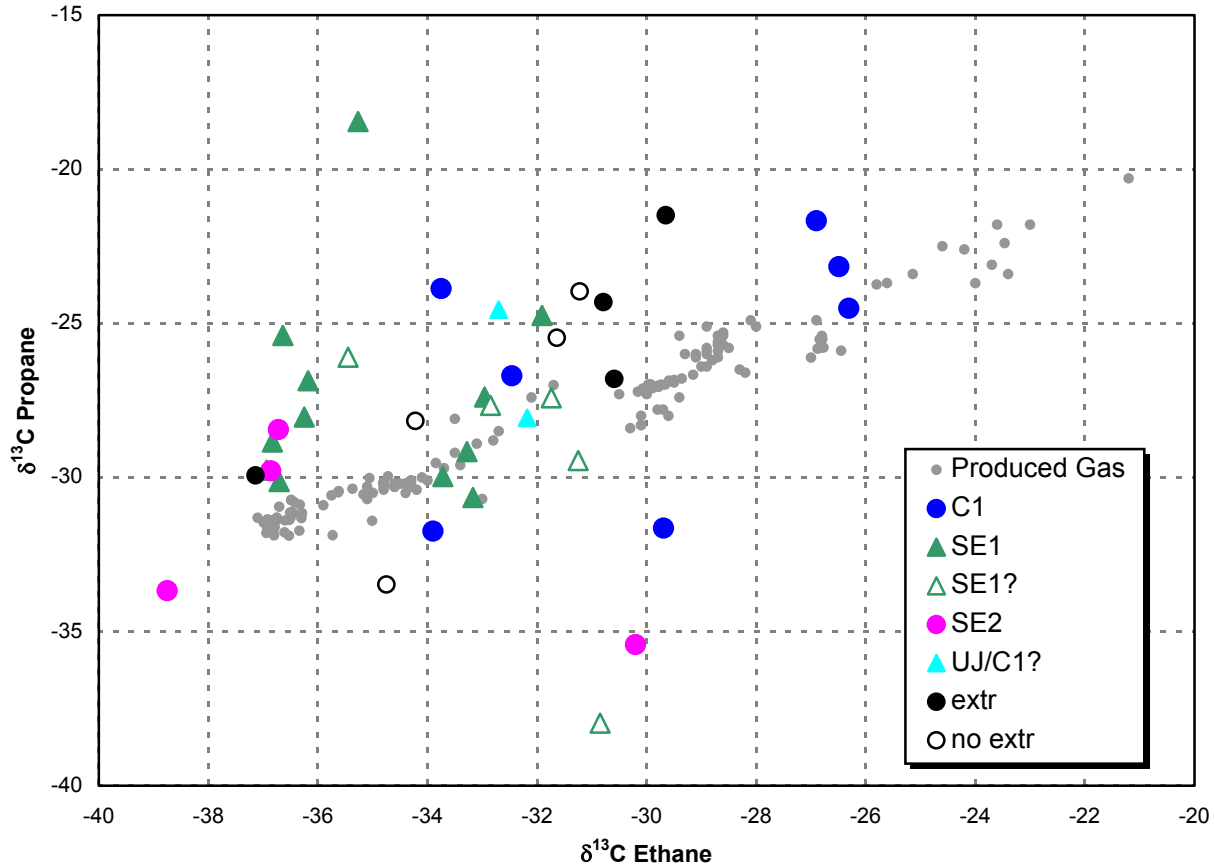


Figure 3. $\delta^{13}\text{C}$ of propane vs. $\delta^{13}\text{C}$ of ethane in near-surface Gulf of Mexico sediments.

The carbon isotopic ratios for ethane and propane in gases taken from near-surface sediments are not nearly as correlated as are those of the well gases. Fractionation of the carbon isotopes of the propane (and of the ethane to a lesser degree) is the most likely explanation. However, a few observations can still be made from these data:

- (1) The near-surface sediment-core gases plot in the general arena as the well gases.
- (2) The gases from cores having oil of the less mature *SE2* oil family plot in the less mature end of the “gas maturity: line.
- (3) The gases from cores having oil of the more mature *C1* oil family plot in the more mature end of the data set.
- (4) The gases from cores having oil perhaps biodegraded from the *SE1* oil family (*SE1?*) seem to cluster near those of the *SE1* family, lending some support to their association with *SE1*.