

## Technical Note:

### Geochemical surveys of sub-marine hydrocarbon seeps in petroleum exploration

Marianne Nuzzo

Cold seeps are areas in which hydrocarbons and water released in buried sediments and rocks are transported to the surface in sub-aerial (Mazzini *et al.*, 2008) or marine settings (Kopf, 2002). They are very common along continental margins and generally involve dewatering of clay-rich sediments undergoing diagenetic clay-mineral transformations at temperatures of ~ 70 to 150°C (e.g. Hensen *et al.*, 2007). The fluids are over-saturated with hydrocarbon gases, predominantly methane, which may be produced in shallow organic-rich sediments by methanogenic microbes or have a deeper thermogenic origin (e.g. Nuzzo *et al.*, 2008 & 2012). In the latter case, the fluid may contain liquid hydrocarbons, in particular in mud volcanoes in which buried sediments are also mobilised and erupted at the surface (e.g. Stadnitskaia *et al.*, 2007; Nuzzo *et al.*, 2009). Seepage may be more or less intense. Very low intensity seeps result from the diffusion of hydrocarbons from shallow accumulations such as gas hydrates or shallow gas reservoirs to the surface. Higher intensity seeps involve the upward advective transport of hydrocarbon-rich water from the subsurface to the seafloor, with seepage intensity increasing for higher fluid advection rates. Transport is generally mediated by faults and seeps are very often associated with strike-slip faults (e.g. Hensen *et al.*, 2007). Seepage is thought to be episodic and to be controlled by complex inter-related factors including pore overpressurisation caused by the generation/influx of clay-water and hydrocarbon gas, tectonics, seismic activity, gas hydrate dynamics, etc.

Hydrocarbon seeps thus hint at the presence of hydrocarbons in the subsurface. They are detectable using relatively simple geochemical methods because the seepage of hydrocarbon-rich fluids in immature seafloor sediments 1) sustains specific, and diagnostic, micro-organisms and biogeochemical processes; and 2) changes the composition of *in-situ* Organic Matter (OM). A geochemical study of the presence and distribution of seeps or microseeps can thus provide insights into the potential occurrence of hydrocarbon reservoirs in the subsurface and can constitute a cost-effective prospective tool for frontier provinces.

As methane-rich fluids are transported to the seafloor, they mingle with sulphate-rich pore water diffusing downward from the bottom seawater along a "mixing front" called the "Sulfate-Methane Transition Zone" (Reeburgh, 2007). Microbial communities often involving sulphate-reducing bacteria and ANaerobic MEthane oxidizers (ANMEs) are able to breathe sulphate and concomitantly oxidize methane to CO<sub>2</sub>, a process referred to as Anaerobic Oxidation of Methane or AOM (Boetius *et al.*, 2000). These microbes are responsible for the simultaneous downward decrease of sulphate (SO<sub>4</sub><sup>2-</sup>) and increase of methane (CH<sub>4</sub>) concentrations that is observed in the SMTZ (Figure 1).

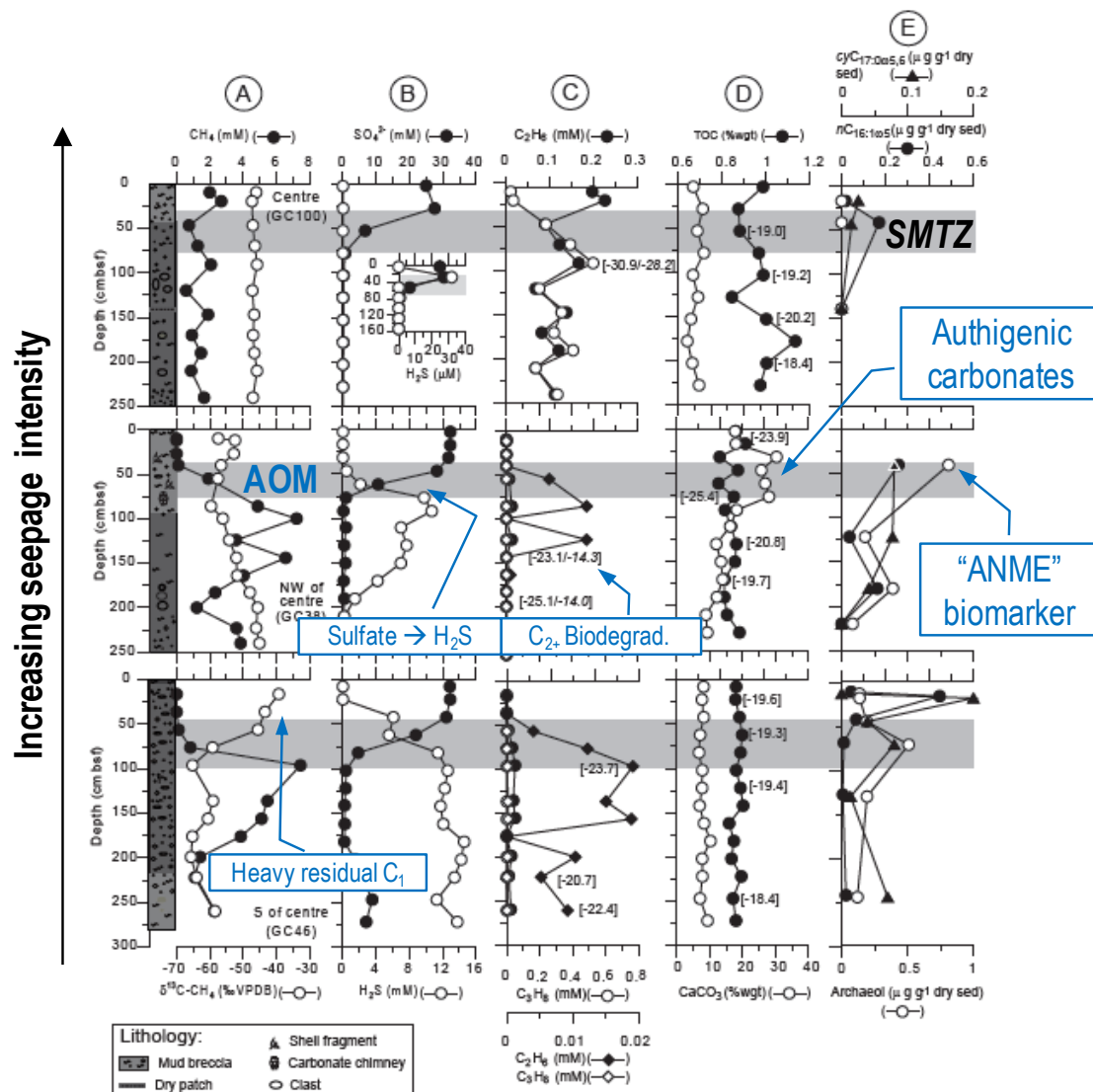
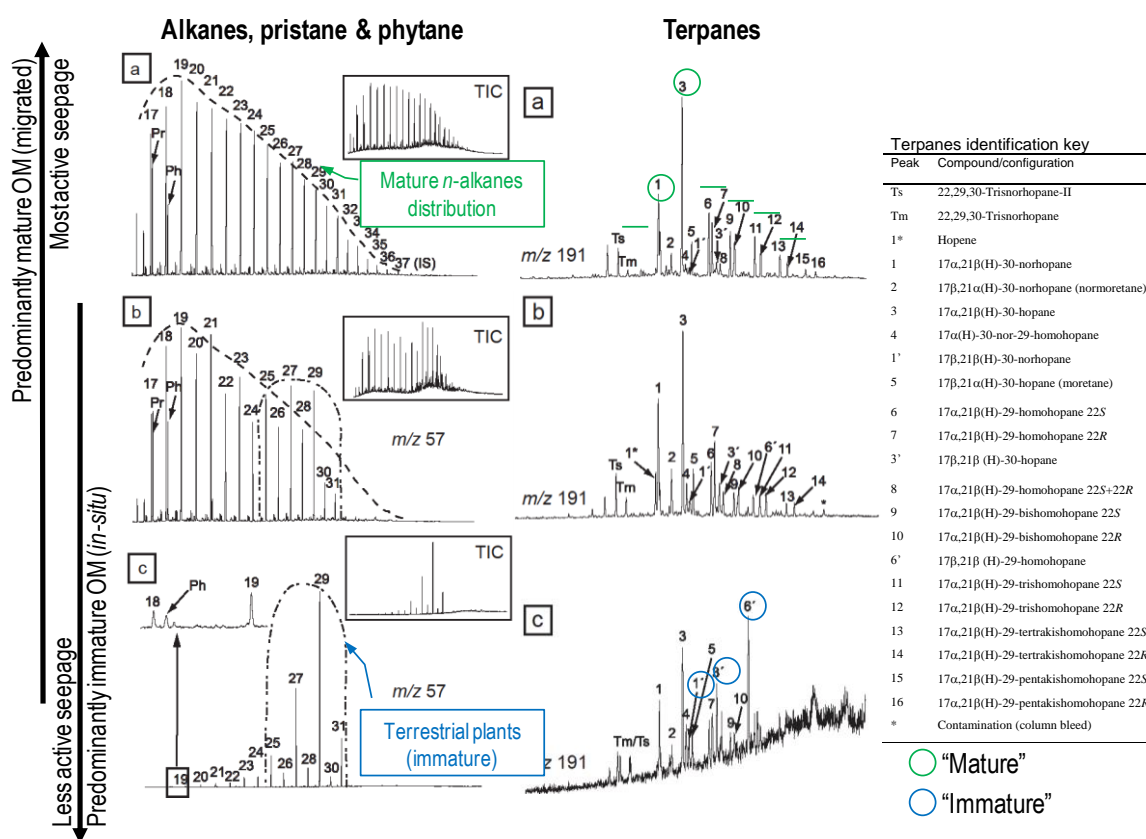


Figure 1: The Anaerobic Oxidation of Methane (AOM) is shallower in the more intense seep area of the mud volcano as indicated by the depth of the Sulfate-Methane Transition Zone (SMTZ, in grey) in which methane concentration decreases and  $\delta^{13}\text{C-CH}_4$  increases upward (A) while sulphate and hydrogen sulphide ( $\text{H}_2\text{S}$ ) concentrations decrease and increase, respectively, downward (B). The concentrations of ethane and propane are higher in the most active centre than where seepage is less intense and they can be biodegraded (C). Authigenic carbonates precipitate from  $^{13}\text{C}$ -depleted bicarbonate produced by AOM (D). Diagnostic biomarkers for sulphate-reducing bacteria and Anaerobic Methane Oxidizers (“ANME”) increase in the SMTZ (E). Modified after Nuzzo *et al.* (2012).

If the seeping gases have a thermal origin, they might be enriched in liquid hydrocarbons whether because they constitute a highly mature gas condensate or because they have “stripped” compounds from oils they came in contact with during migration. This is recognised by the increasing and anomalous presence of mature hydrocarbons mixed with the immature compounds of the *in-situ* sedimentary OM close to the (focussed) seepage locations (Figure 2).



**Figure 2: Distribution of *n*-alkanes, pristane and phytane shown on *m/z* 157 traces (Left) and of terpanes (hopanes) shown on the *m/z* 191 traces (Right). (A) Most intense seepage location (CAMV), with a predominance of mature hydrocarbons. (B) Mixed immature and mature signatures. (C) Predominance of immature hydrocarbons in the least intense seep. Modified after Nuzzo *et al.* (2009).**

Geochemical surveys for seepage and micro-seepage of hydrocarbon fluids in shallow sub-surface marine sediments are often performed using piston or gravity cores about 4 to 10 m long. These are relatively rapid and cost-effective coring techniques, and a survey can involve the collection of a large number of cores distributed over the area of interest. Upon recovery, the core liners are usually immediately cut in half, and sediment plugs collected at one or, preferably, several depths. A sediment plug is used to measure porewater gas concentrations by headspace equilibration. Another sample is collected for extraction in organic solvents and analysis of the biomarker composition of the extracted organic matter. Plastics are a major contaminant and these samples should be collected with clean metal spoons (for example) and stored in sealed furnished glass jars. Other samples are collected for miscellaneous analyses such as total organic and inorganic carbon contents (TOC and TIC, respectively). Organic geochemistry analyses of main interest include the molecular and stable isotope composition of headspace gases, concentrations of gasoline-range hydrocarbons (e.g. by thermal extraction), and the distribution and concentrations of saturated and aromatic biomarkers.

## References

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