AAPG/ASPG RESEARCH SYMPOSIUM
Oil and Gas Petroleum Systems in Rapidly-Subsiding Basins
October 6-9, 1996, Baku, Azerbaijan

Novel Application of Geochemical Inversion to Derive Generation/Expulsion Kinetic Parameters for the South Caspian Petroleum System (Azerbaijan)

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An enigma for basins that experience rapid subsidence is that the actual petroleum source rock is beyond the reach of the drill. As a result, the mechanism for the hydrocarbon charge is usually inferred to have a dominant "vertical" component and crude oil thermal stress analysis is often the only means available to derive the generation/expulsion kinetic parameters. This paper defines the approach and makes the application to the South Caspian petroleum system.

Crude oils examined in this study (n=85) represent the production from 26 oil fields, including samples from 10 fields that are classified as "giants". These samples are interpreted to comprise a single genetic oil type that is differentiated into three subtypes with a combined "biomarker-isotope" technique. The oils are frequently altered by secondary alteration mechanisms, with biodegradation/water washing (76%) and mixing (54%) being the most common. Despite secondary alteration, the molecular traits of these oils can be attributed to marine organic matter deposited in an anoxic to suboxic water column with lesser contributions from terrestrial organic material. Specific evidence includes a terpane fraction with abundant pentacyclics that exponentially decrease with increasing carbon number, accompanied by minor to moderate amounts of gammacerane, oleanane (including des-A variety), 29,30-bisnorhopane, and the C_{24} tetracyclic terpane. The C_{30} diahopane, C_{29}Ts, 2α(methyl)hopanes, and resinous biomarkers (e.g., bicadinanes) occur in minor to trace amounts. The tricyclic terpanes are dominated by the C_{23} and C_{24} members, whereas the C_{15} and C_{16} regular and rearranged drimanes dominate the bicyclic terpanes. It is noted that the oils also contain minor amounts of the C_{25} highly branched isoprenoid (the "diatom" biomarker), β-carotane, and aryl-isoprenoids. The modified Hughes plot shows the oils to be in the "marine shale" sector. The carbon number distribution of the sterane fraction shows nearly equal numbers of the C_{27}, C_{28}, and C_{29} members, but relatively low abundance of the C_{30} and rearranged members. The later observation is extended to include the ring-C monoaromatic steranes as well.

The carbon isotopic composition of the oil samples provide important data. Isotopic compositions for the saturate fraction range between -24.8 and -28.0 per mil, whereas the aromatic fraction ranges from -23.4 and -27.4 per mil. On the modified Sofer-plot, these oils plot below the best fit line; consistent with oils of marine origin. In general, oils produced from onshore fields are isotopically depleted compared to those produced from offshore fields. This data, combined with variation on the molecular level, form the basis for the "biomarker-isotope" technique that resolves these oils into three subtypes (A-1=28%, A-2=44%, and A-3=28%). Correcting the frequency distribution of oil types to reserve size establishes the relationship of A-1<<A-2≈A-3.

The biomarker fraction of the oils contain characteristics consistent with generation at a relatively low level of thermal stress. Over half of the oils display steranes with non-equilibrated $\alpha\alpha\alpha$ members (i.e., conversion of 20R to 20S); this tendency is reinforced with additional maturity dependent biomarker transformations (Fig. 1). The collective results indicate that peak oil generation occurs at a vitrinite reflectance equivalence (VReq) of 0.7 to 0.8. Interestingly, the initiation of hydrocarbon generation does not appear to be significant below 0.6 VReq, since the least mature produced oils (from first expulsion event) have been subjected to this level. It is probable that residual water (related to rapid burial) in the source rock would contribute to aquathermal overpressure to promote an early expulsion event.

The thermal stress analysis of the oils provide significant insights to the generation/expulsion events. The fields that produce the non-equilibrated oils are generally onshore or coincide with a structural uplift; the implication is that the first phase of oil expelled from the source rock (least mature) had access to more continuous migration pathways (preceding deformation events). Subsequent phases of oil expulsion will be more mature (closer to equilibrium), lending support to the contention that the giant fields have a multiple charge history (dilution of low mature oil with more mature oil from the later charges). In circumstances where diverse maturities are observed in a single field (e.g., Bibi Eibat), the reservoir horizon that is responsible for the giant field classification contains the oil that is near the equilibrium point. The giant fields are also in a position to benefit from multiple expulsion/migration events and combined vertical/lateral hydrocarbon charges.

The documentation that these oils were generated at lower thermal stress than is routinely applied to source rocks can be used to refine the threshold for peak oil generation. Combining the crude oil results with the source rock analyses (n=200+) that establish the maturity gradient (Figure 2) enables us to derive the generation/expulsion kinetic parameters. These data establish the effective oil window to occur at the burial depth of 6400 to 8000 meters (peak = 6800 to 7400 meters) for the offshore depocenter; a significant refinement for this petroleum system. Subsequent thermal modeling exercises are used to geologically constrain the kinetic parameters for generation and expulsion of the crude oil. The distribution of activation energies (E_a) are described as asymmetric with the primary burst at 50 kcal/mol with the Arrhenius factor near $9*10^{13}$ (sec^{-1}). It is emphasized that these values are used to describe both oil generation and expulsion instead of simple oil generation. This approach is required to provide a single set of values that can account for the myriad of geologic complexities in the South Caspian petroleum system.

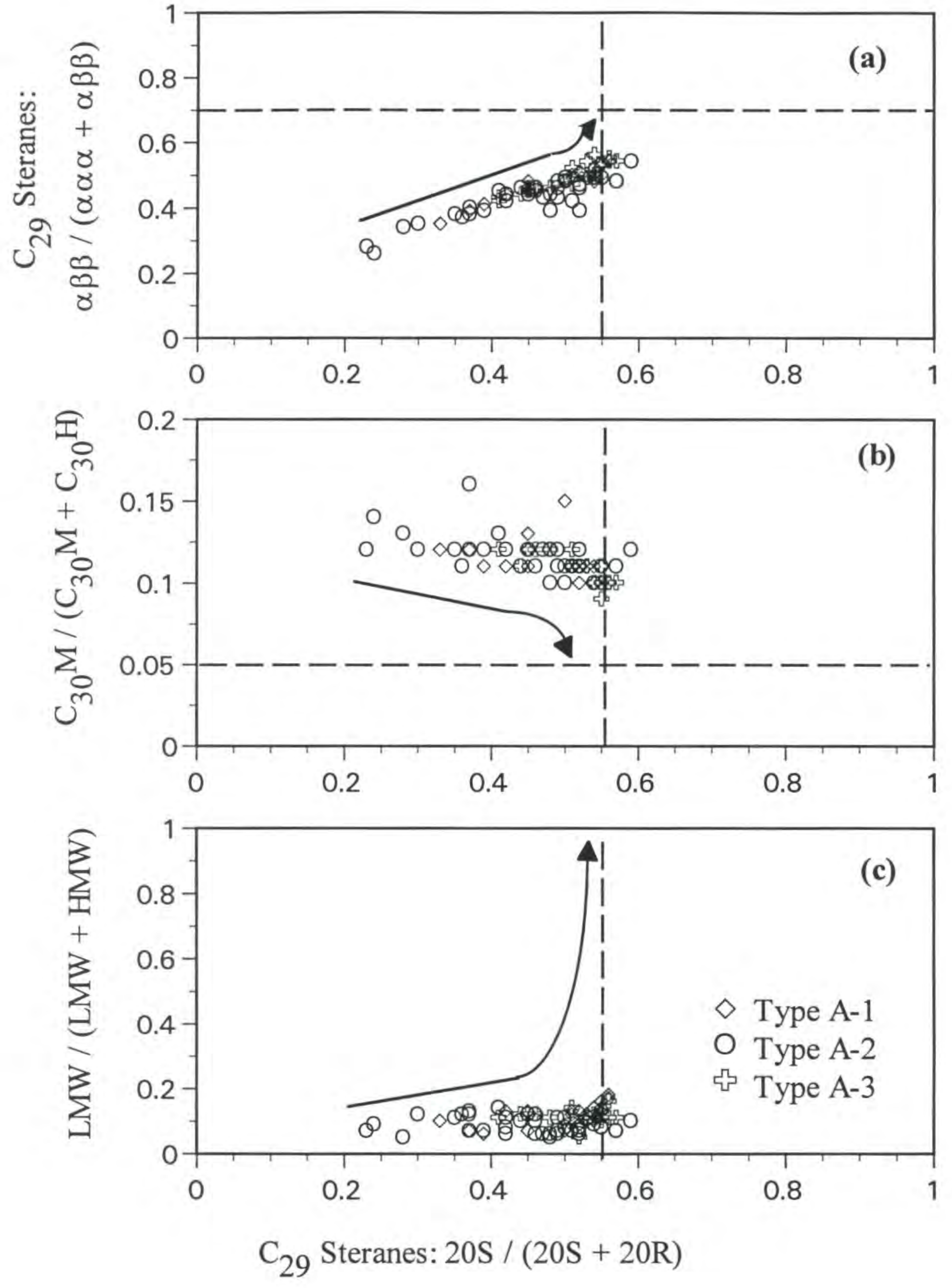

Figure 1. Cross-plots showing the C29 ααα sterane isomerization vs. (a) C29 αββ/(ααα + αββ) ratio, (b) C30 moretane/(C30 moretane + C30 hopane) ratio, and (c) "apparent" triaromatic cracking index. The arrows represent the molecular trends with increasing thermal stress.

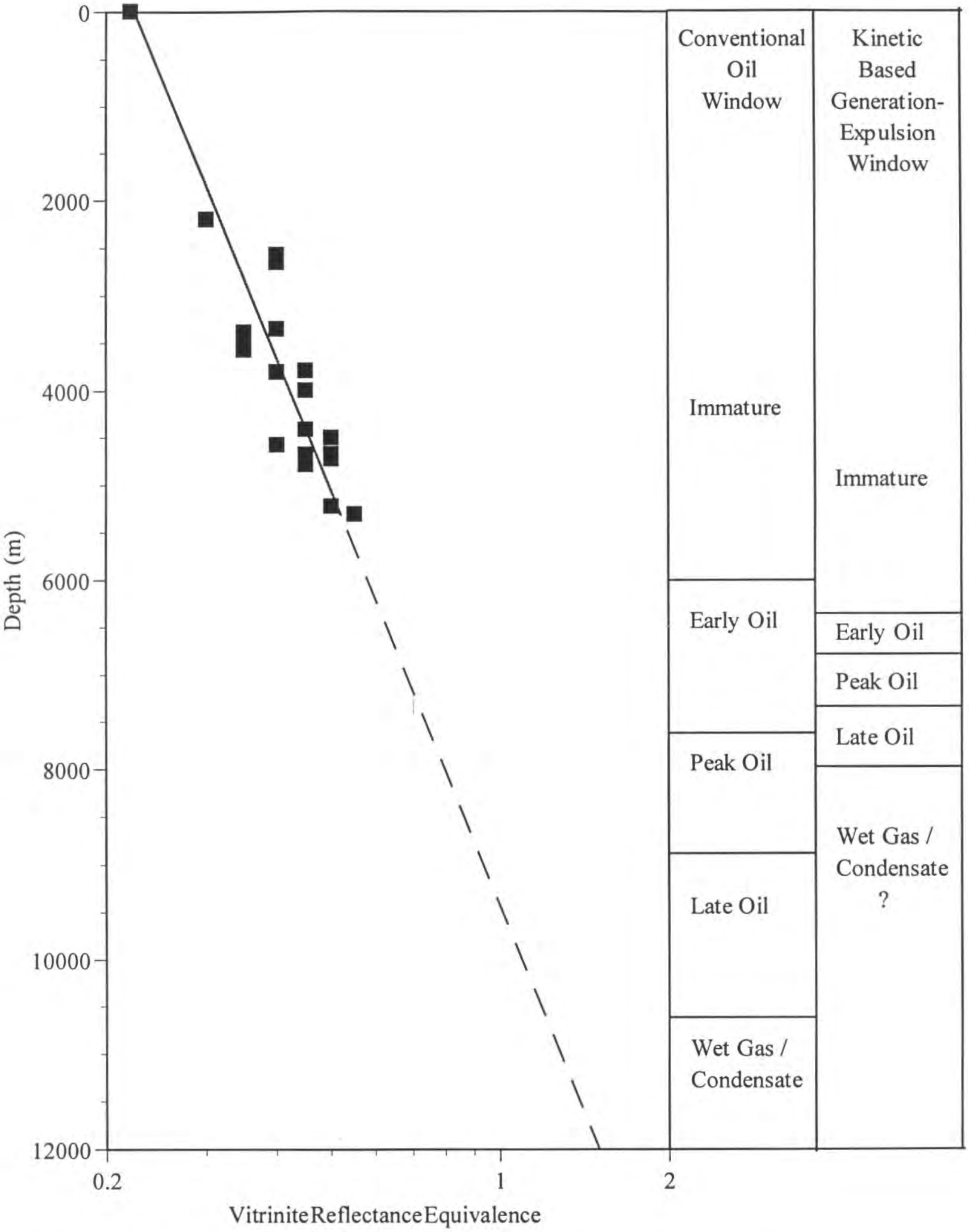

Figure 2. Best fit line ($r^2 = 0.90$) showing the regional maturity profile for the South Caspian basin established by integrating optical (reflected and transmitted light) and chemical (biomarker and pyrolysis) data. A triple weighted data point at 0 meters was used to constrain the maturity at the surface. The "oil window" terminology contrast the conventional and kinetic-based interpretations.