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Processes of Mud Volcanism in the Barbados-Trinidad Compressional System: New structural, Thermal and Geochemical Data

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Subsurface sediment mobilisation in SE Caribbean occurs in a context of plate boundary between the Caribbean plate and the South American plate, at the junction between the Barbados accretionary prism and the transform system of the northern Venezuela. Within this compressional and transpressional system, a several hundred kilometres-long active belt of mud volcanoes and shale diapirs develops from the Barbados tectonic wedge to the thrust belt of Northern Venezuela (Fig. 1). In this system, the mud volcanoes of Trinidad and Venezuela are only the emerged part of a widely developed phenomenon in the offshore area of the Barbados prism (especially in its southern part). This has been notably spectacularly evidenced by the recent results of the CARAMBA survey of the O/V ATALANTE in 2002 (Figs. 2 & 3).

Structural setting

Mud domes and volcanoes developed in different structural settings (Biju-Duval *et al.*, 1982; Valery *et al.*, 1985; Brown & Westbrook, 1987; Brown, 1990; Rutledge. & Leonard 2001; Deville *et al.*, 2003a & b in press, Fig. 1). The front of the tectonic wedge is characterized by an imbricated thrust system mostly devoid of active mud volcanism activity. The main province of active shale diapirs and mud volcanoes is found within the core of the tectonic prism along ramp anticlines and on top of sigmoid rises of mud diapirs (Fig. 2), or else along major transfer zones (especially at the eastern extremity of the El Pilar fault in the Barbados prism; Valery *et al.*, 1985; Griboulard *et al.*, 1991). In the slope between Trinidad and the Barbados prism mud volcanoes have a rather random distribution (Fig. 3). The western part of the Barbados prism is characterized by the occurrence of extension structures overimposed on thrust tectonics (Deville, 2000;Fig. 1), and the very inner part of the prism is devoid of active mud volcanism. Nevertheless, in the inner part of the Barbados prism, fossil mud volcanic activity associated with hydrocarbon migration is known notably on Barbados island (Speed *et al.,* 1991). Laterally, toward the SW, the belt of mud volcanoes is becoming narrower and emerges in Trinidad within the transpressive fold-and-thrust belt of the southern part of the island (Central and Southern Ranges).

Nature of the mud and of the clasts

Combined X-ray diffraction and SEM studies (in the Trinidad and on cores collected from mud volcanoes of the Barbados prism) have shown that the solid particles within the mud are composed of clays (kaolinite, illite, smectite, vermiculite), chlorite and muscovite, but also abundant grains of quartz, feldspar (albite, K-feldspar), carbonates (calcite, dolomite, siderite), titane oxides (rutile, anatase), apatite, baryte, and pyrite. The grain size varies from less than 0.2 µm to more than 200 µm, and the grains are supported within a very thin matrix constituted by a mixing of various clays, micas sheets, and also small fragments (less than 5 µm) of quartz and albite with clearly angular shapes and internal microfractures, especially in quartz. The mechanical damage probably result from shearing during compaction or mud volcanism eruptive processes. Such quartz grains can make up more than 90% of the solid fraction within the mud. In the Trinidad mud volcanoes with a recent eruptive activity (Piparo, Devil's Woodyard, Columbus group, Anglais Point, Moruga), exotic clasts are found (mainly centimetric to pluri-decimetric). The nature of the clasts is polygenic (carbonates, sandstones, shales, calcite, sulphur nodules, …). Some clasts are ancient pebbles initially interbedded within Tertiary formations and mobilized during eruptions, but most of the clasts show angular shapes resulting from intense fracturing. Fractures are filled with carbonate cements (Ca and Ca-Mg). Frequently, real breccias made up of angular and initial joined elements are included within calcite crystallisations. We interpret most of the angular clasts and the breccia as the result of hydraulic fracturing processes. Using nannofossils, it is possible to date precisely the clasts expelled by the mud volcanoes. According to the ages obtained, these elements belong to Tertiary formations, ranging from

Paleocene to Miocene. Cretaceous clasts are expelled by the Piparo mud volcano in the Central Range, the older elements being of Early Barremian age. But in this case, these clasts can come from the base of the Naparima thrust sheet and they do not have necessary a deep origin. On the other hand, the mud shows systematically a mixing of species ranging from Cretaceous to Late Miocene. This suggests that the mud consists of a mixture of microscopic elements of various origins (from Tertiary formations, but also from Cretaceous levels). These data show that the zone of initiation of the mud volcanism is necessarily at least as deep as the Paleogene and probably the Cretaceous, because the mud intrusions do not crosscut thrust sheets involving Cretaceous-Paleogene formations, except for Piparo. In the offshore, the study of nannofossils in cores collected from the south of the Barbados prism suggests that the mobilised sediments in shale domes and mud volcanoes, are of Miocene-Pliocene age (zones NN15 to NN21) at the front of the mud volcanism zone. However, various horizons probably including the Eocene, and certainly including Oligocene (zones NP25 to NP21), Miocene and Pliocene intervals have been mobilised in the inner part of the Barbados Ridge.

Gas composition

In the onshore mud volcanoes of Trinidad, the gas is mainly methane associated with moderate concentrations of ethane, propane and carbon dioxide. This dry gas is characterized by a $\delta^{13}C$ of methane which ranges between -52 and 33‰ (Fig. 4). Such $\delta^{13}C_1$ values associated with very dry gases are generally interpreted as intermediate values between a purely bacterial gas and a purely thermogenic gas. Nevertheless methane $\delta^{13}C$ can be affected by post-genetic phenomena (segregation during migration, chemical bacterial alteration) and it is possible to use the $\delta^{13}C(C_1)$ *vs* C_1/C_2 diagram (Fig. 4) to distinguish some of these processes (Prinzhofer & Pernaton, 1997). This suggests that a mixing hypothesis between bacterial and thermogenic gas must be rejected because in these cases the bacterial end member would have methane $\delta^{13}C$ between -52 et -33 ‰, which are too heavy values, incompatible with a bacterial origin. Therefore, we consider that most of the analysed gas samples have a strictly thermogenic origin. The dryness of the gas would be due to a segregation process, which probably occurred during its migration from depth to the surface (adsorption on the solid grains of the mud, and solubility processes). The concentration in C2+ is higher in the sites where eruptions occurred recently (Piparo and Devil's Woodyard, Columbus). We suppose that adsorption occurs mainly during steady state phases and that C2+ is released only during and after catastrophic eruptions. Though the maturity of the gas is difficult to define precisely because of the segregation processes mentioned above, this thermogenic gas has probably been generated in the oil window. In the case of very recent (Neogene) gas generation, as observed in Trinidad, high flows of thermogenic gas could have been generated at temperature around 150°C, similar to the equilibrium temperature of the deep reservoir that has fed the mud volcanoes (Dia *et al.*, 1999). The chemical and isotopic composition of the gas suggests a cogenetic origin with the hydrocarbon fields of Trinidad, which both exhibit notably atypical heavy values of $\delta^{13}C$ (CO_2). Some values are approaching 30‰, which is very unusual in potential sources of CO_2 in sedimentary basins. It is now well established that the source rock of the hydrocarbon fields of southern Trinidad is of Cretaceous age (Gautier and Naparima Hill formations; Rodrigues, 1988; Talukdar *et al.*, 1990; Heppard *et al.*, 1998). The gas from the mud volcanoes being cogenetic with the gas of the HC fields, we also attribute a Cretaceous source rock for its origin. From another point of view, the analysis of noble gas radiogenic isotopes has shown that the gas expelled from the mud volcanoes exhibits lower $^{40}Ar^*/^{20}Ne$, and $^{4}He/^{20}Ne$ ratios with respect to the gas within the deep HC reservoirs, implying that the gas from the mud volcanoes has a shorter residence time than the gas associated with the oil fields (Battani *et al.*, 2001). So, the gas of the mud volcanoes can not be issued from a direct leakage from the HC fields, but would come directly from deeper kitchens.

Thermal measurements

New heat flow measurements made during the CARAMBA survey, on some active mud volcanoes in the southern area of the Barbados prism, show positive anomalies (values higher than 100mW/m^2, up to 230 mW/m^2 at the vicinity of mud volcanoes in a heat flow background regime lower than 40 mW/m^2). Moreover, at the vicinity of some mud volcanoes, BSRs are shallower compared to the areas around suggesting that the stability field of gas-hydrates is here more restricted to upper levels compared to the surrounding areas. We interpret those anomalies as related to heat diffusion associated to the circulation of hot fluids into the conduits of the mud volcanoes. We also studied the temperature distribution within the mud conduits of some mud volcanoes onshore Trinidad. We noticed an influence of the geometry of the conduits on the fluid circulation and thus on the temperature distribution. Complex temperature distribution implying convection processes were measured in large conduits, whereas linear gradient implying processes close to simple advection were observed in linear mud chimneys. It is worth noting that in both cases one can obtain reverse gradients that can be related either to the geometry of the convective cells or to changes during time of the temperature of the fluid flows at the base of the investigated conduits.

Discussion

Mud volcanoes correspond to sedimentary eruption of liquefied material forming cones or mud pies and associated superficial mud flows, whereas shale dome correspond to percing diapirs of mobilized plastic shales, which have probably never been liquefied. Mud volcanism and shale dome processes are both obviously related to the development of overpressure at depth which contributes to sediment mobilization by reducing the strength within the overpressured layer and which is necessary for mud extrusion (to counterbalance the mud load). Overpressure generation is favored, in this tectonic context, by the conjunction of fast sedimentation rates leading to compaction disequilibrium (sedimentary loading), and compressive stress regimes inducing layer-parallel shortening and tectonic overloading. Also gas-hydrate occurrence in these deep offshore areas is likely to reduce permeability in the superficial levels and so to slow down fluid expulsion, favouring overpressuring. Moreover, the high deformation rates in accretionary prisms (especially compared to onshore mountain belts) probably have an important role in the dynamic development of overpressure (typically non-static phenomena). Moreover, temperature induces the cracking of hydrocarbons in thick prisms, which is an additional factor for overpressure generation. Although the gas expelled by the mud volcanoes in deep water is most likely to be dissolved, the occurrence of free gas bubbles, especially in the shallowest areas, is also likely to reduce the density of the sediments.

Hydraulic fracturing resulting from excess pore pressure tends to be sub-horizontal (Fig. 5). Consequently, lateral hydraulic connectivity may be enhanced. High pore pressures in the center of piggyback basins, if approaching the lithostatic load, may be transmitted laterally towards the anticline crest where sedimentary thickness are smaller. Consequently, if pore pressure overcome the vertical load, upward mud extrusion can occur. Low pore fluid pressure near the surface will favor the lateral emplacement as sedimentary sills or chambers from the main vertical mud conduits toward the surrounding formations. This process is well imaged on some seismic sections (Biju-Duval *et al.* 1985), and has been proven by drilling in Trinidad (Higgins & Saunders, 1974). Mud volcanoes, can significantly modify the flow path of water and hydrocarbons migration within the basin. Both are efficient vertical conduits allowing direct escapes to the surface, as evidenced by methane-rich cold seeps associated to the development of numerous chemiosynthetic communities (Jollivet *et al.,* 1990).

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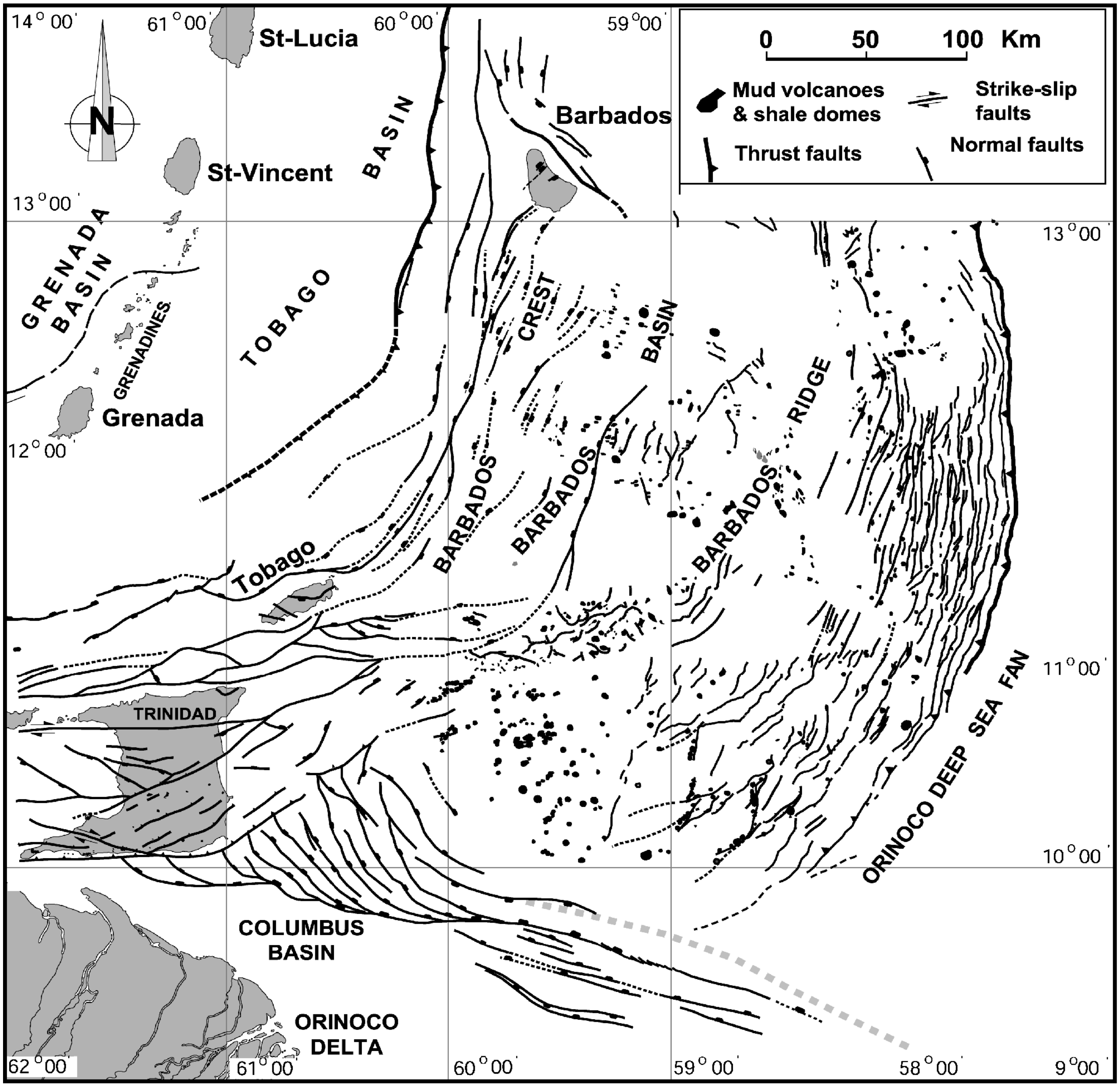

Figure 1 – Location of the mud volcanoes and shale diapirs in the Barbados-Trinidad compressional system (from Deville *et al.*, 2003a in press)

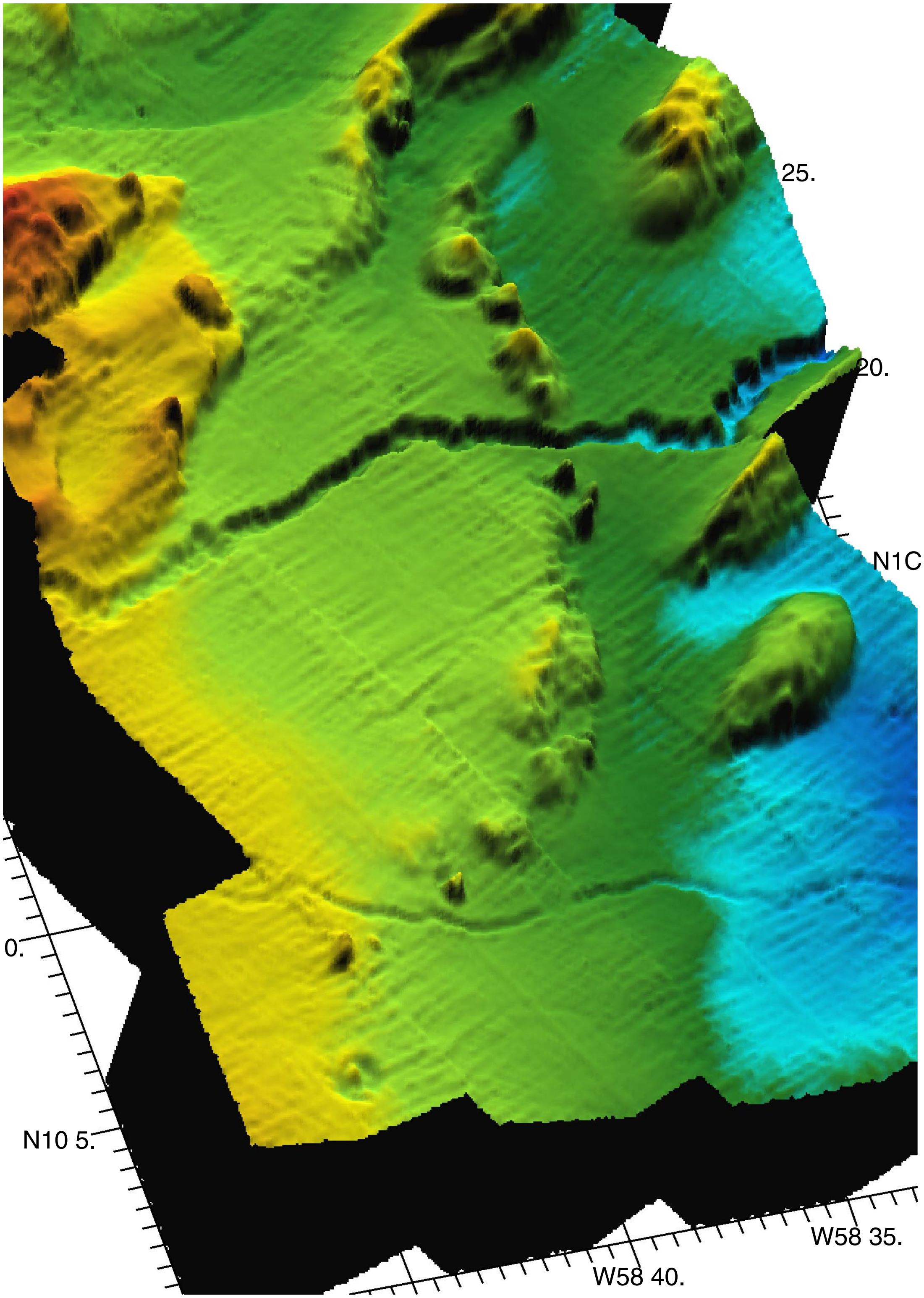

Figure 2 – Sigmoid rise in the Barbados prism

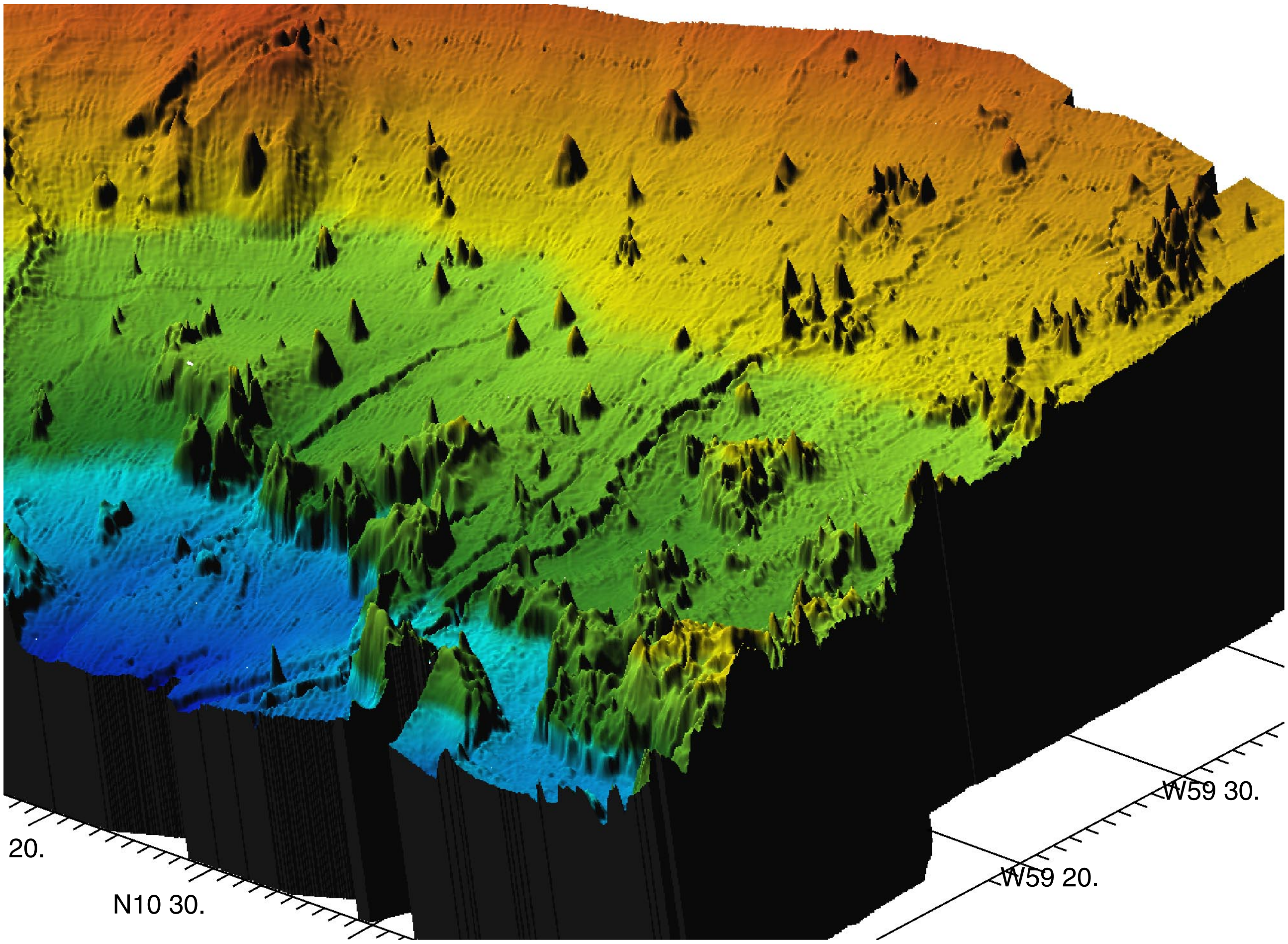

Figure 3 – Random distribution of mud volcanoes in the slope between Trinidad and the Barbados prism

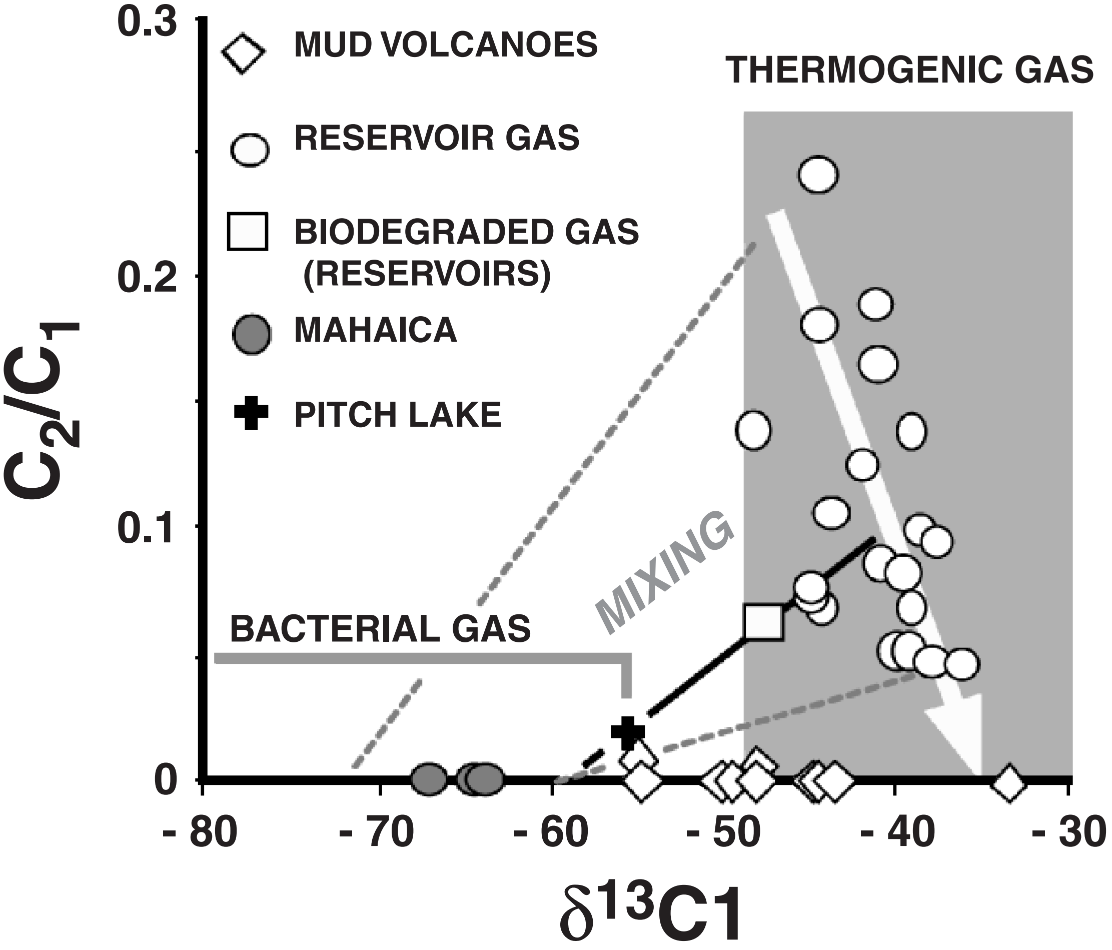

Figure 4 – C_2/C_1 *vs* $\delta^{13}C_1$ diagram in which a mixing between two end members is characterised by a straight line. Only three samples have suffer a bacterial contamination. Most of the mud volcanoes HC gas have a purely thermogenic origin (from Deville *et al.*, 2003a in press).

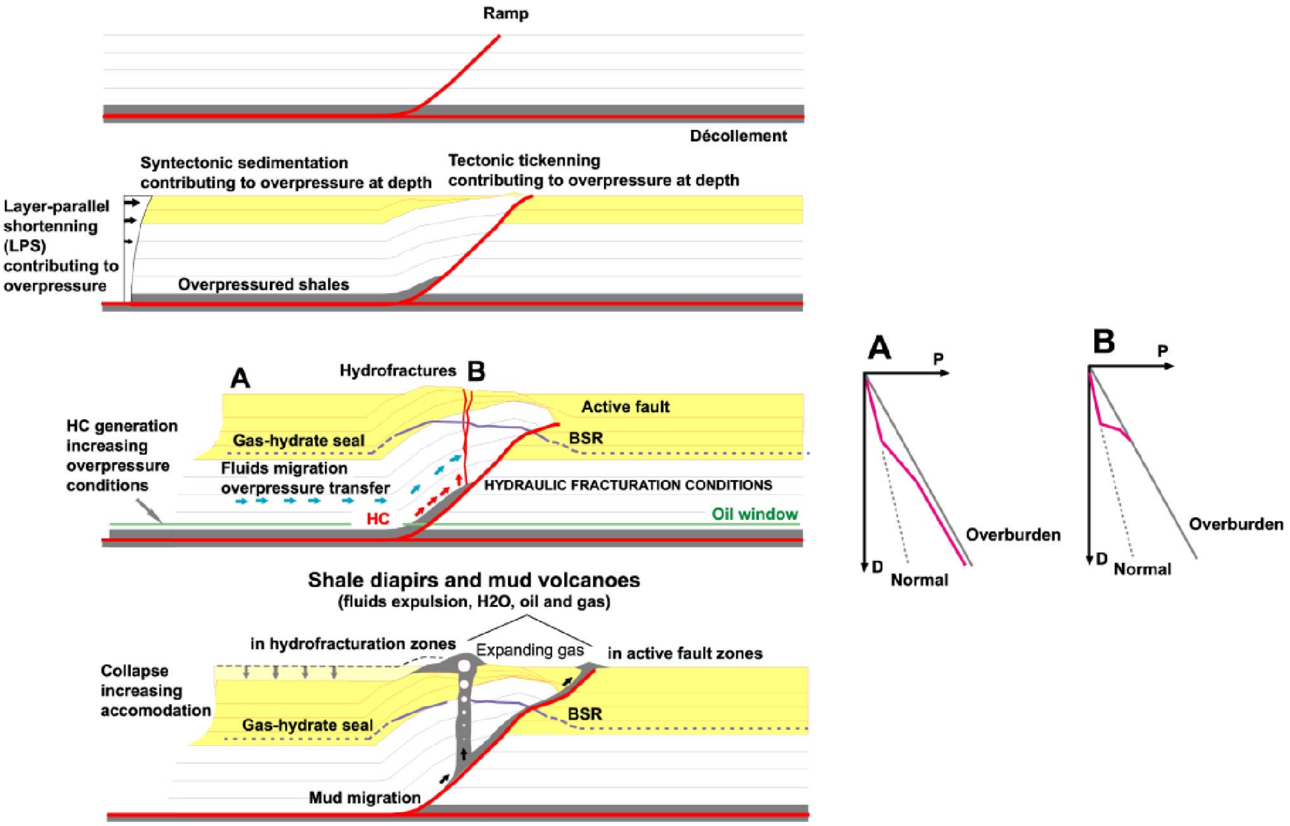

Figure 5 – Proposed pressure distribution leading to the occurrence of mud volcanoes (from Deville *et al.*, 2003b in press).