

AN ABSTRACT OF THE THESIS OF

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Alan R. Niem

Because the origin, source rocks, and maturation mechanism for natural gas in the Mist gas field of N.W. Oregon are not well understood, a source rock and natural gas geochemical study has been performed to 1) characterize the source rocks of the Mist area for the potential to generate hydrocarbon gas, 2) define the source(s) of the natural gas, 3) determine the genetic origin(s) of the natural gases, 4) evaluate mechanisms and possible pathways for methane and nitrogen migration, and 5) determine the source(s) of nitrogen in the natural gas. Standard source rock geochemical analyses (TOC, vitrinite reflectance, rock-eval pyrolysis, visual kerogen, TAI, gas chromatography) were used to assess organic matter richness, quality, maturity, and generative potential for mudstones from the middle to upper Eocene Hamlet formation in the Astoria Basin west of the Mist field and from the Eocene Hamlet and Cowlitz formations in both the Mist field and the North Willamette Basin to the southeast. Coal beds in the Clark and Wilson (C&W) sandstone of the

Cowlitz Fm. were also evaluated. Carbon, hydrogen, and nitrogen stable isotope analyses were performed on gas samples and used along with gas compositional data to help determine the genetic origin of the natural gas. Results from the source rock evaluation indicate that organic matter in Mist source rocks is predominantly terrestrial derived, type III, gas-prone kerogen. The mudstones are characterized by relatively low organic carbon contents (<1.0% TOC) and have little hydrocarbon generative potential. The coal beds in the deltaic C&W sandstone of the Cowlitz Fm. are organic rich (>41% TOC) and represent potentially good source rocks. Mudstones in both basins are thermally immature ($R_o = 0.35$ to 0.72%) with respect to peak gas generation to a depth of at least 9000 ft (2743 m). Below this depth, Eocene Hamlet mudstones in the North Willamette Basin Exxon GPE Federal well exhibit an abrupt increase in maturation level ($R_o = 1.07$ to 1.64%), sufficient to have generated dry thermogenic natural gas. Both burial and elevated geothermal gradients resulting from basaltic intrusions and volcanics during and after the time of Cowlitz sediment deposition have probably contributed to the maturation signature found in the deeper parts of the North Willamette Basin. $\delta^{13}\text{C}$, δD , and gas compositional data indicate that the Mist natural gases have been derived from mixing in situ generated biogenic methane with migrated dry thermogenic gas derived from more distant and deeper buried basinal sources. Sandstone reservoirs with a dominant biogenic gas component are located northeast and southeast of the Nehalem arch and Nehalem Graben, suggesting generation and accumulation soon after structural trap development, perhaps during late Eocene (pre-Keasey) extension

and/or after late middle Miocene uplift that reactivated older faults by wrench tectonics. Reservoirs with a dominant thermogenic gas component are found in and near the Nehalem arch, approximately 20 km northwest of identified mature Eocene source rocks in the Exxon GPE Federal well. Long distance lateral migration of the thermogenic gas component is hypothesized via the Nehalem Graben from the North Willamette Basin southeast of the field. Other possible generation pathways, such as thermal maturation by middle Miocene Columbia River, and upper Eocene Cole Mtn. basaltic sills in the Astoria Basin to the west or vertical migration from mature (?) underplated trench sediment via deep seated faults through the Tillamook Volcanics and Siletz River Volcanics are less likely. Nitrogen concentrations in the gases increase in a general west to east direction, and the highest concentrations are associated with gas pools containing the highest concentrations of biogenic gas. Geologic constraints and $\delta^{15}\text{N}$, N_2 , and N_2/Ar data are consistent with a proposed sedimentary organic matter source for the nitrogen gas and appear to rule out atmospheric, igneous, and metamorphic sources from consideration. The nitrogen gas may have been generated by a combination of microbial (nitrate respiration) and thermal processes, similar to the generation mechanisms proposed for the hydrocarbon gas component. These mechanisms would account for the high-nitrogen, high-biogenic gas mixtures found northeast and southeast of the Mist field and near mature source rocks, as well as the low-nitrogen, high-thermogenic gas mixtures found in Cowlitz sandstone reservoirs near and on the Nehalem arch. Alternatively, others have suggested that nitrogen (in the form of ammonia) may have been generated along with methane solely as a result of deep burial and/or the

heating effects of Eocene intrusions on sedimentary organic matter and coals in the North Willamette Basin. In this scenario, the early release and migration of soluble ammonia eventually would be offset by the greater diffusion rate of methane.

The Mist Gas Field, N.W. Oregon:
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Stable Isotope (C,H,N) Geochemistry

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THE MIST GAS FIELD, N.W. OREGON:
SOURCE ROCK CHARACTERIZATION AND
STABLE ISOTOPE (C,H,N) GEOCHEMISTRY

INTRODUCTION

The Mist gas field, located in western Columbia County, N.W. Oregon (Fig. 1), some 75 km N.W. of Portland, has been producing commercial quantities of natural gas (predominantly methane) since 1979 (Newton, 1979). The field is located on an arch (Nehalem arch) formed by the Tillamook Highlands to the south and the Willapa Hills uplift to the north (Alger, 1985). Although several basins and subbasins bound the field (see Fig. 2), there is a general agreement among investigators that the Astoria Basin to the west and the North Willamette or Nehalem Basin to the southeast represent the best potential candidates as source areas for the Mist field natural gas (Alger, 1985; H. J. Meyer, personal communication, 1986; Armentrout and Suek, 1985; Niem and Niem, 1985). However, the origin, source rocks, and maturation mechanism for the gas of the Mist field are still unknown (Armentrout and Suek, 1985).

Numerous geological investigations, both reconnaissance and local in nature, have been conducted in northwest Oregon and for the Mist field (Niem and Niem,

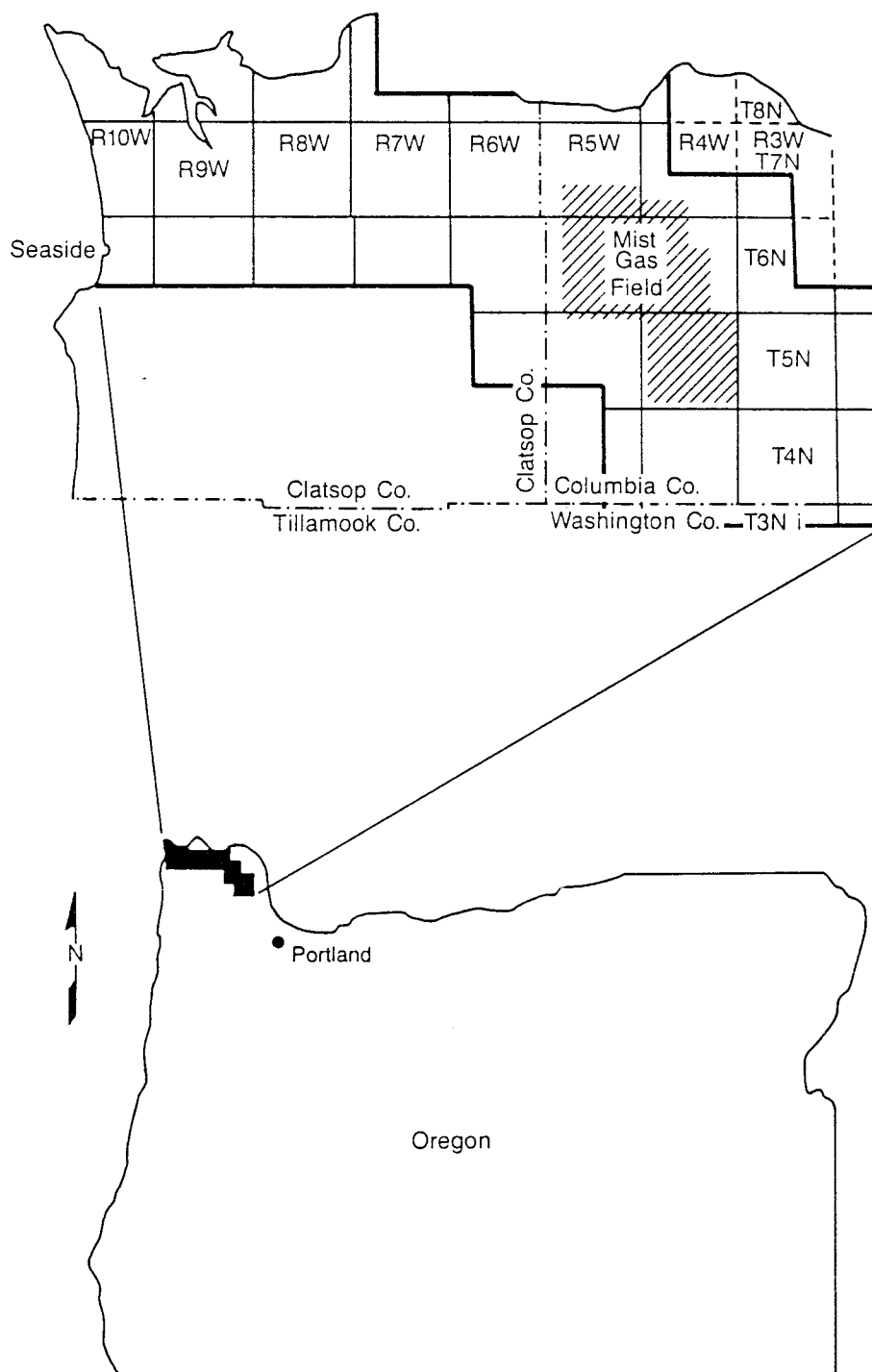


Figure 1. Index map of the study area and location in Oregon.

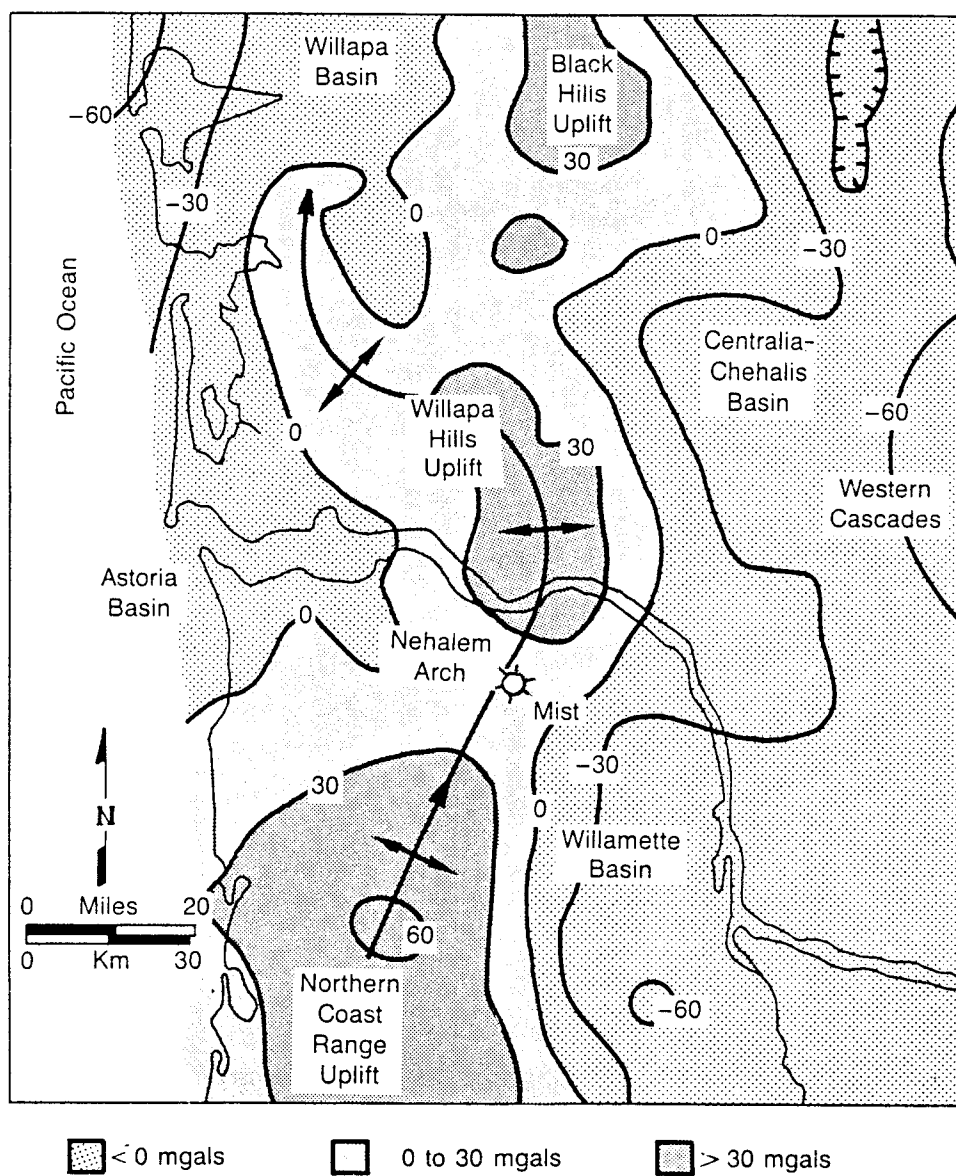


Figure 2. Regional Bouguer gravity anomaly map for northwest Oregon and southwest Washington showing the location of Eocene Coast Range volcanic basement rocks and various basins of Cenozoic sediment deposition. (From Armentrout and Suek, 1985).

1985; Niem et al., 1990; Timmons, 1981; Alger, 1985; Warren and Norbistrath, 1946; Warren et al., 1945; Van Atta, 1971; Berkman, 1990; Farr, 1989). However, no comprehensive organic geochemical study has yet been published, or for that matter completed, which concentrates on questions concerning source area and source rock, organic matter quality and quantity, gas generative history and potential, natural gas genetic considerations or hydrocarbon gas migration - solely with respect to the Mist gas field.

This study was initially undertaken because of concerns related to varying reservoir gas quality resulting from nitrogen contamination. As exploration efforts were directed toward the east and southeast, away from the main Mist field, increasing quantities of nitrogen (N_2) were being encountered in the reservoirs (H. J. Meyer, personal communication, 1985, 1986). The methane-nitrogen reservoir variances brought about questions concerning the genetic origin of the hydrocarbon gases at Mist. Little work has been done systematically in an attempt to characterize the potential source rocks in the area or understand the genetic origin of the gases. Because of the relative absence of existing geochemical data the study was developed into one of constraining the Mist area from an overall organic geochemical approach. Specifically, this study utilizes stable isotope geochemistry ($^{13}C/^{12}C$, D/H, $^{15}N/^{14}N$) and a variety of standard petroleum geochemical analyses (e.g., rock-eval pyrolysis, total organic carbon (TOC), vitrinite reflectance, gas chromatography, and pyrolysis-gas chromatography) in an attempt to:

1. Characterize the source rocks of the Mist area for their potential to generate thermogenic hydrocarbon gas and, if applicable, define the source (basin, rock unit) of the gas.
2. Define the genetic origin of the methane gas.
3. Show trends, if present, suggesting methane migration from source to trap, as well as nitrogen migration.
4. Address the question of nitrogen source and possible reasons for the nitrogen-methane reservoir variability in the field.

Area of Study

The thesis study area encompasses parts of Clatsop and Columbia Counties, N.W. Oregon (see Fig. 1). Access to the study area can be made via highways 26, 47, and 202. The area in and around the Mist gas field is readily accessible by numerous, well-maintained logging roads.

Sample Collection

Fifteen gas samples were collected directly at the well heads by this investigator and subsequently submitted for stable isotope analyses. Gas sampling

bags were of a type commonly utilized in air sample collection. Prior to use, sample bags were evacuated to minimize air contamination. Well heads were flushed for 5 to 10 minutes depending upon well-head pressure and then coupled to the sample bags with tygon tubing.

Source rock samples consisted of well cuttings composited from seven wells, a coal sample from an outcrop of the Clark and Wilson sandstone, and a coal sample from a sidewall core from the Clark and Wilson sandstone. Samples were obtained from the Oregon Department of Geology and Mineral Industries (DOGAMI) - Portland, Oregon Natural Gas Development Company - Portland, Atlantic Richfield Oil and Gas Company (ARCO) - Bakersfield, and Celsius Energy Company - Salt Lake City. It should be noted that the quality of the cuttings, with respect to cleaning and drying procedures, is unknown. Generally, cuttings are collected during well drilling by the well logger, washed, and then dried under a lamp or on a hot plate; the latter procedure being less desirable due to the sensitivity of sedimentary organic matter to heat. Thus it is possible that the results, especially those concerned with maturation parameters, may have been affected by this procedure.

Sample intervals (well cuttings) were chosen from both electric and lithologic logs. The intervals selected consisted of siltstone and mudstone sequences from the Cowlitz and Hamlet formations in the North Willamette Basin, and from the Hamlet formation (informal) in the Astoria Basin. Sample selection was restricted to those

portions of the aforementioned formations representative of probable source rock, and all are Narizian in age (Bruer et al., 1984; Niem and Niem, 1985; Niem et al., 1990; Berkman, 1990).

Experimental Analysis

Carbon, hydrogen, and nitrogen stable isotope analyses were carried out on the gas samples by Coastal Science Laboratories, Inc., Austin, Texas during the Fall of 1986. The reference standards used for carbon-13, deuterium and nitrogen-15 were P.D. Belemnite, Standard Mean Ocean Water (S.M.O.W.) and air nitrogen, respectively. All results are given in the usual δ notation:

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

where R is $^{13}\text{C}/^{12}\text{C}$, D/H, or $^{15}\text{N}/^{14}\text{N}$. The results of the stable isotope analyses (recorded as permil concentrations) are reproducible to within ± 0.5 ‰ for carbon, ± 5.0 ‰ for hydrogen and ± 0.3 ‰ for nitrogen.

Source rock samples were analyzed during late 1986 and early 1987 by Atlantic Richfield Oil and Gas Company (ARCO) at their Plano Research Laboratory and included:

- pyrolysis - gas chromatography
- vitrinite reflectance

- rock - eval pyrolysis
- maceral identification
- extraction and fractionation of solvent soluble organic matter (herein referred to as bitumen or total extract)
- gas chromatography (C_{15}^+ saturates)
- Total Organic Carbon (TOC)
- Thermal Alteration Index (TAI)
- $\delta^{13}C$ (kerogen)

GEOLOGY OF NORTHWEST OREGON

Geologic History

The oldest formations in the Oregon Coast Range date back to the early Eocene and Paleocene (Baldwin, 1981). At that time much of western Oregon and Washington was the site of a eugeosyncline (Snively and Wagner, 1963) or trench and fore-arc basin (Niem and Niem, 1984; Heller and Ryberg, 1983; Johnson et al., 1984; Snively, 1987). The eastern margin extended somewhere beneath the present Cascade Range (Snively and Wagner, 1963). The location of the western margin, as well as the configuration of the eugeosyncline is still debatable. Weaver (1945) presented the Eocene paleogeography of the Pacific Northwest as consisting of an elongate, inland gulf. Snively and Wagner (1963) suggested that the Tertiary embayment was more open and that a submerged sill existed somewhere west of the present coastline, defining the western margin until at least late Eocene-early Oligocene time. The paleogeographic reconstructions presented by Dott (1966) and by Nilsen and McKee (1979) also favor a more open embayment. However, they depict volcanic islands existing offshore with no other land mass to the west. Most of western Oregon was below sea level until middle Tertiary time, with the sea reaching its maximum transgressive extent in early Eocene (Newton, 1969; Niem and Niem, 1985).

The early Eocene was a time of extensive volcanism of oceanic ridge origin (Snively and MacLeod, 1976; Duncan, 1982; Snively and Wagner, 1963). The oceanic plate was carried and rotated clockwise towards the present site of the Oregon and Washington Coast Ranges by subduction between the Pacific (Farallon) and North American plates near the present Cascade Range (Snively and Macleod, 1976; Simpson and Cox, 1977). The oceanic plate, which now forms the basement of the Coast Range, was accreted to the North American plate in the middle Eocene when the subduction zone jumped westward to the present outer continental shelf (Snively et al., 1980; Snively, 1987; Wells et al., 1984). A deep marginal or fore-arc basin formed east of the new underthrust boundary and more than 7000 ft (2134 m) of Cenozoic shallow and deep-marine sediments and mafic volcanics subsequently accumulated in the basin, the axis of which lies along the present north-south axis of the Oregon Coast Range (Snively et al., 1980; Heller and Ryberg, 1983). Alternatively, the early Eocene continental margin may have been a site of oblique subduction with subsequent rifting and in situ tholeiitic basaltic volcanism; a concept that is now gaining favor (Wells et al., 1984; Snively, 1987).

As a result of changing plate motion the boundary between the Pacific and North American plates is inferred to have become a zone of transform faulting in the middle to late Eocene (Snively et al., 1980; Niem and Niem, 1985). Renewed convergence, accompanied by regional uplift and rejuvenation of alkalic basaltic volcanism in the fore-arc occurred in late Eocene, producing a regional unconformity at the base of late Eocene strata (Snively and MacLeod, 1976; Newton, 1969;

Snively et al., 1980). The regional marginal basin was separated into several smaller basins of marine deposition as a result of the late Eocene volcanism and uplift (Snively and Wagner, 1963; Niem and Niem, 1984).

Extension between the Pacific and North American plates appears to have dominated the period from late Eocene to middle Miocene. This extension was accompanied by regional subsidence of these marginal basins and essentially continuous shallow-marine, deltaic, and deep-marine sedimentation of siliciclastics (Snively et al., 1980; Snively, 1987; Niem and Niem, 1985). Middle Miocene Columbia River Basalts erupted in eastern Oregon and eastern Washington (plateau source) and flowed down an ancestral Columbia River to the Astoria, Newport, Tillamook, and Grays Harbor marine embayments to form thick piles of submarine basalt breccias and possible accompanying invasive sills and dikes (Beeson et al., 1979; Pfaff and Beeson, 1989; Niem and Niem, 1985; Rarey, 1986; Wells et al., 1989; Wells and Niem, 1987). Alternatively, these submarine basalt breccias and dikes may be local in origin (Snively et al., 1973). A period of late middle Miocene plate convergence resulted in regional uplift, which subsequently produced a widespread unconformity at the base of upper Miocene strata offshore and uplift of the Oregon and Washington Coast Ranges (Snively, 1987; Niem and Niem, 1984).

Paleomagnetic evidence from Tertiary sedimentary and volcanic rocks of the Coast Range indicates that clockwise tectonic rotation (as much as 70°) has occurred (Magill and Cox, 1980; Simpson and Cox, 1977; Beck and Plumley, 1980). It has

been suggested that this rotation took place about a fixed vertical axis and perhaps in two phases, with the majority of the rotation occurring during the Eocene (Magill and Cox, 1980; Magill et al., 1981). However, more recent evidence suggests that extensive Miocene back-arc spreading and local block rotations between wrench faults may explain much of the paleomagnetic clockwise rotations (Wells, 1984).

General Stratigraphy

For the purpose of this study the nomenclature used for units comprising the stratigraphic profiles in the Astoria and North Willamette Basins is adopted from the recent work of Wells et al. (1983), Niem and Niem (1985), Niem et al. (1990, 1991), Berkman (1990), and Farr (1989). The use of this nomenclature in the Mist-North Willamette Basin area represents a redefinition of the stratigraphy as originally adopted by Warren et al. (1945) and Warren and Norbistrath (1946), and later modified by Armentrout et al. (1983), Armentrout and Suek (1985), Van Atta (1971), Timmons (1981), and Bruer et al. (1984). A correlation chart is provided in Figure 3 which shows the stratigraphic relationship of Tertiary rocks for northwest Oregon and southwest Washington.

The oldest exposed rocks in the northwest Oregon Coast Range are the lower to middle Eocene Siletz River Volcanics, the middle to upper Eocene Tillamook Volcanics, and the middle Eocene Yamhill Formation (Armentrout et al., 1983; Armentrout and Suek, 1985; Alger, 1985; Baldwin, 1981; Wells et al., 1983).

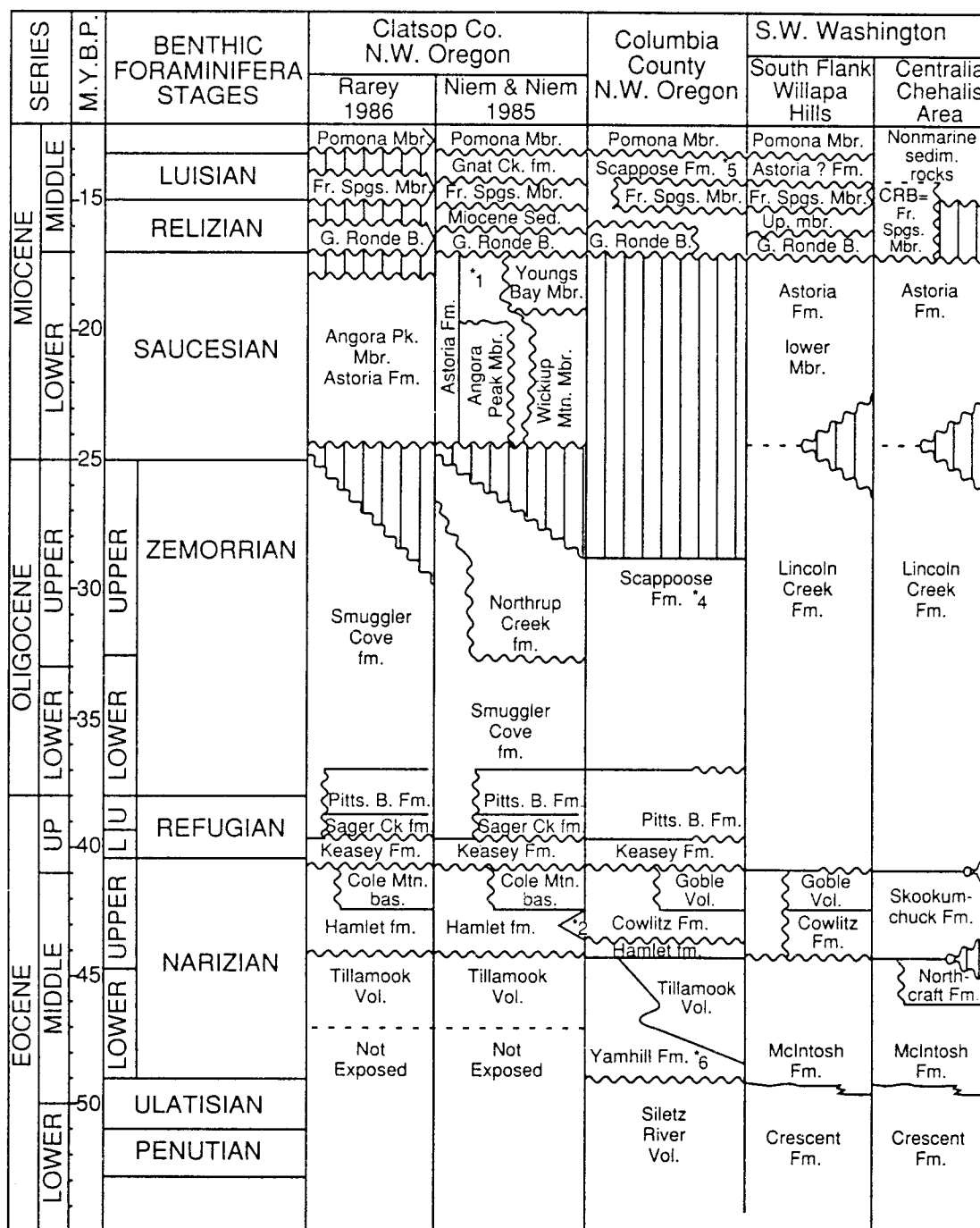


Figure 3. Stratigraphic correlation chart of Tertiary formations in northwest Oregon and southwest Washington (*1 = Cannon Beach mbr.; *2 = Cowlitz Fm.; *3 = Hamlet fm.; *4 = Scappoose Fm. of Norbistrath et al., 1945; *5 = Scappoose Fm. of Van Atta and Kelty, 1985; *6 = Yamhill Fm. of Wells et al., 1983).

The volcanic units consist of submarine and subaerial basalt flows, breccias, and tuffs with estimated thicknesses of 10,000 - 20,000 ft (3048 - 6096 m) (Baldwin, 1981; Newton, 1969; Beaulieu, 1971; Niem and Niem, 1985). The volcanics are associated with dikes and gabbroic sills and minor interbedded mudstone, sandstone, and conglomerate (Wells et al., 1983). The Tillamook Volcanics consist of high TiO_2 tholeiitic basalts. Subaqueous breccia and pillow flow occur at the base (Wells et al., 1983) and subaerial basalts, basaltic andesites and minor andesites-dacites at the top of the unit. This sequence probably represents a series of coalescing volcanic oceanic islands formed in a marginal basin tectonic setting (Niem and Niem, 1985; Rarey, 1986; Safley, 1989; Mumford, 1988; Olbinski, 1983; Berkman, 1990). The 10,000+ ft (3048 m) thick volcanic unit also probably represents the economic basement for the Mist area (Niem et al., 1990; Bruer et al., 1984).

In the Mist-Columbia County area, east and southeast of the Nehalem arch, Yamhill mudstones may interfinger with or overlie the Tillamook Volcanics (Bruer et al., 1984; Alger, 1985). These middle Eocene rocks were deposited predominantly in deep water and consist of tuffaceous siltstone and mudstone, as well as some quartzo-feldspathic sandstones (e.g., Clatskanie sandstone) (Alger, 1985). The Yamhill Formation, first named in the north-central Coast Range by Baldwin et al. (1955), has been correlated to the lower part of the Cowlitz Fm. in Columbia County by Newton (1969) and Newton and Van Atta (1976). However, the lower part of the Cowlitz Fm. of Norbistrath et al. (1945) has been recently redefined in Columbia County by contiguous mapping to the Hamlet fm. (informal) in adjacent Clatsop

County by Berkman (1990) and Farr (1989). Bruer et al. (1984) refer to the Eocene strata in the subsurface of Clatsop and Columbia Counties below the Clark and Wilson sandstone of the Cowlitz Fm. and above the Tillamook Volcanics as the Yamhill Formation. Niem et al. (1990, 1991) and Wells et al. (1983) however restricted the type Yamhill Formation to a sequence of middle Eocene mudstones beneath the Tillamook Volcanics in Tillamook, Washington, and Yamhill Counties, and refer to the Hamlet formation (informal) as mappable middle to upper Eocene mudstone, basal basaltic conglomerate, and arkosic sandstone that occur above the Tillamook Volcanics and directly below the Cowlitz sandstone in Columbia and Clatsop Counties. They have also extended this terminology to the subsurface at Mist and the North Willamette Basin. However, where the Tillamook Volcanics are not present, as in the Willamette Valley subsurface (Bruer et al., 1984), this subdivision is difficult to apply. For the sake of simplicity, the middle Eocene sedimentary rocks below or interfingering with the Tillamook Volcanics will be referred to as the Yamhill Formation. Sedimentary strata between the Tillamook Volcanics and the Cowlitz sandstone will be designated as Hamlet fm. (informal) following the latest terminology of Niem and Niem (1985), Niem et al. (1990, 1991), Berkman (1990), and Farr (1989) in the Mist-North Willamette Basin area. This stratigraphic division recognizes the regional unconformity that exists at the base of the overlying Clark and Wilson (C&W) sandstone of the Cowlitz Formation. The unconformity can be traced in the subsurface from the North Willamette Valley, through the Mist area, and west across the Nehalem arch into eastern Clatsop County (Bruer et al., 1984). This approach is also advantageous with respect to source rock

considerations since potential source rock samples were collected both above and below the C&W reservoir sandstone of the middle to upper Eocene Cowlitz Formation.

The Clark and Wilson sandstone of the middle to upper Eocene Cowlitz Fm. unconformably overlies the Hamlet fm. in the Mist-North Willamette Basin area (Alger, 1985; Timmons, 1981; Bruer et al., 1984; Berkman, 1990; Farr, 1989; Niem et al., 1990, 1991). It is the main reservoir sandstone of the Mist gas field (H. J. Meyer, personal communication, 1986; Alger, 1985; Armentrout and Suek, 1985; Berkman, 1990). A detailed discussion of the C&W sandstone and other potential reservoir sandstone units is presented in the reservoir section of this study. The C&W sandstone is overlain by a thin sequence of siltstone, mudstone, and minor sandstone of the upper Cowlitz Fm. (Timmons, 1981; Van Atta, 1971; Newton, 1969; Alger, 1985; Berkman, 1990; Niem et al., 1990). While the depositional environment of the upper Cowlitz mudstone was predominantly bathyal (Alger, 1985; Berkman, 1990; Niem et al., 1990), several hypotheses exist as to the depositional environment of the C&W sandstone (see reservoir section discussion). Deposition of Cowlitz strata ceased in approximately late Eocene time as a result of active tectonism and erosion (Armentrout and Suek, 1985). In the Mist area, as much as 3000 ft (914 m) of upper Cowlitz strata may have been eroded during this time (Alger, 1985).

Marine strata of the Narizian age Cowlitz Formation are interbedded with the upper Eocene Goble Volcanics in the North Willamette Basin (Fig. 3). These volcanic rocks consist predominantly of subaqueous and subaerial basalt flows and breccias which can be distinguished from both older (middle Eocene) Tillamook Volcanics and younger (Miocene) Columbia River Basalts on the basis of major oxide geochemistry and stratigraphic position (Timmons, 1981; Rarey, 1986; Berkman, 1990). Recently, Farr (1989) and Berkman (1990) recognized ("invasive") intrusive and marine pillow lava equivalents of the type Goble Volcanics in western Columbia County. They informally referred to these units as the Cole Mountain basalts (Mumford, 1988; Rarey, 1986).

Overlying the unconformity at the top of the Cowlitz Fm. is the upper Eocene Keasey Formation (Kadri, 1982; Alger, 1985; Armentrout et al., 1983; Lira, 1990). The Keasey Fm. (Refugian age) consists predominantly of tuffaceous siltstone and mudstone and was probably deposited in a moderately deep-marine environment (Armentrout et al., 1983; Kadri, 1982; Alger, 1985; McDougall, 1975). Fine-grained strata of the upper Cowlitz and Keasey formations act as a regional seal for the Mist gas field reservoirs (Alger, 1985).

Overlying the Keasey Fm. (in decreasing age) in the Mist area are the upper Eocene Sager Creek fm. (informal), upper Eocene to Oligocene Pittsburg Bluff Fm., Oligocene and middle Miocene Scappoose Fm., and the middle Miocene Columbia

River Basalt Group (Warren and Norbistrath, 1946; Kadri, 1982; Armentrout et al., 1983; Niem et al., 1990; Van Atta and Kelty, 1985).

In the Astoria Basin the Tillamook Volcanics are unconformably overlain by the informally named upper Eocene (Narizian) Hamlet fm. (Rarey, 1986; Mumford, 1988; Safley, 1989; Niem and Niem, 1985). This several hundred meter thick formation is composed predominantly of deep-marine siltstone and mudstone. Minor basalt conglomerate and lithic arkosic shallow-marine sandstone occur in the lower part of the unit (Roy Creek and Sunset Highway members, respectively). The formation underlies the C&W sandstone in eastern Clatsop County. Field and subsurface work by Martin et al. (1985), Niem and Niem (1985), and Rarey (1986) in Clatsop County (Astoria Basin) suggests that there is a lateral facies change from the shallow-marine shelf (C&W) sandstone of the Cowlitz Fm. to the deeper marine slope mudstone of the upper Hamlet formation. The Roy Creek basal conglomerate member, Sunset Highway member, and the overlying deep-marine mudstone of the Hamlet fm. reflect a marine transgression over the Astoria Basin and burial of the subaerial Tillamook Volcanics (Niem and Niem, 1985). The shallow-marine lithic arkosic sandstone of the Sunset Highway member of the Hamlet fm. is equivalent to the Clatskanie sandstone of the Yamhill Fm. of Bruer et al. (1984) in the Mist gas field subsurface (Niem and Niem, 1985; Berkman, 1990; Niem et al., 1990, 1991).

The C&W sandstone of the Cowlitz Fm. has been mapped in eastern Clatsop County (Safley, 1989; Nelson, 1985; Olbinski, 1983). Both the C&W and upper Cowlitz mudstone thin eastward towards the Nehalem arch of Armentrout and Suek (1985) (Niem et al., 1990, 1991). On the east flank of this high (in Columbia County) the units thicken eastward (Niem and Niem, 1985; Niem et al., 1990, 1991; Bruer, 1980; Bruer et al., 1984).

Overlying the Cowlitz and Hamlet formations is the upper Eocene (latest Narizian to Refugian) Keasey Formation. In western Clatsop County the contact between the deep-marine Hamlet and Keasey formations appears to be conformable (Martin et al., 1985), although glauconite beds at the base of the Keasey may indicate a disconformity (Rarey, 1986). An unconformable relationship is also indicated between the Keasey and Cowlitz formations in the middle and eastern parts of Clatsop County based upon seismic and well data and field mapping (Niem and Niem, 1985). This local unconformity was also noted by Bruer et al. (1984) in wells and seismic sections and by Berkman (1991) from mapping in western Columbia County. As in the Mist-North Willamette Basin area, the Keasey Formation is characterized by laminated to bioturbated tuffaceous siltstone and mudstone. In contrast to the underlying micaceous Cowlitz sandstone and Hamlet mudstones, the non-micaceous Keasey Fm. contains distinctive glauconitic and tuffaceous mudstone components. These characteristics, along with gamma ray response and trace element geochemistry, were used by Martin et al. (1985), Niem and Niem (1985), Niem et al. (1990, 1991), and Lira (1990) to determine the stratigraphic boundary for

the Keasey in Clatsop and Columbia Counties. Seismic reflection profiles and field mapping show that the micaceous arkosic turbidite sandstone and mudstone of the overlying upper Eocene (Refugian) Sager Creek formation are deeply channeled into the upper Eocene Keasey Fm. in the Mist subsurface and in eastern Clatsop County (Niem et al., 1990, 1991).

Overlying the Keasey Fm. (in decreasing age) are the upper Eocene Sager Creek fm. (informal), upper Eocene to Oligocene Pittsburg Bluff Fm., Oligocene Northrup Creek fm. (informal), upper Eocene to early Miocene Smuggler Cove fm. (informal), late to middle Miocene Astoria Fm., and subaerial lavas and subaqueous pillow breccias and flows of the middle Miocene Columbia River Basalt Group and associated sills and dikes (Niem and Niem, 1985; Armentrout et al., 1983; Fig. 3).

Structure

The structure in the northwest Oregon Coast Range and Mist field is moderately complex. Regionally, the northern Oregon Coast Range is a northward-plunging anticline cored by the Tillamook Volcanics (Snively and Wagner, 1963; Niem and Van Atta, 1973). The Mist field occurs on the southeast flank of the Nehalem arch, a buried segment of this anticlinal trend (Armentrout and Suek, 1985; see Fig. 4).

Superimposed on the Nehalem arch is a complex conjugate fault pattern (Alger, 1985; Niem and Niem, 1985; Niem et al., 1990, 1991). Faults strike northwest-southeast, northeast-southwest, and east-west, although a fairly strong northwest trend might suggest a genetic relationship to the Portland Hills lineament northeast of the field (Alger, 1985). Oblique strike-slip and high-angle normal faults are common (Fig. 4, B-B'; see Plate 2a for cross section location) with some high-angle reverse and thrust faults also present (Newton, 1969; Alger, 1985; Niem and Niem, 1985; Niem et al., 1990, 1991; Rarey, 1986; Nelson, 1985; Safley, 1989; Mumford, 1988; Berkman, 1990; Farr, 1989; R. Jackson, personal communication, 1986). This pattern may reflect wrench tectonics produced by a north-south shear couple due to oblique subduction of the Juan de Fuca plate beneath the North American plate (Niem et al., 1990; Wells and Coe, 1985; Wells et al., 1984). It should be noted that Figure 4 is a composite from two separate cross sections. Although only a few faults have been depicted in cross section B'-B", (in contrast to B-B') they do exist in similar or greater density (R. Jackson, personal communication, 1987; Niem et al., 1990, 1991). Vertical offsets range from several tens of feet to a few thousand feet (meters to hundreds of meters), and many of the northwest-trending faults show right lateral strike-slip movement (Snively and Wagner, 1963; Alger, 1985; Niem and Niem, 1985; Nelson, 1985; Olbinski, 1983). In addition, many normal faults in the subsurface show vertical and lateral offsets which change drastically over short distances suggesting some oblique-slip motion (Alger, 1985). Some normal faults terminate at the Cowlitz-Keasey unconformity (see Fig. 4) with no expression at the surface, reflecting late Eocene deformation

(Alger, 1985; Niem et al., 1990, 1991). Other normal faults show the greatest offsets in upper Eocene strata, but also were reactivated in late middle Miocene by minor oblique-slip or strike-slip motion and can be mapped at the surface cutting younger units (e.g., Pittsburg Bluff Fm., Columbia River Basalt) (Niem et al., 1990).

Understanding the structure of northwest Oregon, especially with respect to fault patterns, is an important task of current exploration effort. This is because most of the sandstone reservoirs in the Mist field are fault traps (see Fig. 4). However, as seismic control in the area gets better, the number of minor faults identified increases dramatically, thus increasing the structural complexity at Mist (H. J. Meyer and R. Jackson, personal communication, 1986). Recent structure information (Niem et al., 1990) indicates that the Nehalem arch is truncated by a large NW-SE trending graben (Nehalem Graben) that roughly follows the trend of the Nehalem River between Mist and Birkenfeld (Fig. 4). Much of the gas production is in upthrown drag-folded fault blocks of C&W sandstone occurring on both sides of the graben (Niem et al., 1990, 1991; see Fig. 4).

Reservoirs

The Clark and Wilson sandstone of the Cowlitz Formation is the main reservoir unit for the Mist field natural gases (H. J. Meyer, personal communication, 1986; Alger, 1985). It is a clean, friable, well-sorted, fine- to medium-grained, micaceous, quartzo-feldspathic sandstone (Armentrout and Suek, 1985; Berkman,

1990; Farr, 1989; Safley, 1989). The excellence of the C&W sandstone as a reservoir unit is illustrated by measured porosity (18-32%; avg. 25%) and permeability (19-1500 md; avg. 250 md) values (see Fig. 6) (Armentrout and Suek, 1985; Newton and Van Atta, 1976). These high values are directly related to the chemically stable quartzo-feldspathic mineralogy, sorting by high-energy, wave-dominated deltaic-shoreface depositional processes, and minor diagenesis of the Clark and Wilson sandstone (Armentrout and Suek, 1985; Berkman, 1990; Farr, 1989; Berkman et al., 1991).

The quartz-feldspar-lithics (QFL) plot of Figure 5 contrasts Cowlitz Formation sandstones (Timmons, 1981; Van Atta, 1971) with typical volcanolithic Cenozoic sandstones of western Washington (Galloway, 1974; Armentrout and Suek, 1985). It is immediately evident that Cowlitz Formation sandstones contain a greater percentage of quartz and feldspar, and fewer lithic grains relative to typical western Washington Cenozoic sandstones. The lithic clasts are predominantly volcanic in origin, and upon diagenesis produce authigenic pore-filling minerals (e.g., smectite-chlorite clays, zeolites) which reduce porosity and permeability (Armentrout and Suek, 1985; Berkman, 1990; Farr, 1989; Berkman et al., 1991). Some secondary K-feldspar and quartz overgrowths have also been recognized in the C&W sandstone (Berkman et al., 1991). However, because of the relative absence of volcanoclastic grains in Cowlitz sandstones, they are less susceptible to development of pore-filling material (Armentrout and Suek, 1985).

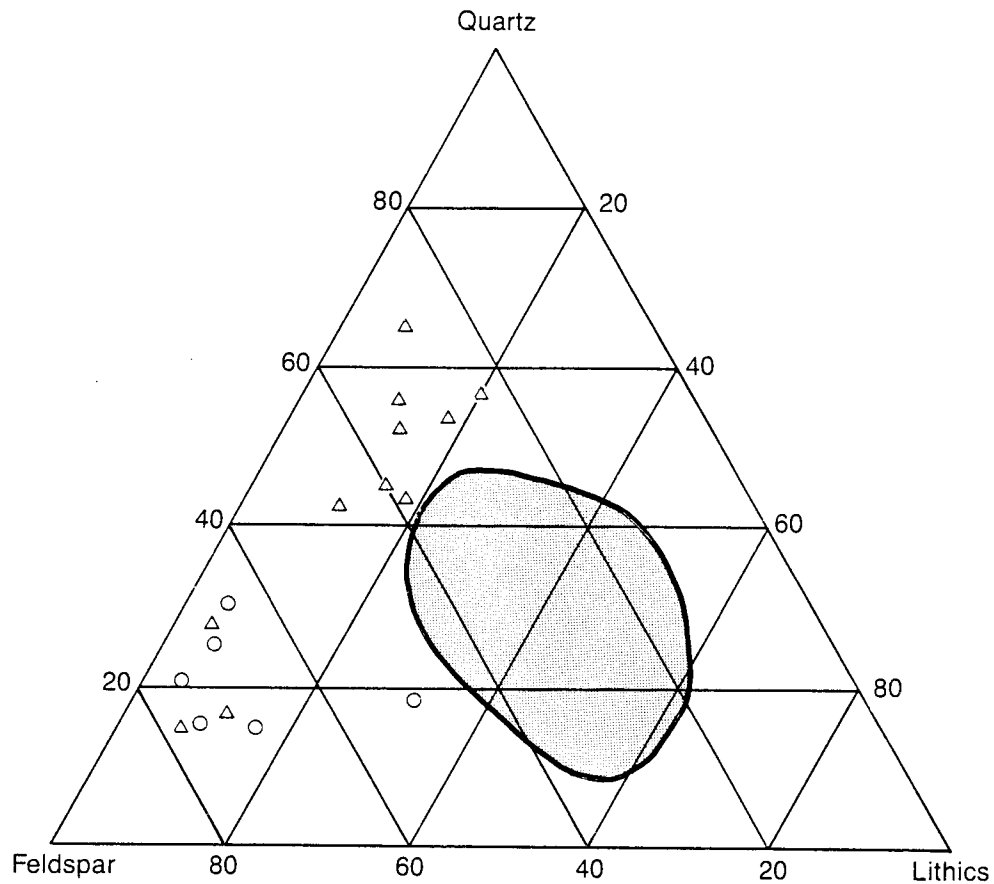


Figure 5. Quartz-feldspar-lithics plot of Cowlitz Formation sandstones (○ - Timmons, 1981; Δ - Van Atta, 1971) versus typical Cenozoic sandstones of western Washington (stippled - Galloway, 1974). Modified from Armentrout and Suek (1985) and Timmons (1981).

There are four sandstone intervals in the Mist area which should be considered as potential reservoir units. Highest to lowest stratigraphically they include the Crown, C&W, Clatskanie (Sunset Highway of Niem et al., 1990, 1991; Berkman, 1990; Farr, 1989), and Yamhill sandstones (Bruer, 1980). The Crown, Clatskanie and Yamhill units are up to 300 ft (91 m), 700 ft (213 m), and 280 ft (85 m) thick, respectively. The C&W sandstone has an average thickness of approximately 330 ft (100 m), but as noted earlier it thins to the west across the Nehalem arch and pinches out in Clatsop County. The Crown, C&W, and Yamhill units have previously been referred to as the upper Cowlitz sandstone, intermediate Clark and Wilson sandstone, and lower Cowlitz sandstone, respectively (Newton 1969; Newton and Van Atta, 1976). The Clatskanie sandstone now correlates with the Sunset Highway sandstone which crops out in both S.W. Columbia and S.E. Clatsop County (Berkman, 1990; Farr, 1989; Nelson, 1985; Rarey, 1986; Mumford, 1988).

A plot of porosity versus permeability measurements for three of these sandstone intervals is shown on Figure 6. The Yamhill sandstone interval is a non-permeable, low porosity unit. Because of its association with basaltic tuffaceous strata and proximity to the Tillamook Volcanics (see Fig. 4, well LF 23-25), Bruer (1980) and Armentrout and Suek (1985) attributed its poor reservoir potential to deep burial and diagenesis of basaltic detritus to clays and other cements. Similarly, early diagenesis of volcanic rock fragments in the lithic arkosic Crown sand unit is the most likely cause of its low permeability (5-90 md) (Armentrout and Suek, 1985). Although no permeability data are available for the Clatskanie sandstones, porosity

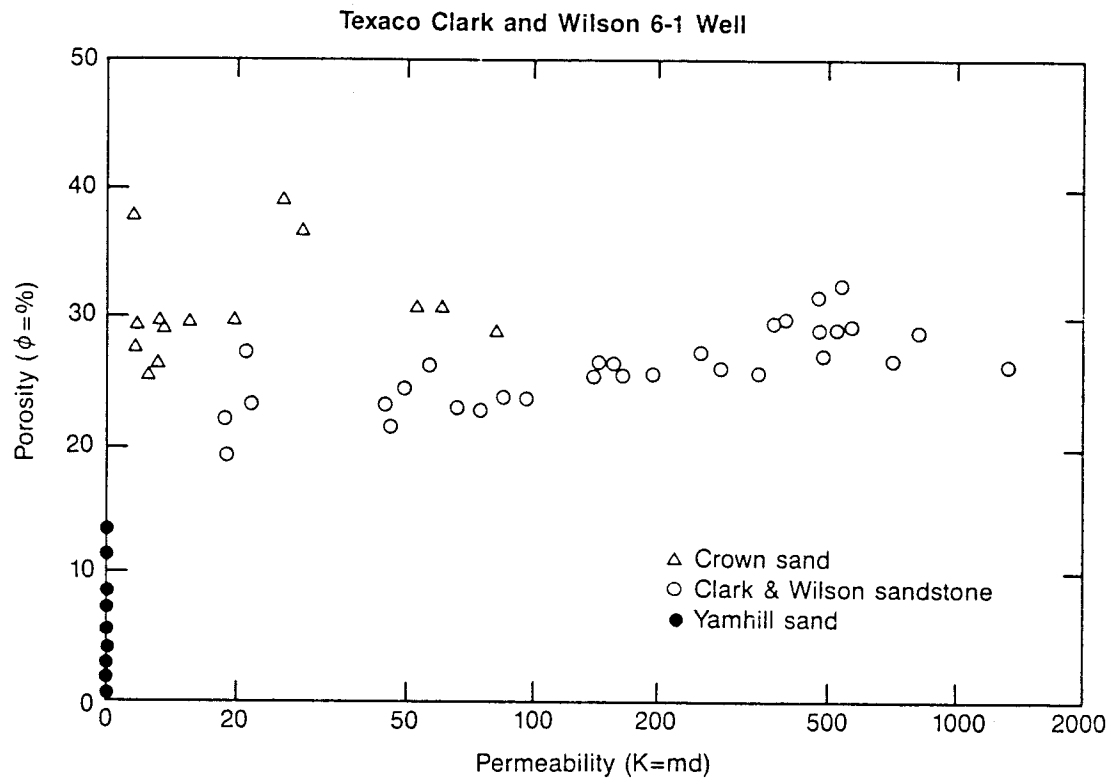


Figure 6. Crossplot of porosity and permeability measurements for the Crown, Clark and Wilson, and Yamhill sandstones. Data from Newton and Van Atta (1976) with units renamed as indicated in the text. Crossplot adapted from Armentrout and Suek (1985).

values range from 18 to 25% (R. Jackson, personal communication, 1987).

According to an appraisal of porosities and permeabilities of common reservoir rock by Levorsen (1967), the Crown, C&W, and Yamhill sandstone units would be classified as fair-good, very good, and poor, respectively, with regard to reservoir potential.

As stated earlier, provenance, mineralogy, and depositional environment are the primary factors resulting in the excellent reservoir quality of the Clark and Wilson sandstone. In addition, some secondary porosity (e.g., dissolution of feldspars) has been produced by diagenetic reactions after burial, which may have caused a minor increase in the porosity and permeability of the unit (Berkman et al., 1991; Farr, 1989). Some authors suggest that deposition of the C&W sands took place during a volcanically quiescent period during the westward jump of the subduction zone during middle to late Eocene time (Snaveley et al., 1980; Armentrout and Suek, 1985). This, in turn, allowed deposition of clean, micaceous quartzo-feldspathic sands derived from granitic (e.g., Idaho Batholith) and metamorphic cratonic source areas farther east via an ancestral Columbia River drainage system, with only minor volcanoclastic input (Van Atta, 1971; Timmons, 1981; Armentrout and Suek, 1985; Berkman et al., 1991; Farr, 1989). The heavy mineral assemblage in the C&W, which is dominated by epidote and euhedral zircons, also suggests a metamorphic and granitic source area (Berkman et al., 1991).

Several other interpretations exist as to the possible depositional environment of the Clark and Wilson (C&W) sandstone. Bruer (1980), based on subsurface geology, suggested that the C&W represents deep-water arkosic sands deposited in a narrow deep-marine gulf or strait that existed during the late Eocene between volcanic highs of Tillamook Volcanics in N.W. Oregon and Grays River Volcanics in S.W. Washington (Wolfe and McKee, 1972). Based on outcrop studies of C&W sandstone, Olbinski (1983), Nelson (1985), Timmons (1981), and Jackson (1983) suggested deposition in a near-shore, wave-dominated, marine shelf environment. A modification of this interpretation is that the C&W sandstone was deposited in a storm- and wave-dominated shallow-water deltaic environment on the late Eocene Oregon and Washington shelves (Alger, 1985; Berkman, 1990; Farr, 1989; Berkman et al., 1991). This interpretation is supported by the presence of wave-dominated sedimentary structures (e.g., hummocky bedding), nearshore biofacies (e.g., trace fossils), abundant lignitic material in cross-beds, and coal beds in both outcrops and cores from the Mist field (Berkman, 1990; Farr, 1989). The coeval Skookumchuck Formation and coal bearing Cowlitz Formation in southwestern Washington are also thought to be of deltaic origin (Buckovic, 1979; Armentrout et al., 1983; Armentrout and Suek, 1985; Alger, 1985; Henriksen, 1956; Wells, 1981; A. R. Niem, personal communication, 1991).

In the Astoria Basin, numerous gas shows have been reported in exploration drilling although no commercial quantities have yet been discovered (Niem and Niem, 1985). Most sandstone dominated formations lack reservoir potential because

of exposure at the surface, restricted deposition, limited thickness, and/or diagenetic alteration. As in the Mist area (east of the Nehalem arch - see Fig. 2), the Clark and Wilson sandstone shows the highest permeability and porosity of all sandstone units in the basin (Olbinski, 1983; Nelson, 1985; Niem and Niem, 1985). It should be noted that the Angora Peak member of the Astoria Fm. has measured permeabilities up to 2 darcies (Cooper, 1981). Although in the onshore area of the Astoria Basin it is probably not buried deep enough to act as a reservoir unit, offshore it has good reservoir potential (Cooper, 1981). As mentioned earlier, the distribution of the Cowlitz Formation is restricted to the eastern part of the Astoria Basin (Niem and Niem, 1985; Niem et al., 1990, 1991; Safley, 1989; Olbinski, 1983; Nelson, 1985; Fig. 7 this report - cross section line shown on Plate 2a). It pinches out to deep-water Hamlet mudstone to the west. If suitable stratigraphic or fault traps can be located, and if the C&W displays sufficient thickness, commercial gas production in the eastern Astoria Basin may be possible (Niem and Niem, 1985). One well (Boise Cascade 11-14) produced 22,000 cfs in a drill stem test (Niem and Niem, 1985).

Traps and Seals

The upper Eocene deep-marine mudstones of the upper Cowlitz and Keasey formations form a regional seal for the Mist gas field reservoirs (Alger, 1985; Armentrout and Suek, 1985; Niem et al., 1990). The tuffaceous character of the overlying Keasey mudstone probably plays an important role in its effectiveness as a seal. Diagenetic alteration of the tuffaceous component produces abundant,

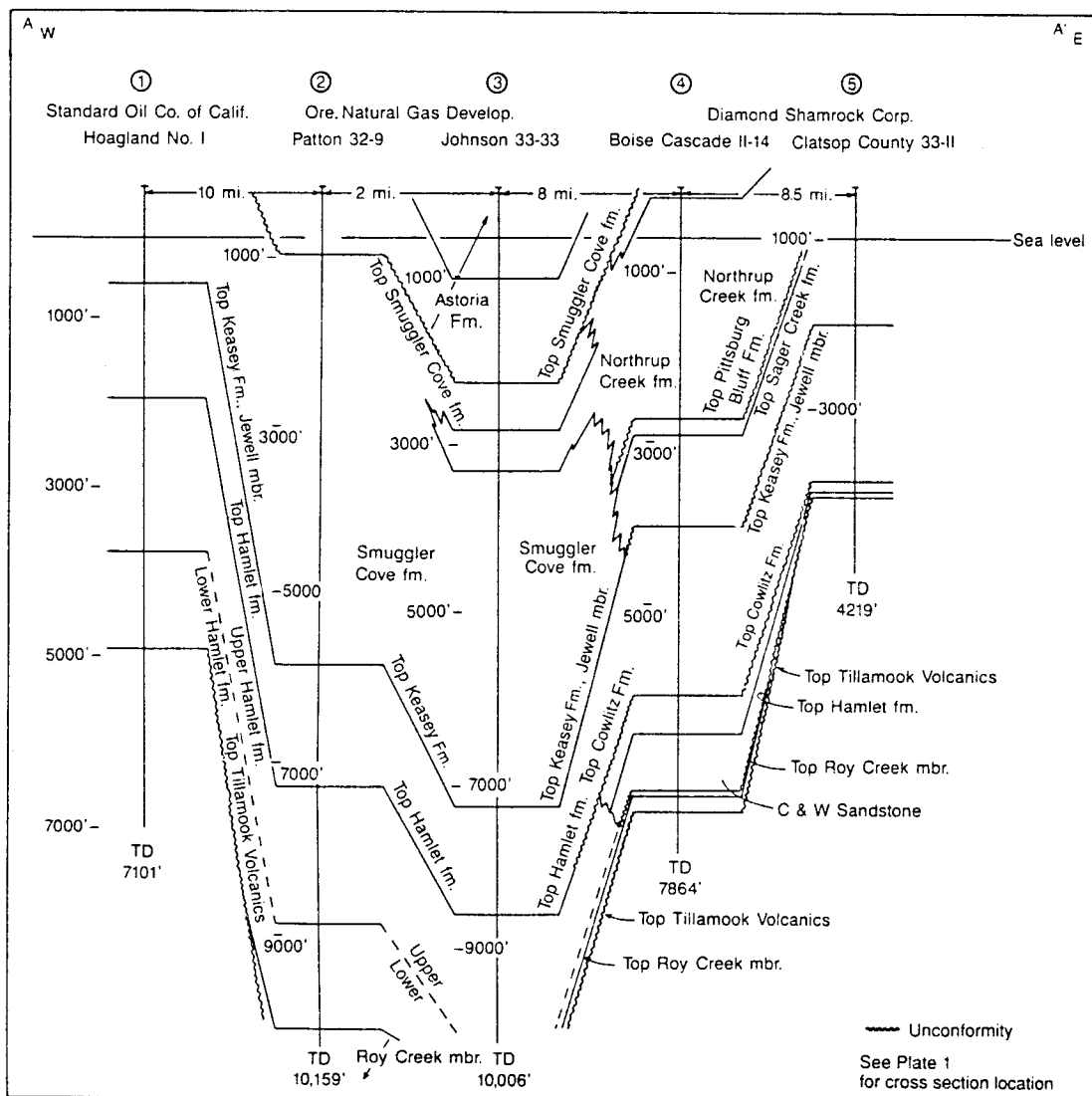


Figure 7. Correlation of exploration wells, Astoria Basin, northwest Oregon. Modified from Martin et al. (1985). See Plate 2a for cross section location.

expandable smectitic clay which can effectively inhibit the movement of fluids and gas. The reservoir-seal relation is shown on the cross section of Figure 4.

With the exception of the Crown Zellerbach 42-1 (CZ 42-1) and the Longview Fiber 12-33 (LF 12-33) RD1 wells, all traps in the Mist field are considered to be fault controlled (Alger, 1985). The structural traps consist of anticline drag-folded C&W strata adjacent to high-angle oblique-slip faults (Niem et al., 1990). Some of the faults are truncated by the unconformity at the base of the overlying Keasey Fm. (see Fig. 4), suggesting their formation as part of an early late Eocene deformational phase (Armentrout and Suek, 1985; Niem and Niem, 1985; Niem et al., 1990, 1991).

The Crown Zellerbach 42-1 well produces from a mudstone-encased, thin, isolated sandstone body in the upper Cowlitz Formation, making it the only pure stratigraphic trap in the Mist field (Armentrout and Suek, 1985). The Longview Fiber 12-33 well may involve erosional truncation of the C&W sandstone and sealing by the overlying tuffaceous mudstones of the Keasey Fm. (Alger, 1985). Other than CZ 42-1, all wells produce from the Clark and Wilson sandstone (Alger, 1985; H. J. Meyer, personal communication, 1986).

There are numerous gas pools, otherwise known as spacing units, in the Mist field (H. J. Meyer, personal communication, 1986). The pools are generally small in size (40-160 acres, 16-65 ha) and the thickest gas column recorded to date is in the Reichhold Columbia County 33-3 well (225 ft, 69 m) (Alger, 1985). Some of the

reservoirs are now depleted (e.g., Columbia County 3, Columbia County 6, etc.) and are being used for gas storage (Oregon Department of Geology and Mineral Industries, 1991).

Mist became the State of Oregon's first and only commercially producing gas field on May 1, 1979 with the reentry, directional drilling, and completion of the Columbia County No. 1 well by Reichhold Energy Corporation (Newton, 1979). Since 1979 over 41.2 Bcf of gas has been produced from the field for an average production rate of approximately 3.7 Bcf per year (Oregon Department of Geology and Mineral Industries, 1991; Wermiel, 1991). At last count, over 140 wells (excluding redrills) had been drilled in the Mist area. Current exploration drilling is being done by Oregon Natural Gas Development Corp. and Nehama and Weagant Energy Corporation (Wermiel, 1991).

SOURCE ROCK GEOCHEMISTRY

Introduction

In an attempt to identify the source area(s) and/or source strata of the Mist field natural gases, various standard petroleum geochemical analyses have been applied to 16 source rock* samples. The Astoria Basin and North Willamette Basin are generally considered to be the best candidates for source areas (Armentrout and Suek, 1985; Alger, 1985; Niem and Niem, 1985). Similarly, a geohistory reconstruction (Lopatin plot) of the North Willamette Basin by Armentrout and Suek (1985) suggests that the Cowlitz Formation and equivalent age or older strata (e.g., Hamlet and Yamhill formations) represent the best potential source rocks that would have been buried deep enough to be thermally matured in these basins. Thus the focus of the source rock investigation for this study has been limited to the Cowlitz and Hamlet formations in the North Willamette Basin and Mist field proper, and the Hamlet formation in the Astoria Basin (see Fig. 8). Yamhill strata as defined by Niem et al. (1991) and Wells et al. (1983), (e.g., Eocene mudstones below the Tillamook Volcanics) are generally not encountered in wells in the Mist-North Willamette Basin area. It should be pointed out that in the older literature

* The term "source rock", as used here, refers to any geologic unit that has generated or has the potential to generate hydrocarbons - independent of thermal maturation levels (Tissot and Welte, 1984).

Bruer et al. (1984) use the term Yamhill for strata now recognized and correlated to the surface as Hamlet formation by Niem and Niem (1985), Niem et al. (1990, 1991), Berkman (1990), and Farr (1989).

In order to avoid confusion during the discussion of source rock data for the Hamlet fm. from the Astoria and North Willamette Basins, the term "Hamlet" will be used in connection with mudstone samples from the Astoria Basin, while the term "Hamlet-Yamhill" will be used in connection with mudstone source rock data collected below the C&W sandstone and above the Tillamook Volcanics from the Mist-North Willamette Basin areas. From wells in the North Willamette Basin and Mist field 10 samples were selected from the Cowlitz and Hamlet-Yamhill formations. The four samples from well cuttings from the Astoria Basin are from the Hamlet formation (equivalent to Cowlitz and Hamlet-Yamhill of the North Willamette Basin). All samples consist of siltstone or mudstone. In addition, two coal samples from the C&W sandstone (one from an outcrop and one from a sidewall core) were analyzed for comparison to the mudstone well cuttings (disseminated organic matter). Figure 8 shows the locations of the wells sampled with respect to the Mist gas field and Table 1 gives the locations of the wells sampled, sample depth intervals, and formation names corresponding to a given interval. The North Willamette Basin wells were selected for sampling because they reflected increasing depth of burial of the target formations from the margin towards the depocenter of the North Willamette Basin. The Astoria Basin wells (Patton 32-9 and Johnson 33-33) were selected in an effort to obtain source rock samples which

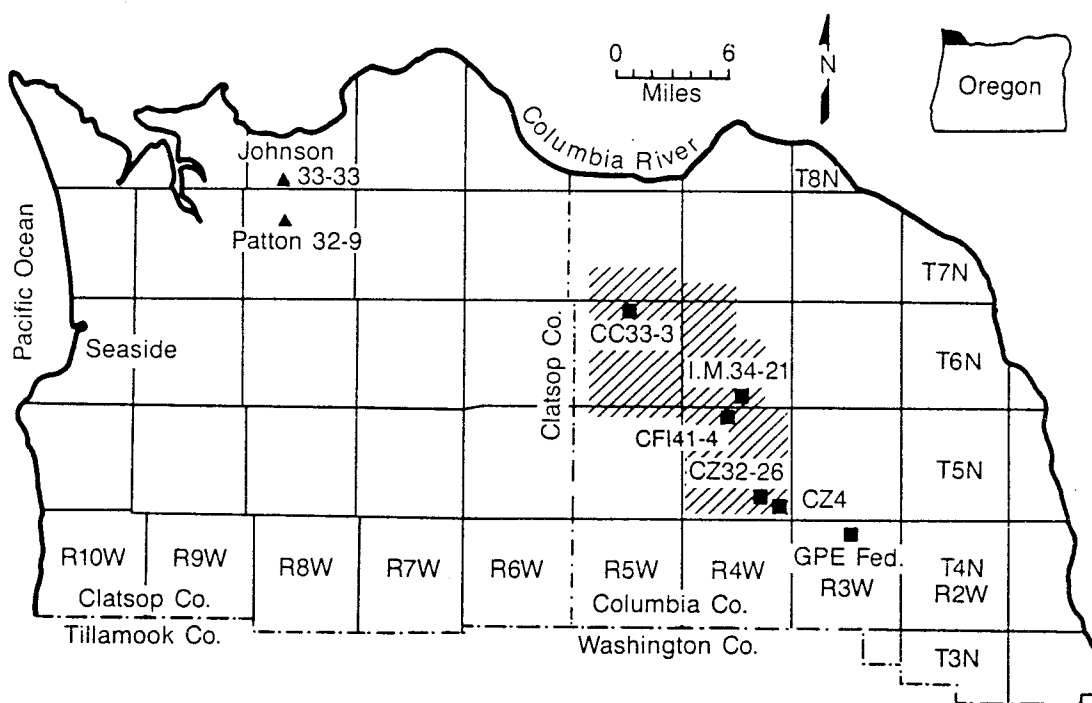


Figure 8. Location of wells sampled for source rock evaluation.

Table 1. Wells and sample depths used in the Mist gas field source rock evaluation.

Operator	Well Name	Location	Formation ¹ Sampled	Depth of Sample Interval - ft (m)	
Oregon Natural Gas Development Co.	Johnson 33-33	SE 1/4 sec. 33, T.8 N., R. 8 W.	Hamlet fm.	8600-8750 8870-8960	(2621-2667) (2704-2731)
Oregon Natural Gas Development co.	Patton 32-9	NE 1/4 sec. 9, T.7 N., R. 8 W.	Hamlet fm.	7170-7260 7860-7950	(2185-2213) (2396-2423)
Reichhold Energy Corp.	Columbia County 33-3	SE 1/4 sec. 3, T.6 N., R.5 W.	Cowlitz Fm.	2000-2270	(610-692)
American Quasar Petroleum Co.	Investment Management 34-21	NW 1/4 sec. 34, T.6 N., R.4 W.	Cowlitz Fm. H-Y fm.	1260-1350 2880-3030	(384-411) (878-924)
Reichhold Energy Corp.	Crown Zellerbach 32-26	NE 1/4 sec. 26, T.5 N., R.4 W.	Cowlitz Fm. H-Y fm.	3370-3520 4570-4720	(1027-1073) (1393-1439)
Reichhold Energy Corp.	Crown Zellerbach 4	NE 1/4 sec. 36, T.5 N., R.4 W.	Cowlitz Fm. H-Y fm.	4010-4130 5360-5420	(1222-1259) (1634-1652)
Exxon Corp.	GPE Federal Com. #1	SE 1/4 sec. 3, T.4 N., R.3 W.	Cowlitz Fm. H-Y fm. H-Y fm.	7900-7920 10250-10270 10760-10780	(2408-2414) (3124-3730) (3280-3286)
ARCO	Cav. Forest Ind. 41-4	NE 1/4 sec. 4, T.5 N., R.4 W.	Clark & Wilson	1917	(584)
ARCO	Outcrop	sec. 20, T.4 N., R.4 W.	Clark & Wilson	Outcrop	

1: H-Y = the Hamlet-Yamhill and represents the Hamlet fm. of Niem et al. (1990, 1991) and the Yamhill Fm. of Bruer et al. (1984) in the Mist-North Willamette Basin area. Cowlitz samples represent the upper Cowlitz mudstone.

represented the best maturation profile resulting from greatest depth of burial in the basin and away from the influence of major igneous intrusions. In addition to data generated from the 16 samples in this investigation, existing published source rock data (Armentrout and Suek, 1985; Niem and Niem, 1985) for the area are also incorporated into this study.

In order to evaluate the source rock samples in terms of hydrocarbon generation, several geochemical parameters need to be elucidated. These parameters include: 1) the quantity and quality of the organic matter, 2) the thermal maturation level of the organic matter, and 3) the generative history and potential of the rock.

The quantity of organic matter in a sedimentary unit refers to its organic richness. This parameter has been measured using total organic carbon (TOC) and whole rock pyrolysis analyses. Sufficient quantities of organic matter must be present in a sedimentary rock before it can be considered as a potential source rock. The concentration of total organic carbon necessary varies depending upon the type of organic matter (OM) present and the type of lithologic unit being considered. In general, TOC values for shale, siltstone, and mudstone have a lower limit of 0.5% to be considered as prospective source rocks (Tissot and Welte, 1984; Barker, 1982).

The quality of organic matter refers to the type of organic detritus (e.g., marine vs. terrestrial) that was incorporated into the sediment during deposition. The type of organic matter plays an important role in determining whether oil or gas will be

generated during maturation, as well as its chemical composition. Data from visual kerogen assessment (e.g., herbaceous, woody, algal, etc.), rock-eval pyrolysis, pyrolysis-gas chromatography (P-GC), and gas chromatography (GC) have been utilized to evaluate this parameter.

Thermal maturity is a measure of the time-temperature history experienced by organic matter (kerogen*) within a fine-grained sedimentary rock. To establish the thermal maturity of organic matter in the Mist area, five techniques have been utilized: 1) the physical measurement of vitrinite reflectance, 2) rock-eval pyrolysis (T-max °C, transformation ratio), 3) thermal alteration index, 4) gas chromatography, and 5) the measurement of specific geochemical criteria which change in a predictable manner with increasing thermal input (e.g., composition of the hydrocarbon range and Carbon Preference Index). Knowledge of organic matter maturation levels allows for characterization of prospective source rocks as immature, mature, or post-mature with respect to their hydrocarbon generating potential.

Inherently related to the time-temperature history (maturation level) of a source rock are hydrocarbon generative history and potential parameters. Pyrolysis data can provide insight as to whether or not a source rock has generated hydrocarbons in the past, as well as its future generative capability.

* Kerogen: Defined as the organic constituent of sedimentary rocks that is not soluble in organic solvents (as opposed to the solvent soluble fraction commonly referred to as bitumen) (Tissot and Welte, 1984).

Organic Richness

The concentration of total organic carbon (% TOC) in a sedimentary unit provides a first approximation of the potential of that rock unit to function as a source rock in generating hydrocarbons. Most identified source rocks have organic carbon contents between 0.8% and 2.0% by weight, although values as high as 10% have been documented (Barker, 1982). Table 2 provides a general guideline for interpreting TOC data in terms of source rock potential.

Table 2. Classification of source rock potential based on Total Organic Carbon content (wt. %) (Geochem Laboratories, Inc., 1980).

% Total Organic Carbon (shales)	% Total Organic Carbon (carbonates)	Descriptive Terminology
0.00 - 0.50	0.00 - 0.12	poor
0.50 - 1.00	0.12 - 0.25	fair
1.00 - 2.00	0.25 - 0.50	good
2.00 - 4.00	0.50 - 1.00	very good
4.00 - 8.00 ⁺	1.00 - 2.00	excellent

Total organic carbon analyses for mudstones in the Hamlet, Hamlet-Yamhill, and Cowlitz formations (see Tables 3 and 4, Figure 9) yield average TOC values of 0.98%, 0.73%, and 0.51%, respectively. All three formations fall within the 0.50-1.00% TOC (shales) range of Table 2, indicating "fair" source potential. Only the Hamlet formation has an average value high enough to warrant consideration as a "good" source rock. The data in Figure 9 suggest that perhaps the Hamlet

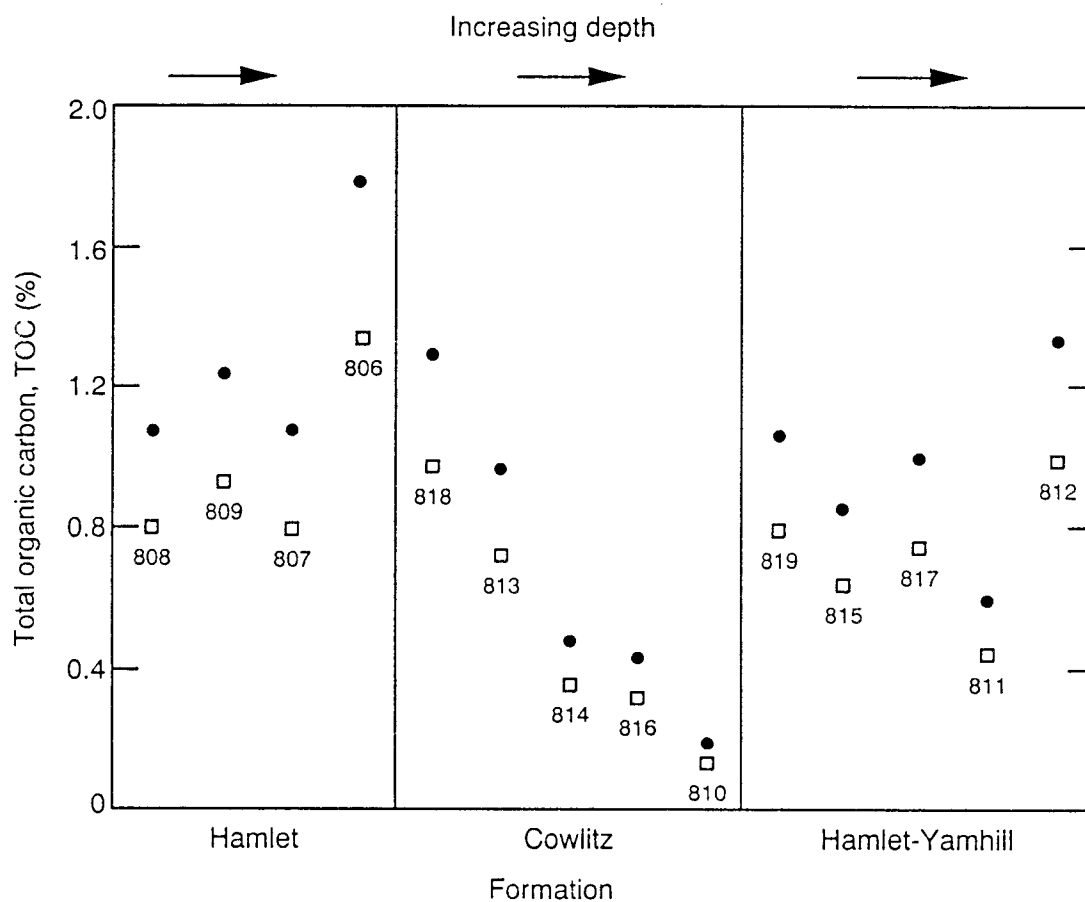


Figure 9. Total organic carbon values (wt%) for mudstones in the Hamlet fm., Cowlitz Fm., and Hamlet-Yamhill* formation. [\square = measured TOC; \bullet = converted TOC based on OM type and maturity (see Tissot and Welte, 1984, p. 496)]. * = Hamlet-Yamhill is the Hamlet fm. of Niem et al. (1990, 1991) and the Yamhill Fm. of Bruer et al. (1984) in the Mist field.

Table 3. Source rock data for organic matter quantity and quality - this report.

Sample Number	Well ^A Name	Avg. Sample ^B Depth - ft (m)	Formation [*]	TOC	S ₁	S ₂	S ₃	HI	OI
806	Johnson 33-33	8675 (2644)	Hamlet	1.35	0.13	1.02	1.84	75.9	136.4
807	Johnson 33-33	8915 (2717)	Hamlet	0.82	0.22	1.13	0.93	137.3	113.6
808	Patton 32-9	7215 (2199)	Hamlet	0.82	0.01	0.71	0.73	86.6	88.4
809	Patton 32-9	7905 (2409)	Hamlet	0.94	0.09	1.09	0.90	115.5	95.5
810	GPE Fed. Com. 1	7910 (2411)	Cowlitz	0.15	0.07	0.00	0.46	0.0	308.4
811	GPE Fed. Com. 1	10,260 (3127)	H-Y	0.46	0.04	0.14	0.41	30.2	89.0
812	GPE Fed. Com. 1	10,770 (3283)	H-Y	1.00	0.10	0.04	0.55	4.3	55.0
813	CC 33-3	2135 (651)	Cowlitz	0.74	0.08	0.35	2.00	47.3	269.7
814	CZ 32-26	3445 (1050)	Cowlitz	0.37	0.05	0.08	0.97	22.5	262.3
815	CZ 32-26	4645 (1416)	H-Y	0.65	0.03	0.13	1.00	19.2	153.1
816	CZ 4	4070 (1241)	Cowlitz	0.33	0.05	0.10	0.65	28.7	197.9
817	CZ 4	5390 (1643)	H-Y	0.75	0.03	0.37	0.62	49.7	82.8
818	IM 34-21	1305 (398)	Cowlitz	0.98	0.03	0.58	1.35	58.7	137.4
819	IM 34-21	2955 (901)	H-Y	0.80	0.02	0.31	1.03	38.7	128.6
820	Outcrop	0	C&W	41.76	1.66	111.62	14.395	267.3	34.5
821	CFI 41-4	1917 (584)	C&W	44.19	4.69	28.89	20.37	65.4	46.1

^{*} H-Y = the Hamlet-Yamhill and is the Hamlet fm. of Niem et al. (1990, 1991) and the Yamhill Fm. of Bruer et al. (1984) in the Mist field.

TOC = Total organic carbon (wt %)

S₁ = mg hydrocarbon/gram of rock

S₂ = mg hydrocarbon/gram of rock

S₃ = mg CO₂/gram of rock

HI = hydrocarbon index (mg hydrocarbon/gram TOC)

OI = oxygen index (mg CO₂/gram TOC)

^A For well and outcrop locations see Figure 8 and Table 1

^B For sample intervals see Table 1

Table 4. Existing published source rock data (From Armentrout and Suek, 1985).

Sample No.	Formation	Rock Type	TOC	S ₁	S ₂	S ₃	HI	OI	R _o
B0075	Cowlitz	Mudstone	1.07	0.10	0.10	1.44	9	135	0.26
B0074	Cowlitz	Mudstone	0.64	0.10	0.10	0.67	16	105	0.20
B0073	Cowlitz	Mudstone	0.61	0.10	0.10	0.68	16	111	0.22
B0072	Cowlitz	Mudstone	0.63	0.10	0.10	0.69	16	110	0.19
B0070	Cowlitz	Mudstone	0.43	0.10	0.10	0.61	23	142	0.18

TOC = Total organic carbon content (wt. %)

S₁ = mg hydrocarbon/gram of rock

S₂ = mg hydrocarbon/gram of rock

S₃ = mg CO₂/gram of rock

HI = hydrogen index (mg hydrocarbon/gram TOC)

OI = oxygen index (mg CO₂/gram TOC)

R_o = vitrinite reflectance as % reflectance in oil

mudstones (Astoria Basin) are enriched in organic matter with increasing depth while the Cowlitz mudstones appear to decrease in organic matter richness with depth. Tissot and Welte (1984) suggested that compensation should be made for other elements (e.g., H, O, N, S) present in kerogen. This is because the elemental composition of kerogen depends on both the type of kerogen under consideration and the level of its evolution. Maturity and organic matter quality data suggest that the majority of the organic matter in the Mist area is predominantly type III and borders the diagenetic-catagenetic boundary (see later sections). Therefore, a conversion factor of 1.33 (see Tissot and Welte, 1984, p. 496) has been applied to the original TOC values and the converted values, which represent total organic matter (TOM), are also shown in Figure 9. Converted values present a more optimistic picture with regard to source rock potential. The Hamlet fm. of the Astoria Basin shows a range of 1.09% to 1.79% with an average of 1.30%. Hamlet-Yamhill mudstones from the North Willamette Basin have a range of 0.61% to 1.33% with an average concentration of 0.97%. Mudstones of the Cowlitz Fm. have the lowest average content (0.68%) with a range from 0.20% to 1.30%. Using the average TOM concentration from the converted TOC values, it can be seen that the Hamlet fm. would fall within the "good" source potential category, the Hamlet-Yamhill fm. would be "fair to good", and the Cowlitz Fm. strata would remain a "fair" source rock. Total organic carbon measurements on five Cowlitz mudstone samples from a study by Armentrout and Suek (1985) show an average of 0.68% (see Table 4) with a converted (TOM) value of 0.90%. Although this converted average is somewhat

higher than that found in the current investigation, the Cowlitz mudstones would still be classified as a "fair" source rock. As seen in Table 3, sample 810 from the Cowlitz Fm. shows an anomalously low TOC value (0.15%). This may be due to the selection of an organically lean sample, and therefore, would probably not be an accurate indicator of the organic richness of the Cowlitz. Alternatively, the low TOC may reflect a decrease in Cowlitz organic richness with increasing depth as noted earlier. When sample 810 is not included in the average TOC calculation, the Cowlitz shows an average TOC of 0.61% and a converted TOM average of 0.81%. While these new values do not change the source potential classification for the Cowlitz, they are more consistent with values measured by Armentrout and Suek (1985). If TOC values from both this investigation and Armentrout and Suek's work are combined the Cowlitz mudstone shows an average TOC of 0.60%. It should be noted that the classification scheme presented in Table 2 is based on TOC, not TOM values. The purpose of the conversion of Mist source rock data to TOM is to illustrate that factors other than baseline TOC, such as maturation level and organic matter type, influence the potential organic richness of a rock unit.

While the average TOC values for the Hamlet, Cowlitz, and Hamlet-Yamhill formations are all less than 1.0%, TOC measurements of the C&W coal samples (41.76% & 44.19%) represent an entirely different picture with respect to organic richness (see Table 3). These TOC values are similar to those found in other Eocene coal deposits of western Oregon and western Washington (Walsh and Lingley, 1991; Niem et al., 1990) and obviously represent a potentially excellent source rock with

respect to oil and gas potential. It is interesting to note that there is increasing evidence that these coal layers are more extensive in the deltaic sandstone in the Mist subsurface than first thought, particularly to the east (R. Jackson, personal communication, 1986; Berkman, 1990).

A second indicator of the organic richness of a sedimentary rock can be obtained using data from rock-eval pyrolysis. Rock-eval is a process whereby a rock sample is heated under controlled temperature conditions for a given time interval (Geochem Laboratories, Inc., 1980). Organic compounds are released in two stages: those released in stage 1 (S_1) represent hydrocarbons already present in the rock in a free or adsorbed state, while those released in stage 2 (S_2) represent the hydrocarbons generated upon pyrolysis of the kerogen (Tissot and Welte, 1984). Generation of hydrocarbons during stage 2 is interpreted to be analogous to the natural process of hydrocarbon generation due to increasing thermal maturation of sedimentary organic matter resulting from increased burial (Tissot and Welte, 1984). In most rock-eval programs a third peak (S_3) is also generated and represents the release of oxygen-containing volatiles (e.g., carbon dioxide) during kerogen pyrolysis (Tissot and Welte, 1984). For a more detailed treatment of the rock-eval process the reader is referred to Tissot and Welte (1984) or Espitalie et al. (1977).

By utilizing data from the S_1 and S_2 peaks (see Tables 3 and 4), a semiquantitative evaluation of the "genetic potential" of a source rock can be determined. The quantity S_1 represents the original genetic potential which has

effectively been transformed into hydrocarbons. The quantity S_2 represents the remaining potential of the rock (Tissot and Welte, 1984). Thus, $S_1 + S_2$ (expressed as kilograms hydrocarbons per ton of rock, kgHC/tRx) is an evaluation of the genetic potential of a given source rock sample.

Tissot and Welte (1984) suggested the following source rock classification with regard to genetic potential:

< 2 kgHC/tRx (<2000 ppm): no oil source rock, some potential for gas

2-6 kgHC/tRX (2000 - 6000 ppm): moderate source rock

> 6 kgHC/tRX (>6000 ppm): good source rock.

Table 5 presents S_1 and S_2 data from Tables 3 and 4, the genetic potential ($S_1 + S_2$) calculations, as well as the characterization according to Tissot and Welte's (1984) proposed classification. It is obvious from Table 5 that the Mist area samples (with the exception of the C&W samples) represent source rocks with some gas, but no oil potential. The Hamlet formation of the Astoria Basin shows the highest genetic values of the three formations under consideration. The organic-rich coal samples (#'s 820 and 821) from the C&W sandstone are justifiably classified as good source rocks. However, the type and quality of organic matter in these samples plays an important role in the type of hydrocarbons generated during maturation (Tissot and Welte, 1984). With respect to the low genetic potential values calculated for the Hamlet, Cowlitz, and Hamlet-Yamhill samples, it should be noted that assessments of

Table 5. Genetic potential ($S_1 + S_2$) evaluation of Mist area source rocks.

Sample* Number	Well	Formation	Average Depth - ft (m)	S_1 kgHC/tRx	S_2 kgHC/tRx	$S_1 + S_2$ kgHC/tRx	Genetic Potential Rating Tissot & Welte 1984
808	32-9	Hamlet	7215 (2199)	0.01	0.71	0.72	Some gas potential; no oil
809	32-9		7905 (2409)	0.09	1.09	1.18	
806	33-33		8675 (2644)	0.13	1.02	1.15	
807	33-33		8915 (2717)	0.22	1.13	1.35	
808	34-21	Cowlitz	1305 (398)	0.03	0.58	0.61	Some gas potential; no oil
813	33-3		2135 (651)	0.08	0.35	0.43	
814	32-26		3445 (1050)	0.05	0.08	0.13	
816	4		4070 (1241)	0.05	0.10	0.15	
810	GPE		7910 (2411)	0.07	0.00	0.07	
819	34-21	Hamlet- Yamhill	2955 (901)	0.02	0.31	0.33	Some gas potential; no oil
815	32-26		4645 (1416)	0.03	0.13	0.16	
817	4		5390 (1643)	0.03	0.37	0.40	
811	GPE		10260 (3127)	0.04	0.14	0.18	
812	GPE		10770 (3283)	0.10	0.04	0.14	
820	Outcrop	C & W	0	1.66	111.62	113.28	Good source rock
821	41-4		1917 (584)	4.69	28.89	33.58	

* See Table 1 and Figure 8 for location and well name. The Hamlet-Yamhill fm. is the Hamlet of Niem et al. (1990, 1991) and the Yamhill of Bruer et al. (1984) in the Mist-North Willamette Basin.

kgHC/tRx = kilograms hydrocarbons per ton of rock.

genetic richness based on whole-rock samples, as is the case with rock-eval pyrolysis, may be affected by sediment mineralogy. Organic compounds (polar and nonpolar) may be retained or altered by sedimentary mineral surface and/or interlayer effects (e.g., clay minerals) (Dembicki et al., 1983; Horsfield and Douglas, 1980; Law et al., 1984). Overall yields may be reduced, and therefore, estimates of genetic richness should be treated as minima (Jurg and Eisma, 1966; Shimoyama and Johns, 1971; Dembicki, et al., 1983; Horsfield and Douglas, 1980).

Both total organic carbon and rock-eval data suggest only that the source rocks in the Mist area contain enough organic matter to generate hydrocarbons. This is especially true for the coal samples from the Clark and Wilson sandstone. By itself, data on quantity of organic matter is insufficient to definitively characterize or evaluate a source rock with regard to hydrocarbon generation. Organic matter quality, as well as organic matter maturation levels, need to be elucidated before making any conclusions on a prospective source rock.

Organic Matter Quality

The quality of the Mist area organic matter has been evaluated using visual kerogen assessment, rock-eval pyrolysis, pyrolysis-gas chromatography (P-GC) and gas chromatography (GC). Source character can be used to predict the nature of the hydrocarbons generated. This is because at intermediate depths of burial (as seen in

N.W. Oregon, 1000 - 10,000 ft; 300 - 3000 m) the type of organic matter exercises primary control over the nature of the petroleum products (Barker, 1982).

There are four main types of kerogen that can be characterized by microscopic visual examination of isolated kerogen (Amorphous- AM, Herbaceous- H, Woody- W and Coaly- C) (Geochem Laboratories, Inc., 1980; L. Lundell, ARCO, written communication, 1987). The composition of organic matter incorporated in sediments reflects the character of its precursors and a distinction can be made between terrestrial and aquatic organic matter (Barker, 1982). The ability to make this distinction stems from the need of terrestrial plants for structural support from polymers such as lignin and cellulose, whereas aquatic organisms, being supported by water, do not require this structural support (Tissot and Welte, 1984). As a result, aquatic and terrestrial derived organic matter exhibit different chemical compositions, as well as morphological differences.

Several kerogen classification schemes exist in the literature which are based on different optical methods available for use in kerogen descriptions. Table 6 provides an approximate equivalence of the various terms. Visual kerogen assessment results for the Mist area source rocks are presented in Table 7. The Hamlet mudstones of the Astoria Basin show a primary amorphous population with a secondary woody population. This suggests mixing of aquatic and terrestrial derived organic matter (see Table 6). This evaluation is consistent with the proposed lateral, deep-water, farther offshore depositional environment (Rarey, 1986) of the Hamlet fm. relative

Table 6. Equivalence of various terms utilized in kerogen classification (From Tissot and Welte, 1984).

Provenance	Terminologies			
Aquatic	Algal	Liptinite	Amorphous	Type I
	Amorphous (A)			
Subaerial (Terrestrial)	Herbaceous (H) (fibrous)	Vitrinite	Humic	Type II
	Woody (W) (plant structure)			Type III
	Coaly (C) (angular to subangular fragments)	Inertinite		Residual

to the Cowlitz mudstones. Similarly, Hamlet-Yamhill kerogens show a predominant aquatic (Am) input with a secondary terrestrial component, also suggesting mixing of organic matter types. The presence of a "Coaly" component in the secondary kerogen population should not be misconstrued as indicating a relationship to coal. A more appropriate term would be inertinite, indicating that the material is more or less inert and thus has little or no hydrocarbon generating capability. In contrast to the Hamlet-Yamhill and Hamlet mudstone units, the Cowlitz mudstones show a predominant terrestrial (W) component with some mixing from aquatic (Am) organic matter.

Table 7. Visual kerogen assessment results for potential Mist area mudstone source rocks.

Sample Number	Well Name	Formation*	Kerogen** Assessment
806	Johnson 33-33	Hamlet	Am;W;-
807	Johnson 33-33	Hamlet	Am;W;-
808	Patton 32-9	Hamlet	Am;-;W
809	Patton 32-9	Hamlet	Am;W;-
810	GPE Fed. Com. 1	Cowlitz	-;-;Am
813	CC 33-3	Cowlitz	W;Am;H
814	CZ 32-26	Cowlitz	W;Am;-
816	CZ 4	Cowlitz	W;Am;C
818	IM 34-21	Cowlitz	Am-W;-;H
811	GPE Fed. Com. 1	Hamlet-Yamhill	Am-W;-;-
812	GPE Fed. Com.1	Hamlet-Yamhill	Am;W-C;-
815	CZ 32-26	Hamlet-Yamhill	Am;W-C;-
817	CZ 4	Hamlet-Yamhill	W;Am;-
819	IM 34-21	Hamlet-Yamhill	Am;W;H

Am = Amorphous

W = Woody

H = Herbaceous

C = Coaly

- = not determined

* Hamlet-Yamhill is the Hamlet fm. of Niem et al. (1990, 1991) and the Yamhill Fm. of Bruer et al. (1984) in the Mist field and North Willamette Basin.

** Kerogen types are arranged in order of primary, secondary, and trace populations. A designation such as Am-W;-;H indicates that kerogen types Am and W are present in approximately equal concentration as the primary kerogen population, with little or no secondary kerogen and only a trace of herbaceous kerogen.

Unfortunately, visual kerogen assessments were not performed on the C&W coal samples. However, their high TOC values are consistent with the coal deposits of the Skookumchuck Fm. of S.W. Washington, which consist predominantly of terrestrial (structured) organic matter (Walsh and Lingley, 1991; Armentrout and Suek, 1985).

Table 6 shows that amorphous kerogen corresponds to type I or II kerogen, whereas woody and coaly kerogen corresponds to type III. The importance of this distinction is related to the nature of the hydrocarbons produced. Most petroleum geochemists (e.g., Tissot and Welte, 1984; Hunt, 1979) agree that type I kerogens are oil-prone, whereas type III kerogens generate natural gas as the principal hydrocarbons. Visual kerogen data suggest that mudstones of the Hamlet and Hamlet-Yamhill formations are oil-prone source rocks and that Cowlitz Fm. mudstones are gas-prone. However, no liquid hydrocarbons or wet gas have been produced from the Mist field (see later section on gas chemistry). In addition, this apparently straight forward interpretation of the visual kerogen assessment data is somewhat inconsistent with regard to other source rock quality data.

There are a number of hypotheses that can be put forward to help explain the inconsistency of visual kerogen data with respect to other source rock quality data:

1. Mist natural gases are solely sourced from the Cowlitz Fm. (e.g., coals and mudstones).

2. The natural gases have not been thermally generated from available source rocks, but rather are biogenic in origin.
3. Visual kerogen data is not an accurate indicator of source rock quality without taking into consideration other organic matter quality parameters.

It is unlikely that the Cowlitz Fm. is the sole source rock for the Mist field. Maturation data from this investigation indicate that the older Hamlet-Yamhill fm. has the best potential to generate hydrocarbons. In addition, there are no geologic constraints which would indicate that hydrocarbons generated in the Hamlet-Yamhill mudstone could not migrate to available C&W sandstone reservoirs as easily as from the mudstone in the Cowlitz Formation.

Carbon and hydrogen stable isotope data for the Mist field natural gases from this investigation (see section on reservoir gas geochemistry) show values intermediate between purely biogenic and a purely thermogenic origin. This information favors, at least in part, a thermogenic origin for the gases.

Tissot and Welte (1984) have noted that the precipitation or adsorption of dissolved colloidal organic matter, such as humic acids, could result in structureless, amorphous organic matter having low petroleum potential. They also point out that intense microbial reworking of organic detritus or deposition in an oxidizing environment may destroy the various morphological structures of different origins.

Given the low to intermediate maturation levels (see discussion on maturation) of the three formations in question, especially the Hamlet and Cowlitz formations, it is possible that humic acids are a significant organic matter component. In addition, whole rock pyrolysis data (e.g., hydrogen and oxygen indices) could be interpreted as indicating an oxidizing depositional environment where microbial activity would potentially be high. Visual kerogen and rock-eval pyrolysis data presented by Armentrout and Suek (1985) suggest both an oxic depositional environment and terrestrial derived organic matter for the Mist area source rocks. Kerogen assessments in the Astoria Basin also indicate a predominance of structured organic matter suggesting a terrestrial (higher plant) origin (Niem and Niem, 1985). This is generally consistent with the overall organic matter quality determination for this study, suggesting that the amorphous kerogen may either be of a sapropelic origin, an altered terrestrial origin, or more likely, a combination of the two. Recognition of possible multiple sources of amorphous organic matter is important for interpreting hydrocarbon generating capability of Mist source rocks. Work by Mukhopadhyay (1989) on different types of organic matter has shown that both the overall yield and the type of hydrocarbons generated can be significantly influenced by the type of amorphous organic matter being investigated. Because either the primary or secondary kerogen population from all three formations has been identified as amorphous, it is important not to place undue weight on the visual kerogen assessments without examining other organic matter quality parameters.

Data from rock-eval pyrolysis can also be used in organic matter quality determinations. Kerogen type is characterized by two indices: the hydrogen index - HI (S_2/TOC) and the oxygen index - OI (S_3/TOC) (Tissot and Welte, 1984). The indices are strongly related to the elemental composition of kerogen. In other words, there is a good correlation between HI and the H/C atomic ratio and between OI and the O/C atomic ratio (see Fig. V.I.II, Tissot and Welte, 1984). A plot of these two indices can therefore be interpreted in the same way as a normal Van Krevelen diagram which is based on elemental composition analysis of the organic matter. Three kerogen types can be distinguished from a plot of HI vs. OI (Fig. 10), corresponding to types I, II, and III of Table 6.

Figure 10 represents a plot of the hydrogen index versus oxygen index values calculated for the Mist area source rock samples (see Tables 3 and 4 for actual values). The Hamlet-Yamhill and Cowlitz mudstones plot well within the type III kerogen field. Pyrolysis data suggest a dominant terrestrial organic matter input for the Cowlitz and Hamlet-Yamhill formations from the North Willamette Basin. The Hamlet data points may indicate a slightly greater contribution of marine or aquatic organic matter relative to the other two formations although the terrestrial contribution still represents the major component of the organic matter. Similar to the disseminated organic matter from the mudstone samples, the sidewall core coal sample from the C&W plots in the type III kerogen field. On the other hand, pyrolysis of the C&W outcrop coal sample yielded a relatively high hydrogen- and low oxygen-index value. This suggests that the type II kerogen of the outcrop coal

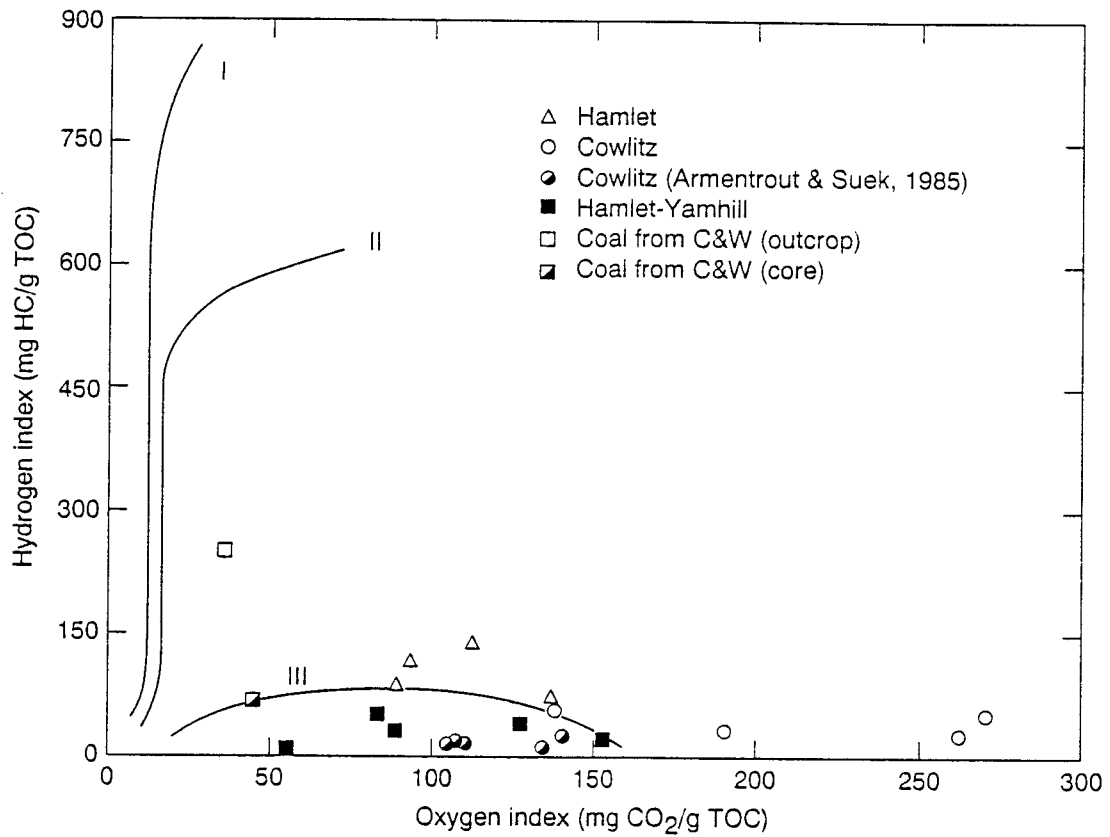


Figure 10. Plot of hydrogen index versus oxygen index values from rock-eval pyrolysis data for the Mist area source rocks.

has moderate hydrocarbon yield potential. With the exception of the C&W outcrop coal sample, hydrogen and oxygen-index values suggest organic matter deposition in an oxidizing environment. As a result, the mudstone source rocks (e.g., Hamlet, Cowlitz, and Hamlet-Yamhill) appear to contain low hydrocarbon-yielding kerogens with potential for gas generation but not oil. Overall, the predominant terrestrial signature shown by rock-eval data is in excellent agreement with the fact that the Mist field produces only dry (methane rich) natural gases.

Another pyrolytic technique, pyrolysis-gas chromatography (P-GC), has found increased application with regard to kerogen typing. Larter and Douglas (1980) utilized pyrolysis-gas chromatography to characterize kerogens by their chromatographic "fingerprint", as well as by employing a numerical "type index" (R) as determined by the peak height ratio of m(+p) xylene/n-octene in the pyrogram. Van de Meent et al. (1980) analyzed several kerogens and kerogen precursors using pyrolysis-gas chromatography and pyrolysis gas chromatography-mass spectrometry. Using parameters such as abundance of long chain products and n-alkene/n-alkane ratios in different carbon number ranges they were able to provide a semiquantitative evaluation of kerogen types. Additionally, the relationship of aliphatic to aromatic constituents in pyrolysates has been used by various investigators as an indicator of a kerogen's aromaticity (Giraud, 1970; Larter and Douglas, 1978, 1980; Leplat, 1967, etc.). For example, Giraud (1970) showed that kerogens derived from terrigenous organic matter gave aromatic pyrolysates.

In this investigation, the numerical "type index" system of Larter and Douglas (1980) and the signature of the pyrogram "fingerprint" produced by pyrolysis-gas chromatographic analysis have been utilized by this investigator to examine the quality (organic matter type) of the Mist area source rocks. Figure 11 (a-c) shows the pyrograms generated by pyrolysis-gas chromatography. Also shown are the measured type index (R) values for each pyrogram.

With the exception of m(+p) xylene and n-octene, peak identifications have been made only to the extent of reflecting aromatic or aliphatic character. Compound class assignments for selected peaks were made based on identification and comparison of pyrolysis product GC retention indices with available library/reference data.

At first glance, obvious differences in pyrogram character are apparent both between and within the mudstone dominated formations under consideration. Pyrograms of Hamlet kerogens (Fig. 11a, i-iv) exhibit products mainly in the carbon number range below C_{16} . Overall, the pyrograms are characterized by a relatively smooth n-alkene/n-alkane distribution to C_{30} and a relatively low concentration of aromatic species. The kerogen pyrolysates from both the Cowlitz (Fig. 11b, i-v) and the Hamlet-Yamhill (Fig. 11c, i-v) contrast markedly with those of the Hamlet kerogens. The n-alkene/n-alkane distributions and concentrations are similar to the Hamlet mudstone, at least for samples 819, 815, and 817 (Hamlet-Yamhill) and 818, 813, 814, and 816 (Cowlitz). However, the pyrograms for kerogens from both

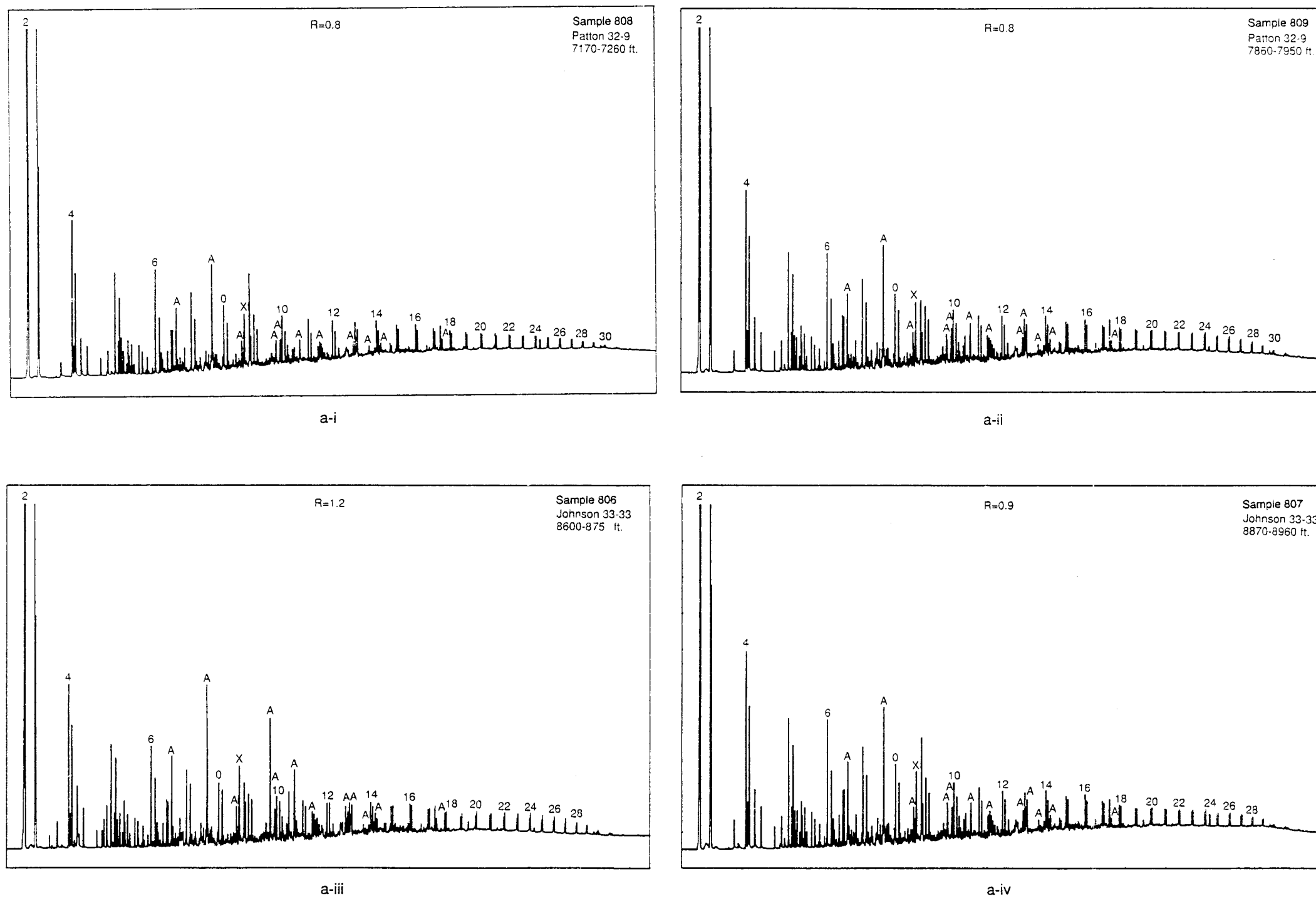


Figure 11a. Pyrolysis gas chromatograms of kerogens isolated from the Hamlet formation mudstone. Numbered peaks represent carbon number range of n-alkene/n-alkane doublets, A = aromatic compounds, x = m(+p)xylene, o = n-octene, R = peak height ratio of x/o.

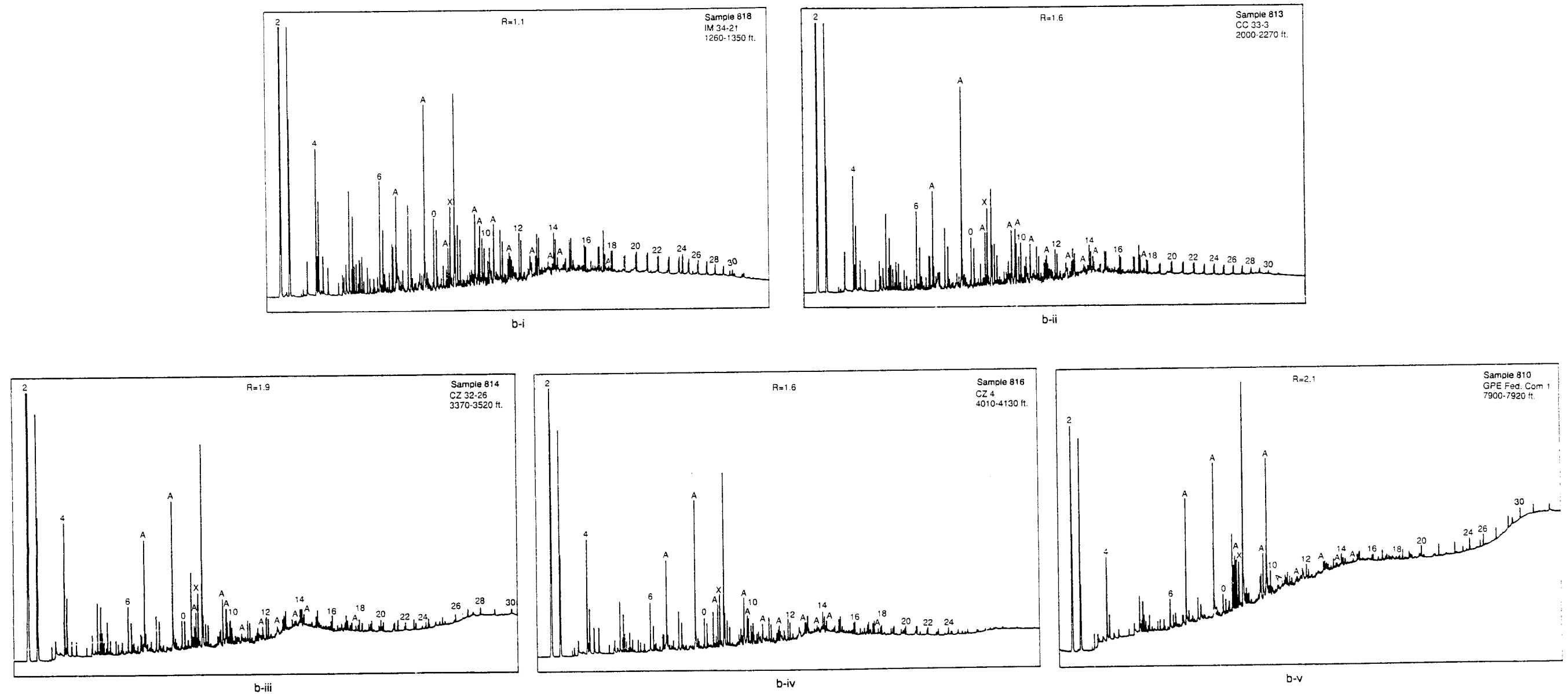


Figure 11b. Pyrolysis gas chromatograms of kerogens isolated from the Cowlitz Formation mudstone. Numbered peaks represent carbon number range of n-alkene/n-alkane doublets, A = aromatic compounds, x = m(+p)xylene, o = n-octene, R = peak height ratio of x/o.

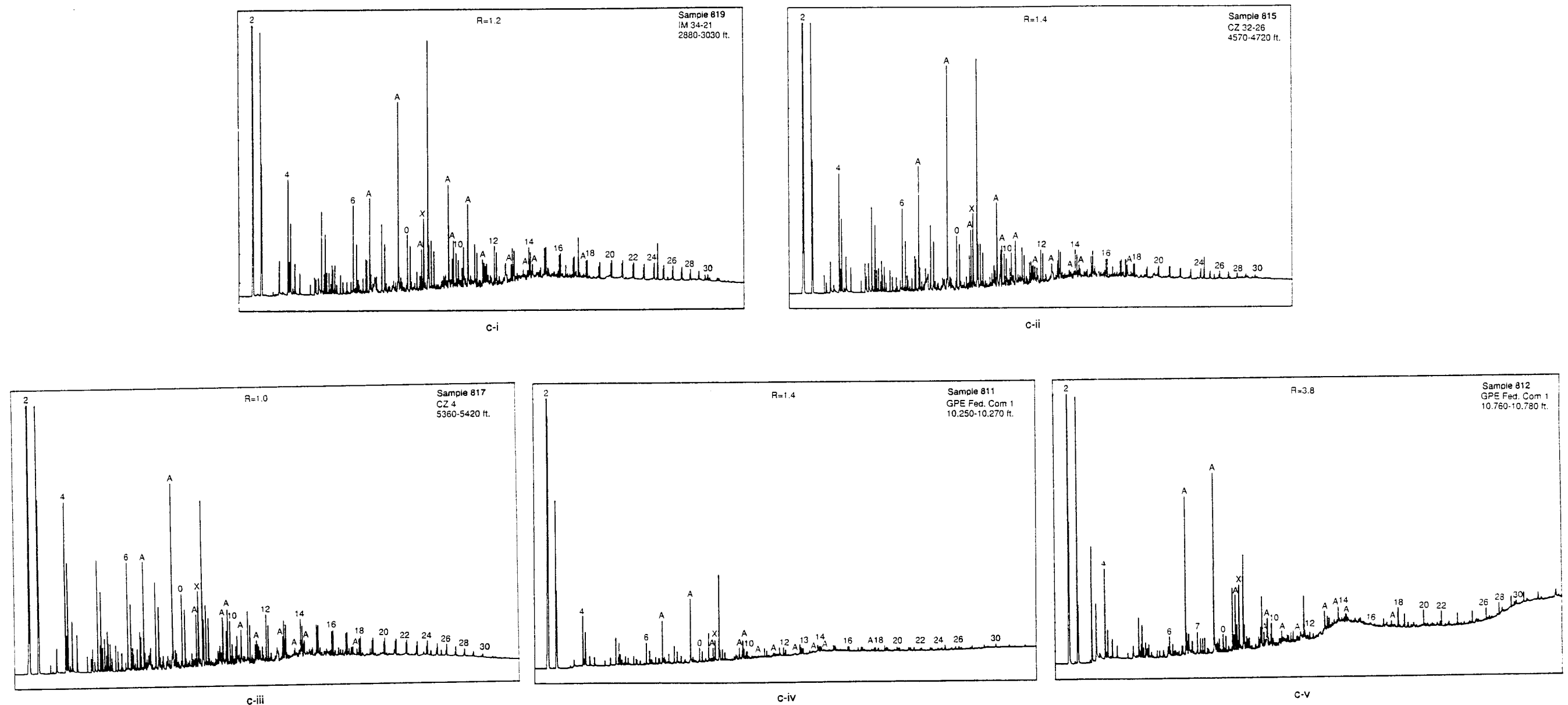


Figure 11c. Pyrolysis gas chromatograms of kerogens isolated from the Hamlet-Yamhill formation mudstone. Numbered peaks represent carbon number range of n-alkene/n-alkane doublets, A = aromatic compounds, x = m(+p)xylene, o = n-octene, R = peak height ratio of x/o.

formations are dominated by the presence of aromatic constituents suggesting greater terrestrial input than for the Hamlet.

Samples 810 (Cowlitz), 811 and 812 (Hamlet-Yamhill) show a distinct intraformational change in pyrolysate character. Although all three samples retain the predominant aromatic signature, overall yields are significantly reduced. A pyrolysis study carried out by Mukhopadhyay (1989) on various types of amorphous organic matter suggests that the fingerprints of the above samples could be accounted for by the presence of low hydrocarbon-yielding inertinite. Although the hydrogen index versus oxygen index data presented earlier could be interpreted as indicating organic matter with low hydrocarbon potential, gas chromatographic data from this investigation suggest that the fingerprints for samples 810, 811, and 812 may also be the result of maturation influences.

Peak height ratios of m(+p) xylene/n-octene are used here as a semiquantitative means of evaluating the aromaticity of Mist kerogens. In other words, the aliphatic to aromatic character of a given pyrolysate is thought to reflect the general terrestrial versus marine/aquatic input to the system. In a study of 85 kerogens of different origin, Larter and Douglas (1978) showed that type I kerogens gave type index (R) values generally less than 0.3, while type III kerogens gave R values greater than approximately 1.2. Kerogens of mixed assemblages (e.g., marginal marine facies) generally plotted with intermediate values.

From information already presented, the Mist kerogens appear to be dominated by terrestrial organic matter with variable amounts of marine input. Type index values measured for the Mist kerogens reflect this general mixing and, in fact, reflect a progression in the relative input of various organic matter types. Type index values (R) are presented at the top of each pyrogram and in Table 8. A small but obvious shift in index values is evident, progressing from the low to high end of what Larter and Douglas (1978) would interpret as the mixed assemblage area. Hamlet kerogens from the Astoria Basin have the lowest values ($R = 0.8 - 1.2$, avg. 0.9), followed by Hamlet-Yamhill kerogens from the North Willamette basin which range from 1.0 - 1.4 (with one notable exception - sample 812, $R = 3.8$). The Cowlitz samples have R values slightly higher than for the Hamlet-Yamhill with a range from 1.1 to 2.1 (avg. 1.7).

The shift of type index values indicates a relatively small but progressive change in terrestrial organic matter contribution to the three formations. The Hamlet fm., which is predominantly bathyal mudstone and siltstone (Niem and Niem, 1985; Rarey, 1986), appears to have the smallest terrestrial component of the three. Although the Hamlet-Yamhill mudstones are also considered to be predominantly deep-water deposits, deposition closer to the Eocene coastline may have resulted in a slightly greater terrestrial contribution. The Cowlitz mudstone is considered a lateral equivalent of the deeper slope mudstone of the Hamlet fm. (Niem and Niem, 1985), and thus its type index values may also be a reflection of proximity to the middle to late Eocene coastline.

Table 8. Type index (R) values for Mist area kerogens.

Sample Number	Formation	Average Depth-ft (m)		R*	
808	Hamlet	7215	(2199)	0.8	
809	Hamlet	7905	(2409)	0.8	
806	Hamlet	8675	(2644)	1.2	
807	Hamlet	8915	(2717)	0.9	avg. 0.9
818	Cowlitz	1305	(398)	1.1	
813	Cowlitz	2135	(651)	1.6	
814	Cowlitz	3445	(1050)	1.9	
816	Cowlitz	4070	(1241)	1.6	
810	Cowlitz	7910	(2411)	2.1	avg. 1.7
819	Hamlet-Yamhill	2955	(901)	1.2	
815	Hamlet-Yamhill	4645	(1416)	1.4	
817	Hamlet-Yamhill	5390	(1643)	1.0	
811	Hamlet-Yamhill	10,260	(3127)	1.4	
812	Hamlet-Yamhill	10,770	(3283)	3.8	avg. 1.8

*R = peak height ratio of m(+p) xylene/n-octene

Data from gas chromatography can be used as one last parameter for evaluating organic matter quality. Work by Didyk et al. (1978) and Powell and McKirdy (1973) suggest that pristane to phytane ratios (Pr/Ph) of sediments reflect paleoenvironmental conditions of sedimentation. In particular, pristane to phytane ratios are thought to reflect relative oxicity/anoxicity during sediment deposition, which itself influences organic matter predation and degradation by bacteria. Anoxic conditions tend to preserve the C₂₀ isoprenoid (phytane) leading to low Pr/Ph values (less than one), whereas oxic environments cause greater degradation of the phytol side chain of chlorophyll, leading to generation of pristane and thus higher Pr/Ph ratios. Both maturation and microbial activity have been shown to affect the Pr/Ph

ratio. However, the general relationship of anoxic environments giving $\text{Pr/Ph} < 1$ and oxic environments providing Pr/Ph greater than unity appears to be retained (Didyk et al., 1978). Pristane to phytane values for the Mist source rocks (see Table 9) suggest that the majority of the strata were deposited under oxic conditions. Sample 810 may reflect deposition under an alternating oxic/anoxic environment. The overall indication of an oxic depositional environment is actually not unexpected in light of the low hydrogen-index and high oxygen-index values calculated from rock-eval pyrolysis.

Maturation Levels

Attention must now be focused on the maturation level and generative potential of source rocks in the Mist area. By characterizing maturation and using this information in conjunction with other geochemical data it should be possible to identify which basins and/or formations are capable of generating thermogenic gas, and which are the most likely sources of the Mist natural gases. A number of geochemical parameters have been utilized in order to evaluate these two areas: 1) vitrinite reflectance, 2) rock-eval pyrolysis (T-max, transformation ratio and genetic potential), 3) thermal alteration index, and 4) gas chromatography and related geochemical criteria such as Carbon Preference Index and n-alkane distribution. The geochemical data for maturation are presented in Table 9, and generative potential

Table 9. Maturation indices for Mist area source rocks.

Sample Number	Formation ¹	Avg. Sample Depth- ft (m)		R _o ²	TAI ³	Kerogen color	T-max ⁴	TR ⁵	Pr/Ph ⁶	CPI ⁷
808	Hamlet	7215	(2199)	0.53	2.2	N.D.	443	0.02	3.50	1.44
809	Hamlet	7905	(2409)	0.63	2.3	N.D.	445	0.07	--	--
806	Hamlet	8675	(2644)	0.39	2.3	N.D.	440	0.11	2.42	1.38
807	Hamlet	8915	(2717)	0.48	2.3	N.D.	440	0.16	--	--
818	Cowlitz	1305	(398)	0.48	2.2	N.D.	433	0.05	N.D.	N.D.
813	Cowlitz	2135	(651)	0.49	2.3	N.D.	430	0.19	1.26	1.35
814	Cowlitz	3445	(1050)	0.66	2.0	N.D.	430	0.37	1.18	1.38
816	Cowlitz	4070	(1241)	0.58	2.5	N.D.	443	0.35	1.42	1.53
810	Cowlitz	7910	(2411)	0.56	N.D.	yellow	N.D.	1.00	1.00	1.47
819	H-Y	2955	(901)	0.49	2.2	N.D.	437	0.06	N.D.	N.D.
815	H-Y	4645	(1416)	0.52	2.0	black	444	0.19	1.32	1.42
817	H-Y	5390	(1643)	0.72	2.3	N.D.	450	0.06	2.97	1.11
811	H-Y	10260	(3127)	1.07	N.D.	org bm,bm	471	0.24	3.11	1.08
812	H-Y	10770	(3283)	1.64	N.D.	brn, drk brn	511	0.69	--	--
820	C&W	0		0.35	N.D.	N.D.	424	0.01	N.D.	N.D.
821	C&W	1917	(584)	0.36	N.D.	N.D.	426	0.14	N.D.	N.D.

1 = H-Y is the Hamlet Fm. of Niem et al. (1990, 1991) and the Yamhill Fm. of Bruer et al. (1984).

2 = Vitrinite reflectance as % reflectance in oil

3 = Thermal alteration index

4 = Temperature of maximum hydrocarbon yield

5 = Transformation ratio derived from rock-eval pyrolysis [$S_1/(S_1 + S_2)$]

6 = Pristane to Phytane ratio

7 = Carbon Preference Index

-- = Samples combined to obtain sufficient extract for analysis (e.g., 806+807, 811+812, 808+809).

data are presented in Tables 3 and 4. Additional information generated from source rock analysis (e.g., vitrinite reflectance histograms, C_{15+} saturate data, etc.), but not used in interpretations are included in Appendix B.

The physicochemical evolution of sedimentary organic matter resulting from progressively increased burial has been the subject of numerous investigations and is well documented (Tissot and Welte, 1984; Dow, 1977; Durand, 1980; Hunt, 1979; Ishiwatari et al., 1976; McIver, 1967, etc.). Three stages of evolution are generally recognized - diagenesis, catagenesis, and metagenesis. A schematic representation of this evolution from the time of deposition to the beginning of metamorphism is illustrated in Figure 12. A brief discussion of the three stages follows. For a more detailed discussion, the aforementioned literature should be consulted.

The diagenetic stage of organic matter evolution corresponds to shallow burial depths where the principal agent of organic matter transformation is microbial activity and the main hydrocarbon generated is biogenic gas (Tissot and Welte, 1984). The end of this stage corresponds to vitrinite reflectance values of about 0.5% (Tissot and Welte, 1984; Hunt, 1979; Schoell, 1980, 1983). The second or catagenetic stage corresponds to vitrinite reflectance values between 0.5% and 2.0%. Most evolutionary schemes depict this stage as the principal zone of hydrocarbon formation, progressing from liquid hydrocarbons (petroleum) to wet gas and condensates, and finally to thermogenic natural gas generation (Schoell, 1980, 1983;

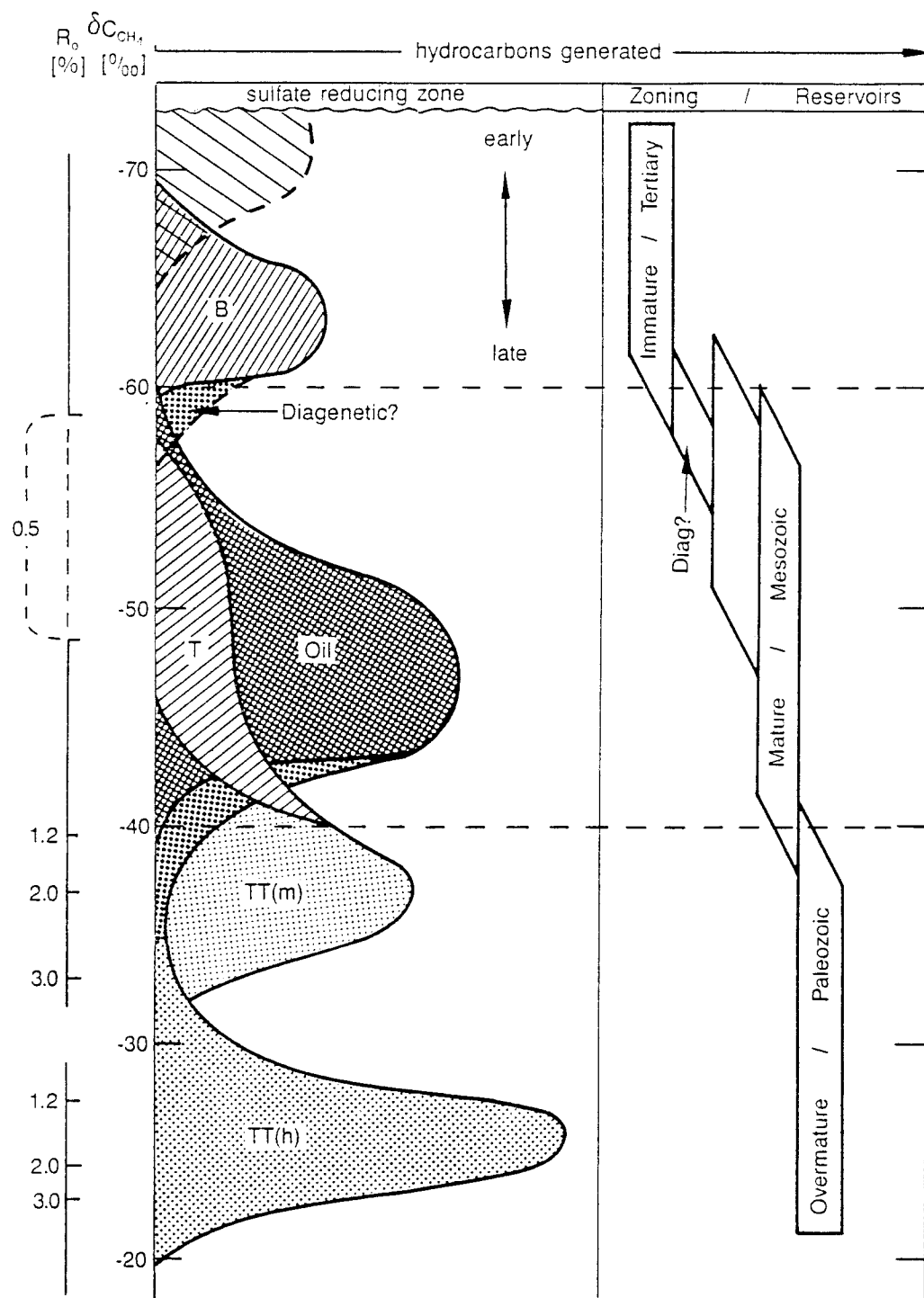


Figure 12. Illustration of the formation of natural gas and petroleum in relation to organic matter maturity (From Schoell, 1980).

Tissot and Welte, 1984; Hunt, 1979). Because organic matter quality data (e.g., type III kerogen) suggest that source rocks in the Mist study area have little capacity for generating wet gas and condensates, it is the thermogenic portion within the catagenetic stage that is important to this investigation (see Figure 12). The point where this generation commences may be affected by such factors as organic matter quality, burial rate and geothermal gradient (Barker, 1982).

The third stage (metagenesis) is generally thought to begin at vitrinite reflectance values of about 2.0%. This stage corresponds to greater burial depths (~3000 m depending on maturation factors), and the predominant hydrocarbon is thermogenic natural gas (Schoell, 1980; Tissot and Welte, 1984; Hunt, 1979).

Vitrinite reflectance (measured as % reflectance in oil - R_o) is an optical microscope technique commonly utilized in the petroleum industry to measure the degree of thermal maturation of sedimentary organic matter. Definitive boundaries for maturation levels, and thus hydrocarbon generation zones, are difficult to pinpoint. This, in part, is a consequence of the chemical structure and composition of the kerogen in question, strengths of the various bonds, and the kinetics associated with generation (Tissot and Welte, 1984). As illustrated in Figure 12, generation of thermally derived methane for kerogens commences at R_o values as low as 0.9%, although peak gas generation may not occur until approximately $R_o = 1.2$ to 1.5%.

In the study area, vitrinite reflectance values of indigenous organic matter show the following range:

- $R_o = 0.48 - 0.66\%$ Cowlitz Fm.
- $= 0.49 - 1.64\%$ Hamlet-Yamhill fm. of the North Willamette Basin
- $= 0.39 - 0.63\%$ Hamlet fm. of the Astoria Basin.

In addition, Armentrout and Suek (1985) noted that R_o measurements in the Mist field proper average 0.21% (see Table 4), indicating that organic matter in the shallow buried field itself is immature and still in the diagenetic stage of evolution. This led Armentrout and Suek to suggest that Mist natural gases were probably sourced in the deeper parts of either the North Willamette Basin or Astoria Basin with subsequent migration to their present location. The vitrinite measurements in this investigation provide supportive evidence for their theory. Figure 13 and Table 9 illustrate that the shallowest samples from both the Cowlitz and Hamlet-Yamhill formations have the lowest reflectances. These samples were collected from wells located closest in proximity to the Mist field proper (in other words, closest to the Nehalem arch of Armentrout and Suek, 1985). Proceeding towards the southeast, into the deeper parts of the North Willamette Basin, reflectance values for the Hamlet-Yamhill fm. show a gradual increase to approximately 9000 ft (2743 m), with a dramatic increase below this depth. The deepest Hamlet-Yamhill samples, taken from the Exxon G.P.E. Federal Commission #1 well at 10,260 and 10,770 ft (3127 and 3283 m), show the highest reflectance values (1.07 and 1.64% R_o),

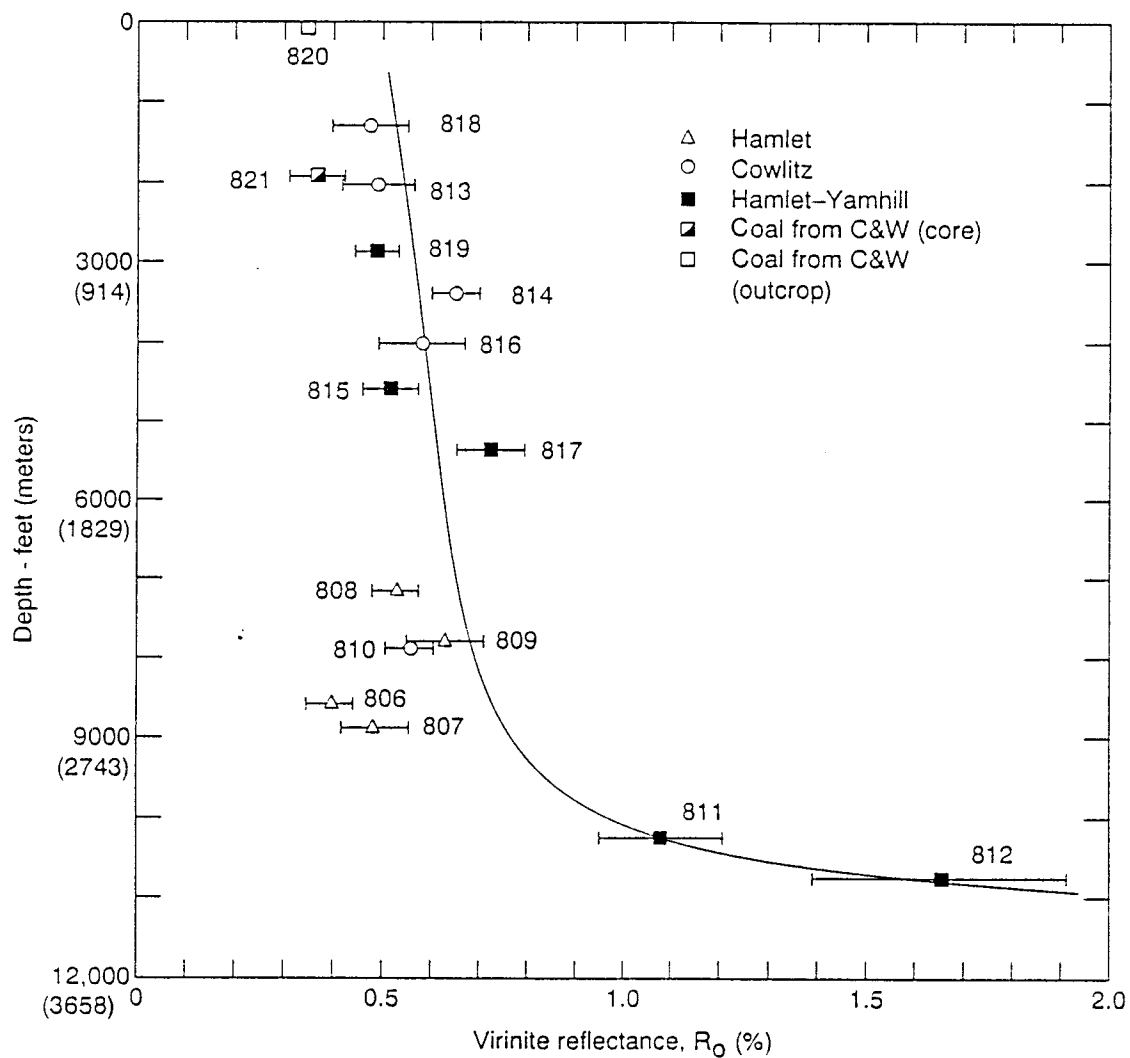


Figure 13. Vitrite reflectance of Mist area source rocks as a function of depth, (error bars represent one standard deviation).

respectively). The Cowlitz Formation, on the other hand, shows little reflectance variance or increase with depth. The maximum reflectance measured for the Cowlitz Fm. was 0.66%. The deepest Cowlitz sample (no. 810) was collected from a depth of 7910 ft (2411 m), yet exhibits an R_o of only 0.56% (Fig. 13). It should be pointed out that the reflectance measurement for sample 810 is based on only three vitrinite counts and its value for assessing deep Cowlitz mudstone maturity is questionable. However, the overall immature signature (e.g., small R_o increase) of the Cowlitz mudstone with depth is generally consistent with the maturity signature reported in other investigations of Pacific Northwest Eocene basins (Armentrout and Suek, 1985; Niem and Niem, 1985; Niem et al., 1990; Summer and Verosub, 1987; Walsh and Lingley, 1991).

The time-temperature paleohistory reconstruction (Lopatin plot) of the North Willamette Basin by Armentrout and Suek (1985) indicates that at depths greater than 10,000 ft (3048 m) the strata of Cowlitz and pre-Cowlitz age (e.g., Hamlet-Yamhill) should be sufficiently mature due to burial to generate hydrocarbons. Data in this study generally support this hypothesis. Extrapolation of the data presented in Figure 13 for the Cowlitz Formation suggests that at about 9,000 ft (2743 m) the maximum R_o to be expected is approximately 0.60%. This indicates that Cowlitz mudstones are still relatively immature at this depth and probably incapable of generating significant quantities of thermogenically derived hydrocarbons. Tissot and Welte (1984) and Schoell (1980) show that thermogenic gas generation may commence at approximately $R_o = 0.9\%$. No attempt has been made to estimate

vitrinite reflectance values for the Cowlitz below the 9,000 ft (2743 m) interval for two reasons: 1) data is lacking for the Cowlitz Fm. below 9000 ft (2743 m) in North Willamette Basin wells, but Hamlet mudstones, which are interpreted to be the deep-water lateral equivalent of the Cowlitz and Hamlet-Yamhill (Niem et al., 1990, 1991), were collected at 9000 ft (2743 m) in the Astoria Basin (e.g., Patton 32-9 and Johnson 33-33 wells). They also show a maximum R_o value of 0.55%, which is consistent with estimates for the Cowlitz and suggests a similar burial history for the two formations; 2) deeper buried Hamlet-Yamhill mudstones show an abrupt increase in R_o between 9000 ft (2743 m) and 10,770 ft (3283 m) - 0.90 to 1.64% (Fig. 13), which is perhaps indicative of thermal maturation influences and processes not associated with geothermal gradients due to deep burial, such as intrusions and/or an abrupt increase of the geothermal gradient associated with Goble volcanism.

Using a best fit curve for the Hamlet-Yamhill data (Fig. 13), it can be shown that at 9000 ft (2743 m) reflectance values for this formation should be approximately 0.90% - a maturation level high enough to generate thermogenic gas. At depths greater than 10,000 ft (3048 m) R_o values show a significant increase well into the catagenetic stage of hydrocarbon generation (e.g., beyond the oil window and into the thermogenic gas window, see Fig. 12).

Data from this investigation indicate that mature source rocks should be encountered at approximately 9000 ft (2743 m) based on current burial depths. This is generally consistent with, although somewhat shallower, than estimates by

Armentrout and Suek (1985) based on time-temperature reconstructions for the North Willamette Basin. It is not possible to constrain Cowlitz mudstones with regard to maturity versus depth of burial below 9000 ft (2743 m) due to the limited deep well control in the North Willamette Basin.

Sediment maturation levels within the North Willamette Basin could also have been affected by the heat derived from Tertiary volcanic intrusive and extrusive events. These volcanic units include: the upper Eocene Goble Volcanics and Cole Mtn. Volcanics, emplaced contemporaneously with and after the Cowlitz Fm. in the North Willamette Basin (Niem et al., 1991), the Oligocene through Miocene calc-alkaline volcanics and granodiorite plutons of the Cascade mountain range located along the eastern edge of the Willamette Basin and Puget lowland (Walsh and Lingley, 1991), as well as the older middle Eocene Tillamook Volcanics. The regional effect of these regional volcanic and local intrusive thermal events on maturation is unknown. However, due to the relatively low maturation level of a Cowlitz mudstone sample (no. 810 - Table 9) below the Goble Volcanics from the Exxon G.P.E. Federal Commission #1 well (7910 ft, 2411 m), a regional geothermal heating event associated with the extrusive Goble Volcanics does not appear to be a significant influence (see Fig. 4). However, the abrupt increase in Hamlet-Yamhill fm. maturation levels below approximately 9000 ft (2743 m) may have been influenced by the intrusives of the Goble or Cole Mtn. encountered in this well (Niem et al., 1991), and/or by residual regional higher geothermal gradients during

deposition of the Hamlet-Yamhill mudstone after the middle Eocene Tillamook Volcanics. A. R. Niem (personal communication, 1991) noted that descriptions on drillers logs for the Exxon GPE Fed. well suggest that some of the gray Hamlet-Yamhill mudstones are locally bleached white, which is suggestive of cooking effects on the organic matter. Similar bleaching to white mudstone by nearby Miocene and Eocene intrusions is widespread in the Astoria Basin (Niem and Niem, 1985; Cressy, 1974; Mumford, 1988; Safley, 1989). In the Gulf of California, Simoneit et al. (1984) have shown that the heat derived from shallow basaltic sills can create profound effects on Pleistocene sediment organic matter maturation levels (e.g., petroleum-like products generated by flash heating of immature organic matter). Therefore, this potential influence should not be dismissed, especially in light of the abrupt change of vitrinite reflectance data for the Hamlet-Yamhill mudstones in the Exxon GPE Federal well and also because of the potential widespread occurrence of these intrusions (Niem and Niem, 1985; Safley, 1989).

Evaluating the maturation level of the Hamlet fm., and thus the Astoria Basin, from vitrinite data requires more careful consideration. The presence of numerous middle Miocene invasive sills and dikes of Columbia River basalt has been documented in several wells by Martin et al. *in* Niem and Niem (1985). Down hole vitrinite measurements in these wells (see Fig. 14) exhibit significantly elevated R_o values in the vicinity of the sills, providing thermal maturation signatures similar to those found in the Gulf of California but on a much larger scale (e.g., effects seen on strata up to 300 m above underlying gabbroic intrusions). In order to

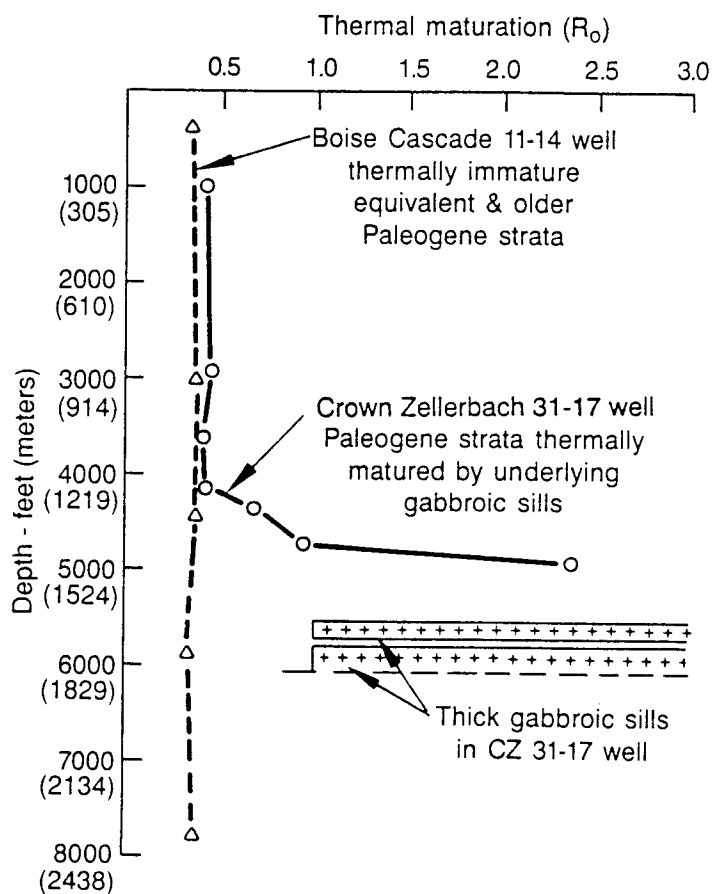


Figure 14. Comparison of thermal maturation of similar age Oligocene and Eocene strata in Crown Zellerbach 31-17 and Boise Cascade 11-14 wells from the Astoria Basin (From Niem and Niem, 1985).

show the organic matter maturation level in the Astoria Basin which has resulted from burial and the normal geothermal gradient, selection of mudstone samples for this study was restricted to those wells (e.g., Patton 32-9 and Johnson 33-33) where little or no intrusive bodies were present in the proximity of the Hamlet formation.

Vitrinite data from the Hamlet fm. indicate that sedimentary organic matter in the Clatsop County part of the Astoria Basin is relatively immature (R_o max = 0.63%). Comparison with R_o data from the Cowlitz Fm. (upper Hamlet equivalent) shows that there is a good correlation between the two formations at depths ranging from 7100 to 8900 ft (2164 to 2713 m), indicating similar maturation and burial histories. It appears that normal burial (at least to a depth of 9000 ft, 2743 m) within the Astoria Basin has not been sufficient to thermally mature the Hamlet fm. organic matter to a quantitatively important degree, at least with regard to being a hydrocarbon source for the Mist field. However, the heat derived from upper Eocene and middle Miocene intrusions may have accelerated maturation in local areas, and thus the importance of the igneous activity with respect to organic matter maturation should not be ignored, at least until the spatial distribution and overall effects are better understood. This conclusion is supported by the fact that areas of the basin not associated with igneous events have maximum measured vitrinite reflectances of 0.63% (see Fig. 13, and Table 9 this report, and discussions by Niem and Niem, 1985), whereas Oligocene and Eocene mudstones in the immediate proximity of intrusive dikes and sills have recorded reflectances as high as 2.36% (see Fig. 14). These 1000+ ft (305+ m) thick sills have been traced for tens of miles in the offshore

and onshore parts of the Astoria Basin and may reflect important widespread regional heat sources for maturation. Thick gabbroic and basaltic Cole Mtn. sills (>150 m thick) and dikes that intrude the Hamlet mudstones in Clatsop County have locally thermally matured these mudstones 100's of meters away from the contact according to some data reported by Safley (1989). The regional effect of past high geothermal gradients on these strata in the buried eastern part of the North Willamette Basin near the Western Cascades is unknown. However, Walsh and Lingley (1991) noted the abrupt increase in maturation and rank of the Eocene coals of western Washington from lignite to bituminous A, B, C and even to anthracite as one approached the granitic intrusion of the Western Cascades in the Puget Group.

Vitrinite reflectance measurements of the coal samples from the C&W sandstone (#'s 820 & 821) indicate that the organic matter in these samples from the Mist area is immature and in the diagenetic or nongenerative maturation state. Both samples exhibit very low reflectance values -- $R_o = 0.36\%$ (typical of lignitic coal rank) for both sample 820 and 821 (see Table 9).

Whole rock pyrolysis data also provide a number of parameters which have application in maturation evaluations. Plots of T-max versus depth and transformation ratio (TR) versus depth are presented in Figures 15 and 16, respectively. T-max represents the temperature of maximum hydrocarbon yield during rock-eval pyrolysis. The transformation ratio $[S_1/(S_1 + S_2)]$ is the ratio of

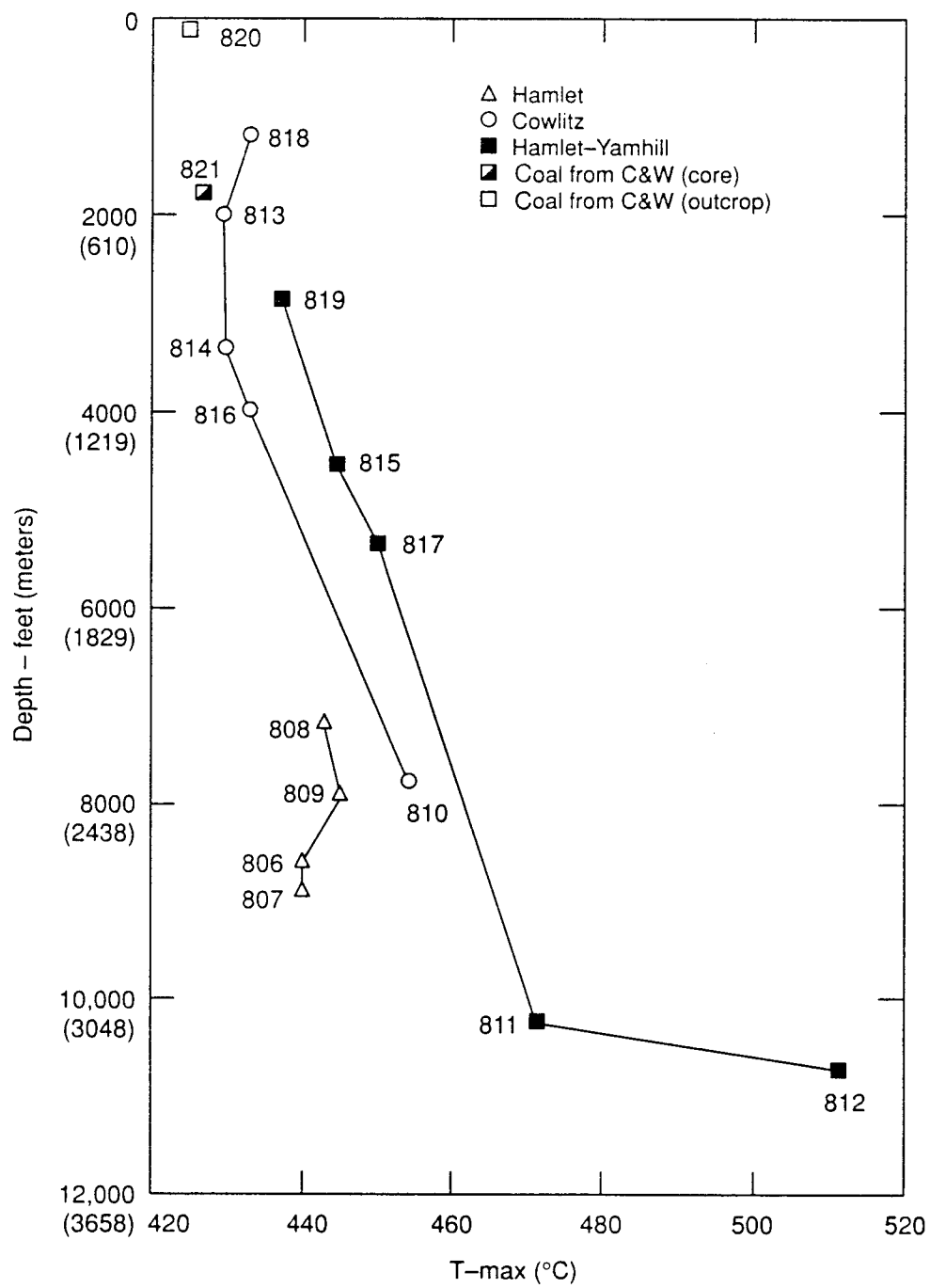


Figure 15. Plot of T-max (°C) versus depth.

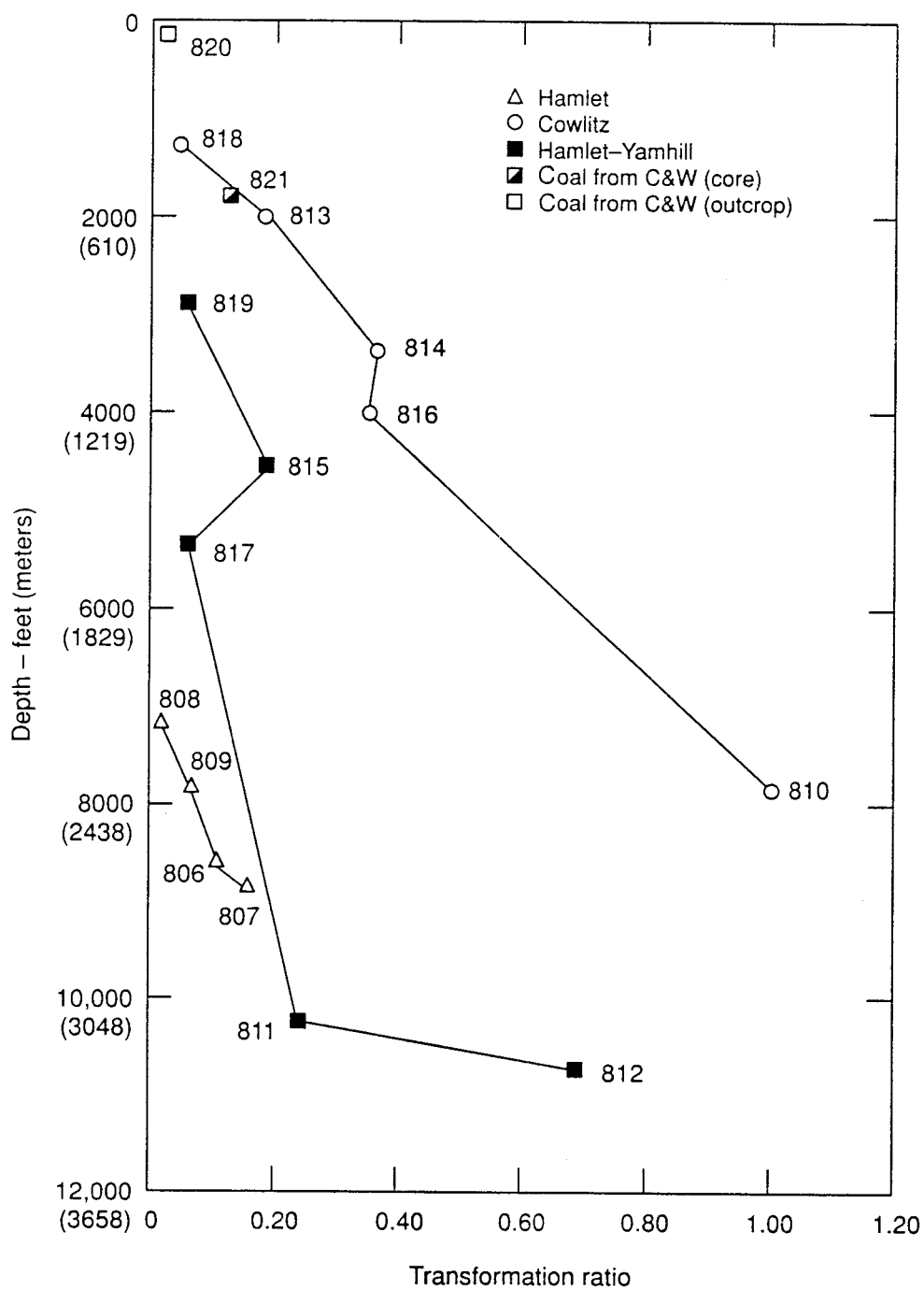


Figure 16. Plot of transformation ratio versus depth.

petroleum actually formed by the kerogen to the amount of petroleum the kerogen is capable of generating (Tissot and Welte, 1984). Both parameters have been shown to increase with depth making them useful indices of maturation (Barker, 1982; Tissot and Welte, 1984; Espitalie et al., 1977; Claypool and Reed, 1976). Because T-max may be affected by the type of organic matter being evaluated and TR by hydrocarbon migration, these parameters are being examined only for their overall trends and for correlation to other maturation indices (Tissot and Welte, 1984).

In both Figure 15 and Figure 16, the Hamlet-Yamhill fm. of the North Willamette Basin shows a progressive increase in T-max and TR down to a depth of approximately 10,000 ft (3048 m). At this point, both maturation indices show dramatic increases. These trends mimic quite well the vitrinite reflectance signature displayed in Figure 13. Sample 817 (Well CZ4) shows a lower than expected value for the transformation ratio which could be the result of migration of previously generated hydrocarbons as mentioned earlier. However, the overall consistent trend exhibited by the Hamlet-Yamhill samples with respect to %R_o, T-max, and TR suggests that these mudstones have experienced gradual maturation down to approximately 10,000 ft (3048 m) and then an abrupt increase in maturation well into the catagenetic window (perhaps due to thermal effects of possible basalt intrusions in the Exxon GPE Federal well; A. R. Niem, personal communication, 1991).

T-max and TR data for the Cowlitz and Hamlet formations are not as easily interpreted as for the Hamlet-Yamhill. Small, but noticeable deviations from

expected maturation signatures are evident, providing evidence of the limitations of these parameters. The TR trend for the Hamlet mudstone samples of the Astoria Basin does show the increase expected with increasing depth of burial. The increase is, however, small when compared with Hamlet-Yamhill data and is a reflection of the overall immature character of the formation. T-max values, on the other hand, decrease slightly with increasing sample depth. It is not clear why this reverse trend is occurring, although vitrinite reflectance data (Table 3, Fig. 13) also show a slight decrease with depth. It is possible that the type of kerogen is slightly different between the two sets of Hamlet mudstone samples (e.g., 808 and 809 vs. 806 and 807), although this was not seen in either visual kerogen or pyrolysis-GC data (see Fig. 11 and Table 7).

The T-max versus depth profile for the Cowlitz Fm. is generally consistent with the immature character shown by vitrinite reflectance measurements. The dashed line between Samples 816 and 810 in Figure 15 is an estimate based on an expected increase with depth. The pyrolysis S₂ peak for Sample 810, from which T-max is calculated, was too small for accurate integration/measurement most likely due to the sample's low TOC (L. Lundell, ARCO, personal communication, 1988). The trend for TR values, although increasing with depth as would be expected independent of other maturation information, is high with respect to kerogen color and vitrinite reflectance data. These indices indicate that the Cowlitz mudstones are relatively immature and in a more or less nongenerative maturation state. TR data alone would suggest that the Cowlitz has generated a significant portion of its potential

hydrocarbons, especially for Sample 810 at 7910 feet (2411 m). The TOC value (Table 3) for Sample 810 is very low (0.15%). If hydrocarbons have been generated the remaining potential would be expected to be low based on the sample's organic leanness. Alternatively, hydrogen index versus oxygen index data (Figure 10) indicate that the Cowlitz is a type III kerogen with a low hydrocarbon-yield potential. Additionally, if a significant portion of the kerogen is inertinite (residual kerogen) or oxidized then the calculated transformation ratios are probably accurate with respect to generative potential (see later discussion), but not necessarily a reliable indicator of the formation's maturation state.

The T-max and TR values presented in Table 9 and Figures 15 and 16 for the two C&W coal samples indicate that both are immature. Both samples exhibit T-max values which are lower than all other analyzed samples. Transformation ratio values also indicate that both samples (#'s 820 & 821) have realized little of their hydrocarbon potential.

Optical techniques using transmitted (versus reflected) light have also been used for evaluating source rock maturity by observing changes in the color and/or structure of palynological kerogen. The thermal alteration index (TAI) is a value (1 to 5) based preferably on the cuticle, or secondarily the spore-pollen, coloration over the range yellowish-green (immature), yellow (immature), orange, light brown, dark brown (mature), and black (supermature) (Geochem Laboratories, Inc., 1980). Thermal alteration index values for some of the Mist source rock samples are

presented in Table 9. Using the numerical and descriptive scales developed by Geochem Laboratories, Inc. (1980), TAI values and colors can be evaluated for maturity in relation to other maturity parameters.

TAI values determined for the Mist area range from 2.00 to 2.50. Values in this range reflect source rocks which are moderately immature to moderately mature, and correspond to vitrinite reflectance values between 0.5 and 0.8% (Geochem Laboratories, Inc., 1980). For samples where both TAI and R_o have been determined, TAI values suggest an overall, slightly greater degree of maturity than vitrinite measurements. If additional maturity parameters (e.g., TR, T-max, and CPI) are taken into account, the overall immaturity of these samples is evident. While providing a relative indication of maturity, TAI values are considered slightly high and do not reflect the maturation level of the Mist kerogens as accurately as other indices.

Unfortunately, TAI determinations were not made for samples 810, 811, and 812. However, kerogen color was determined for these samples and can be evaluated with respect to other maturity parameters. Sample 810 appears yellow in transmitted light, which agrees fairly well with its low vitrinite value (see Table 9, Figure 13) and indicates a relatively immature sample. On the other hand, all maturity parameters for samples 811 and 812, including the brown-dark brown kerogen color determination, suggest that these samples have reached the catagenetic stage of hydrocarbon generation.

As with vitrinite reflectance, gas chromatography is commonly used as a method for evaluating source rock maturity. Gas chromatography provides several indices which are valuable in assessing not only maturity, but source rock quality as well (Tissot and Welte, 1984; Geochem Laboratories, Inc., 1980). As a result of the widespread use of this method, both the values assigned individual indices, and the overall chromatographic signatures exhibited by various types of source material at various maturation levels, are well understood and have been shown to be reliable in maturation evaluations.

Figures 17, 18, and 19 represent gas chromatograms of the C_{15}^+ saturate fraction from extracts of the Hamlet, Cowlitz, and Hamlet-Yamhill mudstones, respectively. Several samples had to be combined to provide enough material for analysis (e.g., 806+807, 808+809, 811+812). In general, the following information should be kept in mind when evaluating chromatograms of the C_{15}^+ saturate fraction:

1. Marine organic matter is characterized by n-alkanes of medium molecular weight (C_{12} - C_{20}) with a frequent predominance of C_{15} , C_{17} , and C_{19} n-alkanes (Tissot and Welte, 1984; B. R. T. Simoneit, written communication, 1984).
2. Terrestrial organic matter is derived predominantly from higher plants and exhibits mainly odd n-alkanes of high molecular weight

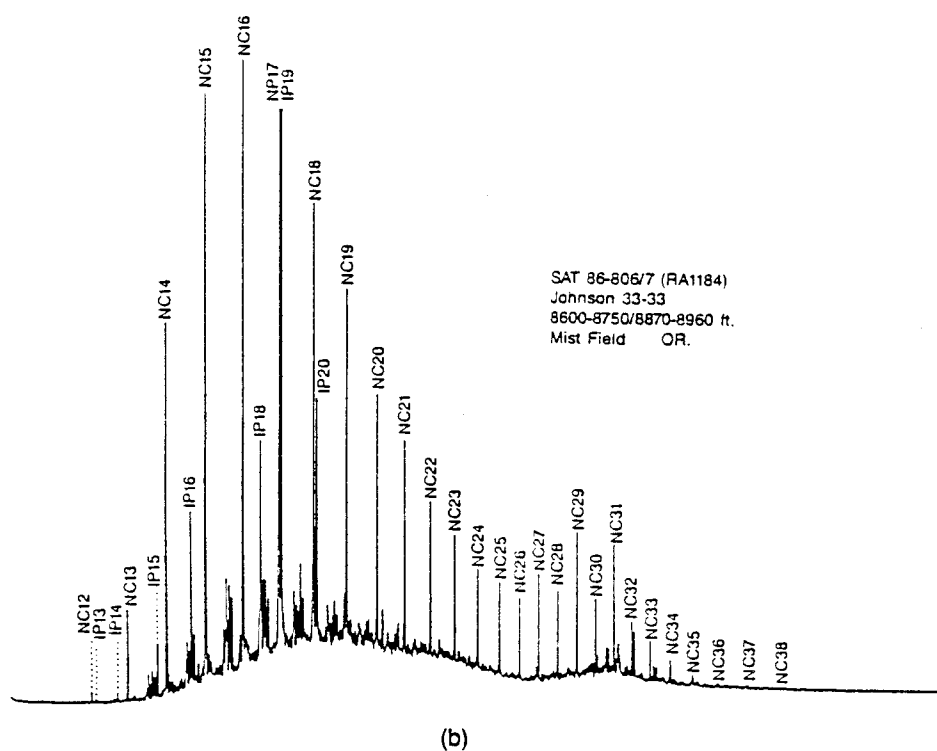
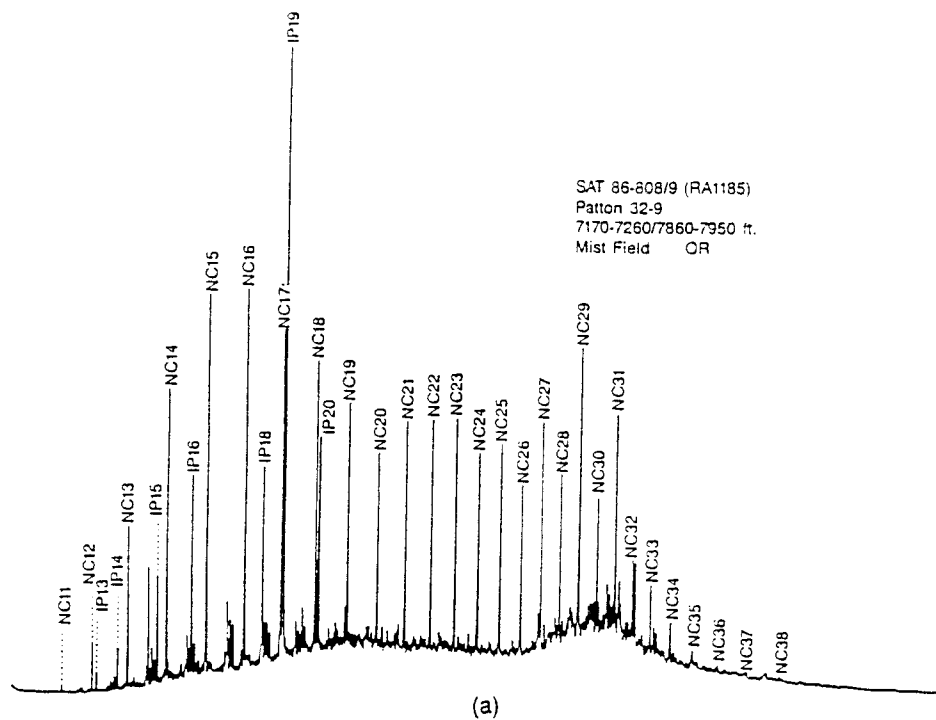


Figure 17. Gas chromatograms of C_{15}^+ saturate fraction for the Hamlet formation mudstones. Analyses performed by ARCO Oil and Gas Company.

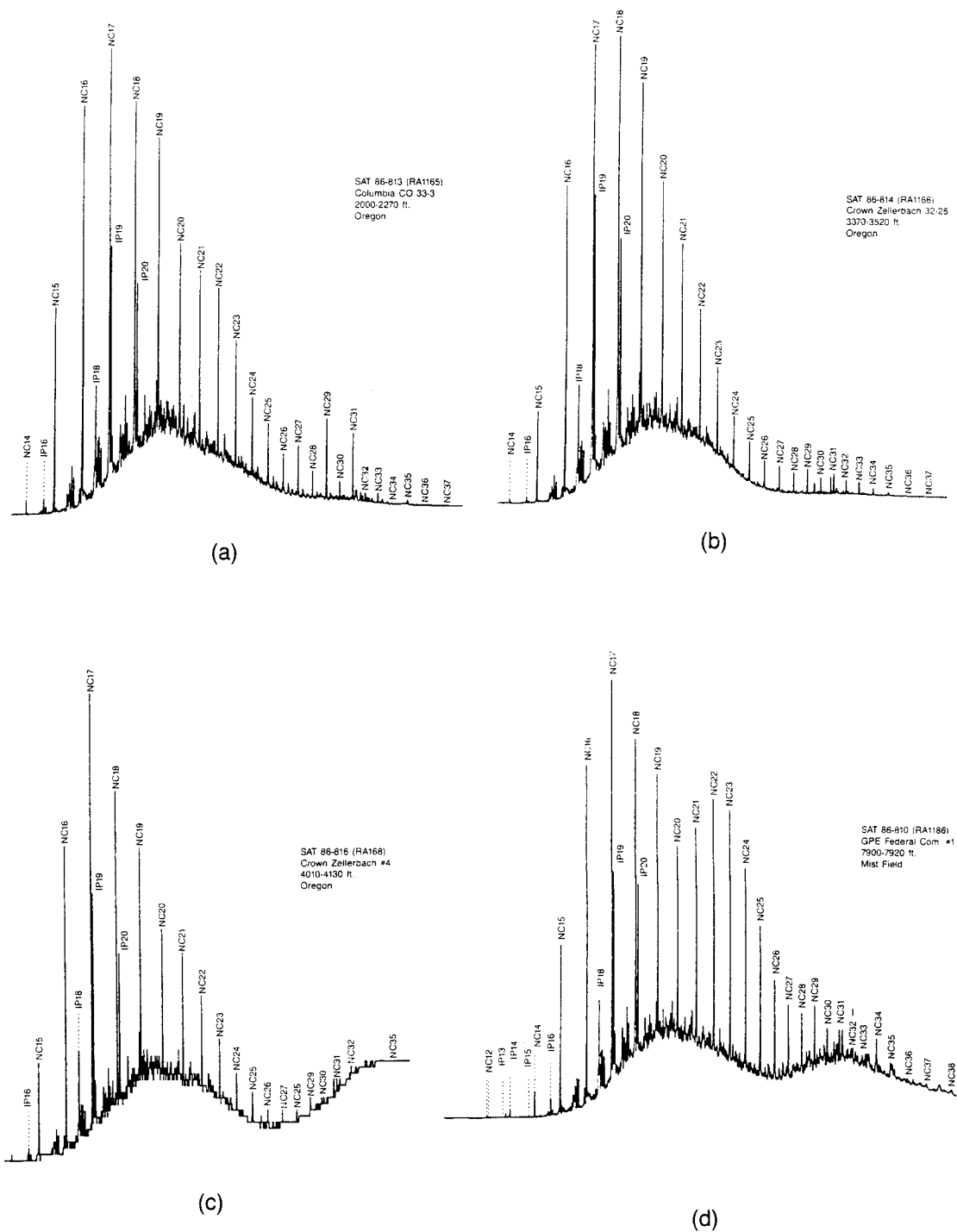


Figure 18. Gas chromatograms of C_{15}^{+} saturate fraction for the Cowlitz Formation mudstones. Analyses performed by ARCO Oil and Gas Company.

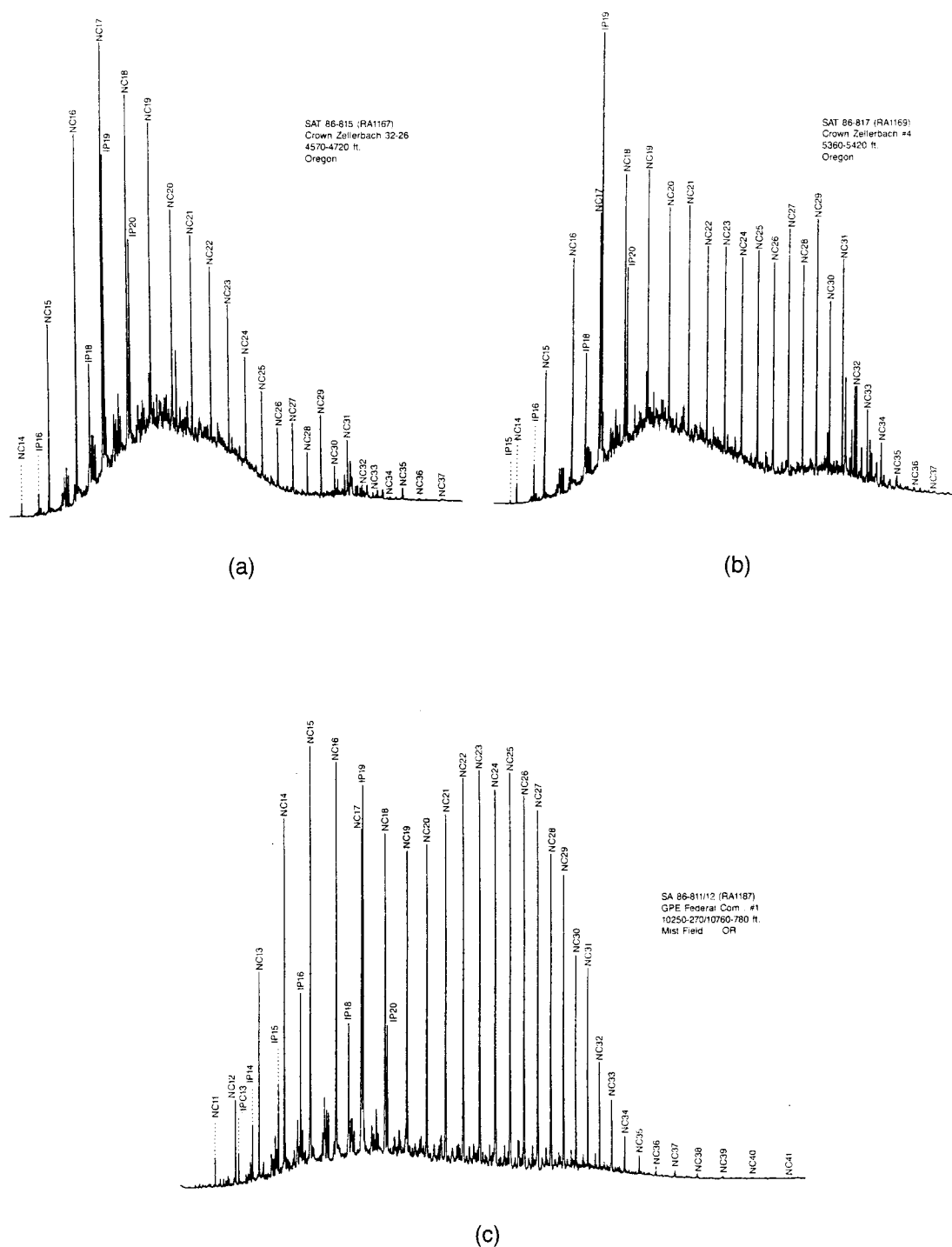


Figure 19. Gas chromatograms of C_{15}^+ saturate fraction for the Hamlet-Yamhill formation mudstones. Analyses performed by ARCO Oil and Gas Company.

(C₂₅ to C₃₃) (Tissot and Welte, 1984; B. R. T. Simoneit, written communication, 1984).

3. The n-alkane content of terrestrial derived organic matter is usually higher than in marine organic matter. Therefore, in systems where both types of organic matter are present, terrestrial organic matter tends to dominate the n-alkane distribution pattern (Tissot and Welte, 1984).

As noted earlier, the Hamlet, Cowlitz, and Hamlet-Yamhill mudstones are characterized by a mixed marine-terrestrial organic matter assemblage. This interpretation is supported by the bimodal n-alkane distribution pattern on the C₁₅₊ saturate fraction gas chromatograms (Fig.'s 17, 18, and 19).

For the purpose of this discussion the most useful indicator of maturation is provided by the carbon preference index (CPI) (Table 9). The carbon preference index is based on the distribution of long chain n-alkanes and shows a progressive change with maturation (Tissot and Welte, 1984). It is calculated using the ratio of odd to even numbered alkanes as shown in the following example.

$$CPI = \frac{1}{2} \left[\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right]$$

The premise behind using CPI as a maturation index is based on the fact that plants usually do not synthesize even n-alkanes, but rather even-numbered acids and alcohols which are important constituents of fats and waxes (Tissot and Welte, 1984). It is thought that in normal environments, the alcohols are oxidized to acids with subsequent decarboxylation to yield additional odd n-alkanes besides those directly derived from waxes (B. R. T. Simoneit, personal communication, 1991). During catagenesis new alkanes are generated with little or no odd-preference, causing the progressive disappearance of the odd/even predominance by dilution (Tissot and Welte, 1984). It should be noted that n-alkane distributions exhibiting an even n-alkane preference have been documented, but are less frequent than an odd-predominance and are thought to occur as a result of alcohol or acid reduction (Tissot and Welte, 1984). Because CPI values are influenced by both the type of organic matter and level of maturation, it is the progressive decrease in CPI, as well as the actual values which are used in evaluating organic matter maturity.

Carbon preference index values are presented in Table 9. The Hamlet samples show CPI values of 1.44 and 1.38 with increasing depth. Although there is a slight decrease in the CPI, these values are still relatively high and are interpreted as immature (L. Lundell, ARCO, personal communication, 1989). Similarly, samples from both the Cowlitz and Hamlet-Yamhill formations (with one exception) are interpreted as immature based on their CPI values, their chromatographic signatures, as well as other maturity indices. The exception is the combined 811/812 sample.

This sample has a CPI value approaching unity, indicating dilution of the odd-carbon number predominance by the generation of new n-alkanes.

Generative History and Potential

In a variation of the genetic "richness" potential presented earlier, rock-eval data can also provide an indication of both the generative history and potential of the Mist source rocks. Through a series of histograms, Figures 20, 21, and 22 illustrate the amount of generative potential already realized (S_1), as well as the remaining potential (S_2) of the three formations to generate hydrocarbons. In an ideal system, the S_1 peak would get progressively larger with a corresponding decrease in the S_2 peak as more and more hydrocarbons are generated as a function of increased burial and maturation. Before evaluating these two parameters for the Hamlet, Cowlitz, and Hamlet-Yamhill formations, it should be noted that there are significant differences in the scaled concentrations between the formations.

The progressive change in S_1 and S_2 is well illustrated in the three formations being investigated. The Hamlet formation (Fig. 20) shows a small but noticeable increase in the S_1 peak with depth. The remaining potential (S_2) does not show a corresponding decrease with depth, but this is due to slight variations in the overall original potential (e.g., $S_1 + S_2$) of each sample. Although the Hamlet formation of the Astoria Basin shows an increase in hydrocarbons generated as a function of depth, the amount is small with respect to its generative capability. However, what

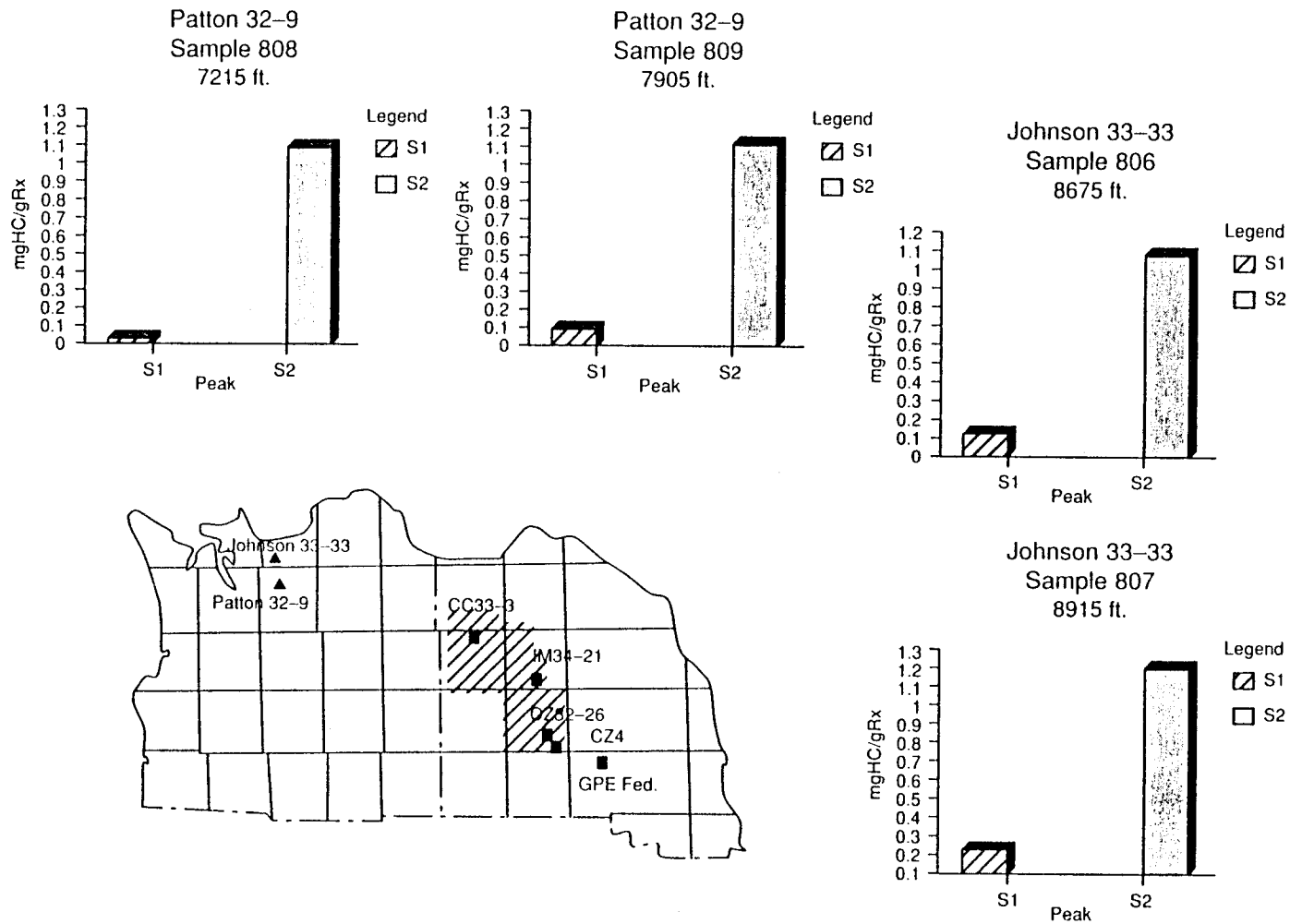


Figure 20. Histograms showing generative history and potential (S₁ vs S₂) of the Hamlet formation. Note differences in scale (Y-axis) for the various mudstone samples.

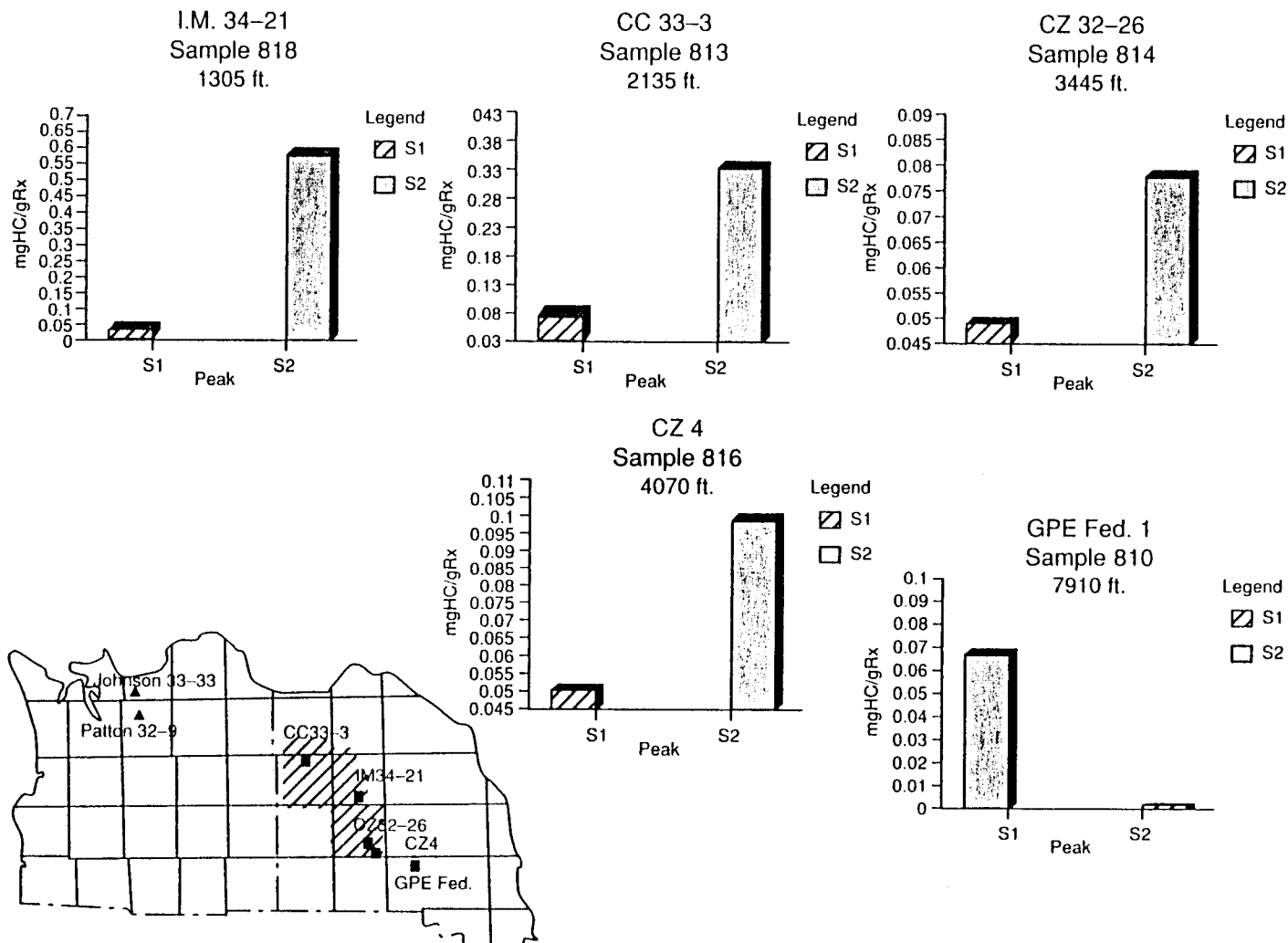


Figure 21. Histograms showing generative history and potential (S_1 vs S_2) of the Cowlitz Formation. Note differences in scale (Y-axis) for the various mudstone samples.

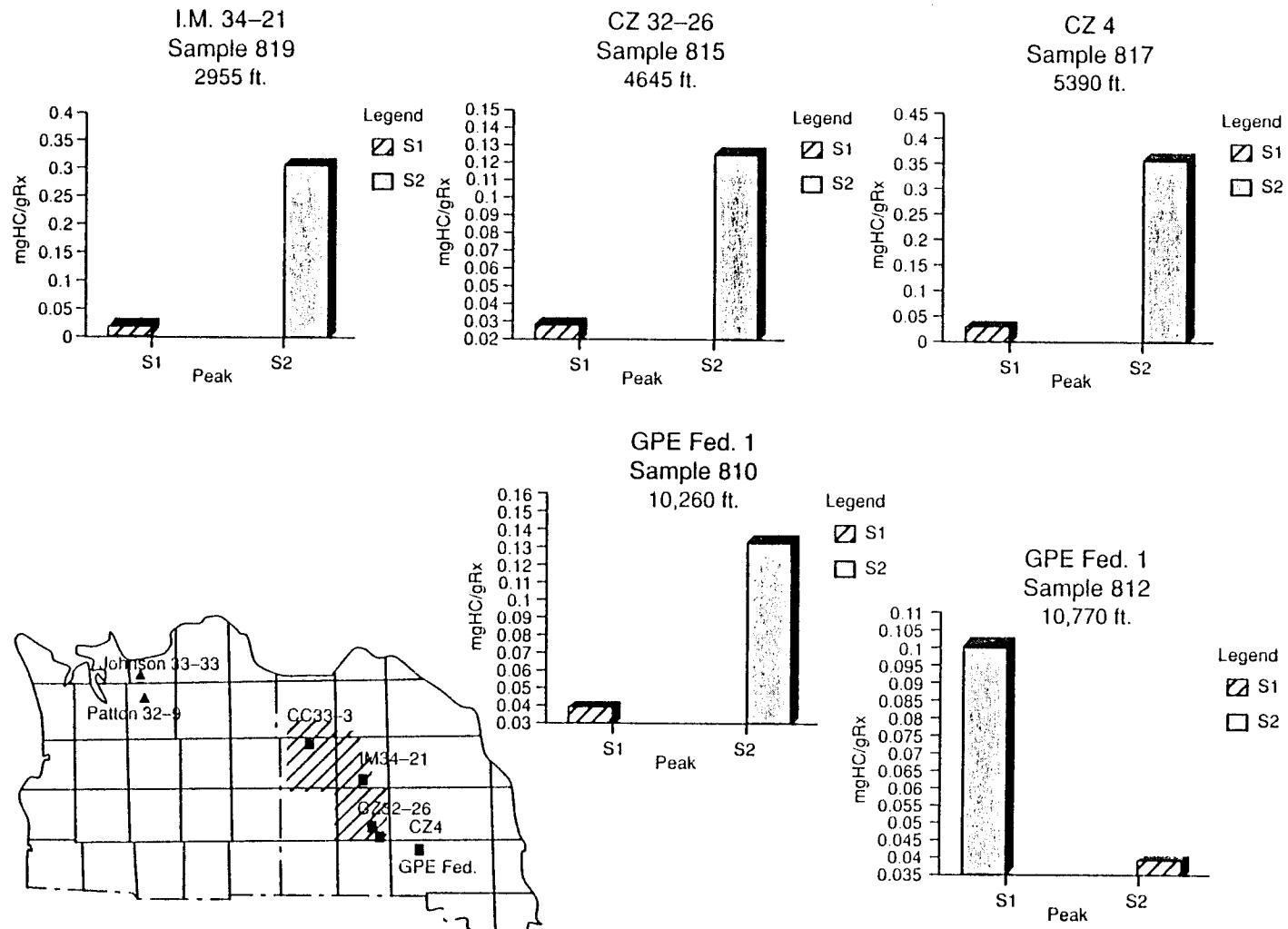


Figure 22. Histograms showing generative history and potential (S_1 vs S_2) of the Hamlet-Yamhill formation. Note differences in scale (Y-axis) for the various mudstone samples.

must be kept in mind is that the Hamlet has the best hydrocarbon generating potential of the three formations (see Table 5). Because of its overall nongenerative history and moderate to good source rock classification (TOC), the Hamlet still retains a significant portion of its generating capability.

What is immediately evident from the histograms of the Cowlitz mudstones (Fig. 21) is the very low concentration of hydrocarbons generated. The samples show an average realized potential of 0.05 mgHC/gRx, which is less than half the average evolved hydrocarbon concentration of the Hamlet formation. There also appears to be little increase in realized potential with depth. This points to a rather nongenerative history, with the overall low concentrations in both peaks indicative of a low hydrocarbon-yielding source rock unit. Sample no. 810 (GPE Fed. #1) appears to have a much different character than the other four samples. Upon closer examination of the y-axis scale, it is evident that this sample has generated approximately the same concentration of hydrocarbons as the others. However, what is different about sample 810 is that it has essentially no future generative capability, while the others retain some, albeit small, future potential. As has already been mentioned, the signature of sample 810 may only be a reflection of the low organic carbon content of the sample. In other words, with a low initial potential, any subsequent hydrocarbon generation would result in a low remaining potential.

The Hamlet-Yamhill fm. of the North Willamette Basin has a generative history and potential signature similar to the Cowlitz. However, the cause of this similarity

is important with respect to the ability of these two formations to act as source rocks. The histograms for the Hamlet-Yamhill mudstones (Fig. 22) show little realized potential down to a depth of approximately 10,700 feet (3261 m). Sample 812 (10,770 ft 3283 m) shows a significant jump in evolved hydrocarbon concentration. Taking into account the maturity of this sample ($R_o = 1.64\%$), it would be surprising if sample 812 had not generated hydrocarbons. Its low remaining potential (S_2) is the result of hydrocarbon generation, as might be expected from a sample that had been matured well into the catagenetic stage of evolution.

RESERVOIR GAS GEOCHEMISTRY

Chemical Composition of Reservoir Gas

The chemical composition of Mist reservoir gas is dominated by two compounds, methane (CH_4) and molecular nitrogen (N_2), in highly variable amounts. Reservoir gas chemical data presented in Table 10 were provided by W. T. Aimes and H. J. Meyer of the Northwest Natural Gas Company, Portland, Oregon. The data represent analyses carried out by Northwest Natural Gas (or various subcontractors) between 1982 and 1990. In general, for wells with multiple analyses (e.g., monthly, quarterly, semi-annual, etc.), gas compositions are fairly consistent with only small fluctuations over time. The hydrocarbon fraction of the gas is dominated by methane (>99.93%). The ethane, propane, butane, and pentane hydrocarbon components are detectable only in trace amounts (<0.07%). From these observed concentrations Mist gases can be classified as "dry" (methane rich) gases (Tissot and Welte, 1984; Schoell, 1980, 1983). Among the non-hydrocarbon components (e.g., CO_2 , N_2 , O_2) nitrogen is dominant (>99.49%) with only trace amounts of CO_2 and essentially no free O_2 . Whole gas data (Table 10) show that methane - nitrogen concentrations range from 98.77 - 1.21% (Paul 34-32) to 48.98 - 51.02% (Crown Zellerbach 31-16).

Table 10. Chemical composition of Mist field reservoir gases (mole or volume %).

Well Name	CH ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₈ (%)	iC ₄ H ₁₀ (%)	nC ₄ H ₁₀ (%)	C ₂₊ (%)	O ₂ (%)	CO ₂ (%)	N ₂ (%)
Crown Zellerbach 42-1	91.014	0.054	ND	ND	ND	0.054	ND	0.017	8.916
Longview Fiber 23-36	85.586	ND	ND	ND	ND	0.000	ND	ND	14.414
Columbia County 13-34	97.583	0.012	ND	ND	ND	0.012	ND	ND	2.405
Columbia County 23-22	96.789	0.017	ND	ND	ND	0.017	ND	ND	3.194
Longview Fiber 12-33	98.313	0.016	ND	ND	ND	0.016	ND	ND	1.671
Columbia County 43-27	90.680	0.021	ND	ND	ND	0.021	ND	ND	9.300
Columbia County 43-22	96.466	0.015	ND	ND	ND	0.015	ND	ND	3.519
Columbia County 6-RD2	90.479	0.024	ND	ND	ND	0.024	ND	0.035	6.855
Columbia County 10	96.512	ND	ND	ND	ND	0.000	ND	0.006	3.482
Columbia County 3	90.930	0.023	ND	ND	0.006	0.023	ND	0.014	9.033
Paul 34-32	98.773	0.021	ND	ND	ND	0.021	ND	ND	1.206
Columbia County 4	92.766	0.032	ND	ND	ND	0.032	ND	ND	7.192
Columbia County 1	90.885	ND	ND	ND	ND	0.000	ND	ND	9.115
Columbia County 13-1	78.884	ND	ND	ND	ND	0.000	ND	0.009	21.107

Table 10. (Continued).

Well Name	CH ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₈ (%)	iC ₄ H ₁₀ (%)	nC ₄ H ₁₀ (%)	C ₂₊ (%)	O ₂ (%)	CO ₂ (%)	N ₂ (%)
Crown Zellerbach 12-1	73.570	ND	ND	ND	ND	0.000	ND	ND	26.430
Crown Zellerbach 31-16	48.977	ND	ND	ND	ND	0.000	ND	ND	51.023
Columbia County 41-28	95.407	ND	ND	ND	ND	0.000	ND	ND	4.593
Busch 14-15	95.869	ND	ND	ND	ND	0.000	ND	ND	4.131
Columbia County 33-3	95.961	0.020	0.017	ND	ND	0.037	ND	ND	4.012
Columbia County 44-21	93.095	0.013	ND	ND	ND	0.013	ND	0.035	6.855
Crown Zellerbach 23-15	65.000	ND	ND	ND	ND	0.000	ND	ND	35.000
Columbia County 32-32	95.390	ND	0.040	0.030	ND	0.070	0.170	ND	4.380
Columbia County 24-9-64	85.091	ND	ND	ND	ND	0.000	ND	ND	14.909
CER 41-16-64	87.674	ND	ND	ND	ND	0.000	ND	ND	12.326
CFW 12-15-64	84.197	ND	ND	ND	ND	0.000	ND	ND	15.803
CER 11-16-64	88.530	ND	ND	ND	ND	0.000	0.030	ND	11.440
Columbia County 42-8-54	77.352	0.010	0.038	ND	ND	0.048	0.023	0.045	22.530

Analytical data provided by Northwest Natural Gas Co. (W. T. Aimes and H. J. Meyer).
ND = Not detected

The chemical composition of gas can provide a first indication of its origin. Very low concentrations of ethane and higher hydrocarbon homologs suggest the presence of microbial methane generating processes. Analysis and evaluation of gas compositional data from numerous natural gas fields by Schoell (1983) suggests that biologically derived gas deposits rarely have C_{2+} concentrations greater than about 0.05 to 0.2%. When C_{2+} concentrations exceed this range, it is generally an indication of the presence of thermally derived gas. Although low C_{2+} concentrations might suggest the presence of biogenically derived methane in the Mist field (see Table 10), thermogenic gas and/or mixing processes should not be eliminated from consideration based on source rock maturation and gas stable isotope data.

In addition to providing clues to the genetic origin of natural gas, compositional data for non-hydrocarbon components can also be evaluated. The presence of variable but significant amounts of nitrogen might suggest gas derivation from terrestrial organic matter or possibly coal sequences, as opposed to marine organic matter (Tissot and Welte, 1984). However, genetic interpretations of natural gas origin based solely on chemical composition can lead to erroneous conclusions. For example, natural gases enriched in methane can be of a bacterial origin, derived from high-rank coals, or result from secondary processes such as mixing and migration (Schoell, 1984a, 1983). For this reason, carbon and hydrogen stable isotope data have been evaluated in conjunction with compositional data in an attempt to determine the genetic origin of the Mist natural gas.

Carbon and Hydrogen Isotope Signature: Natural Gas Genetic Characterization

Natural gas originates from two basically different processes: 1) by microbially mediated transformation processes (biogenic natural gas), and 2) by the cleavage of gaseous products from organic matter during the thermal alteration/maturation of the organic matter (thermogenic natural gas) (Schoell, 1980, 1983, 1984a). Figure 23 is a schematic representation of natural gas occurrence as related to its vertical distribution in the earth's crust, and also reflects increasing maturity of the overall system as a function of $\delta^{13}\text{C}_{\text{CH}_4}$ and R_o . A brief discussion of the various types of natural gas illustrated in Figure 23 is presented below.

Biogenic natural gases (B) are formed in areas of high sedimentation rates and where sedimentary organic matter is immature (Schoell, 1984a, 1983; Mattavelli et al., 1983). These gases have been documented in a variety of environments including glacial tills (Coleman, 1976), marine sediments (Claypool and Kaplan, 1974), and Tertiary basins (Colombo et al., 1969; Schoell, 1977; Mattavelli et al., 1983). Work by Schoell (1980), Rice and Claypool (1981) and others suggests that CO_2 reduction (methanogenesis) is the dominant pathway by which biogenic gas is formed.

Carbon and hydrogen stable isotope analyses of natural gases from various geologic settings show that biogenic natural gases have a definable isotope composition, where $\delta\text{D}_{\text{CH}_4}$ ranges from approximately -150 to -250‰ and $\delta^{13}\text{C}_{\text{CH}_4}$ is

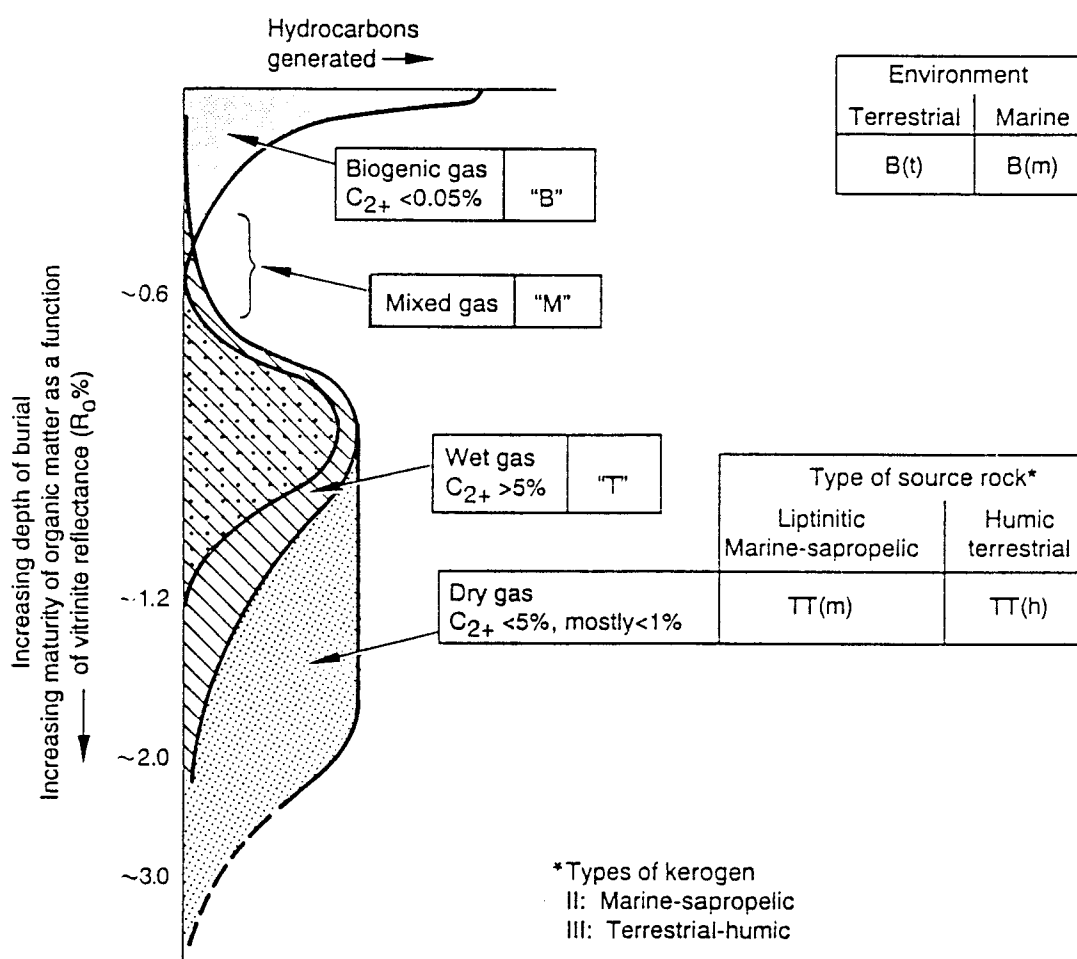


Figure 23. Schematic illustration of natural gas occurrence as a function of depth and organic matter maturity (adapted from Schoell, 1983).

generally less than -55 to -60‰ (Schoell, 1983). Natural gases which have greater $\delta^{13}\text{C}$ isotopic values (less negative) also show the presence of small quantities of ethane and higher hydrocarbon homologs. Since methane is essentially the sole hydrocarbon generated from bacterial processes, the presence of a C_{2+} component greater than about 0.05 - 0.2% is indicative of at least some input from thermally derived gas (Schoell, 1980, 1983).

Thermogenic natural gases (T and TT) result from increased burial of sedimentary organic matter. The organic matter is restructured with increasing thermal stress leading to the formation of low molecular weight hydrocarbons (Tissot and Welte, 1984; Durand, 1980). Schoell (1980, 1983) identified two genetic types of thermogenic gas: 1) gases formed during or immediately following oil formation and 2) "dry" gases formed after the main stage of oil formation. The former type is genetically related to gas formed in association with oils or condensates (T_o/T_c), whereas dry thermogenic gas (TT) is thought to originate from cracking reactions in kerogens, or perhaps from thermal alteration of deeply buried petroleum in overmature environments (Schoell, 1983). Associated gases (T_o/T_c) and non-associated gases (TT) can be differentiated by their C_{2+} concentrations, where the use of C_{2+} in discriminating genetic origin is based on the fact that the highest concentrations are formed during the main stage of oil generation (Schoell, 1983). With increasing organic matter maturity the concentration of these C_{2+} hydrocarbons decreases (Evans et al., 1971; Schoell, 1980; Stahl et al., 1977).

In cases such as the Mist field, where gas composition alone cannot provide a definitive explanation of natural gas origin, stable isotope relationships ($^{13}\text{C}/^{12}\text{C}$ and D/H) together with C_{2+} compositional data can be utilized to help determine gas genetic origin. Schoell (1983) has shown that these three indices can be used to distinguish not only biogenic gases from thermogenic gases, but also thermogenic associated ($\text{T}_\text{o}/\text{T}_\text{c}$) from non-associated gases (TT), non-associated marine (TT_m) derived from terrestrial sourced (TT_h) gases, as well as gases resulting from the mixing (M) of different sources.

The natural gas genetic fields used in this investigation (see Figures 24a and 25a) are adopted from work by Schoell (1980, 1983, 1984b). Schoell based the design of these diagrams and their compositional fields on published and unpublished data from over 500 natural gas analyses. His approach attempts to explain compositional variations due not only to processes during gas formation but compositional changes resulting from secondary processes (e.g., migration, mixing) as well. It should be noted that the fields developed by Schoell are for primary gases which have retained the basic isotopic signature of their precursor material and/or generation process. Secondary processes such as migration and mixing may alter the original gas genetic signature, especially as related to C_{2+} data, and this must be taken into account when making genetic interpretations of natural gases.

For this investigation, gas samples from 15 wells were collected directly from the well heads by this investigator during the later part of 1986 and subsequently

submitted to Coastal Science Laboratories, Inc. in Austin, Texas for measurement of the $^{13}\text{C}/^{12}\text{C}$ and D/H isotopic ratios of the methane component. The carbon and hydrogen isotopic concentrations (expressed in δ -notation) and C_{2+} gas concentrations are presented in Table 11. Also presented in Table 11 are carbon and hydrogen isotopic concentrations from seven wells from a previous investigation (unpublished data, Rice et al.). Mist gases are characterized by $\delta^{13}\text{C}$ values of their methane between -53 and -40 ppt, and δD values between -169 and -128 ppt. C_{2+} concentrations are below 0.07% in these gases (see Table 11).

Figure 24a is an illustration of the genetic fields defined by Schoell (1983) from the correlation of C_{2+} and $\delta^{13}\text{C}$ data. Figure 24b illustrates where Mist gases plot with respect to these genetic fields. With the exception of gases from wells CZ 23-15 and CZ 12-1 (see Table 11), all samples plot within the genetic field corresponding to gases associated with condensates (T_c). The samples from the two Crown Zellerbach (CZ) wells plot within the "mixed" (M) gas field. This graphical correlation suggests that the majority of the gas is thermally derived and originated during or immediately following the main stage of hydrocarbon generation in association with condensate formation. However, associated gas (e.g., gas generated in association with condensate or oil) typically exhibits the highest C_{2+} concentration of all the genetic types of gas, and as illustrated in Figure 24b Mist gases are essentially devoid of C_{2+} hydrocarbons. In addition, although higher hydrocarbons have been detected in mud chromatographic analysis during drilling of several wells,

Table 11. Carbon and hydrogen stable isotope data and C₂₊ concentrations of the Mist natural gases.

Well Name	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	δD (‰)	C ₂₊ (%)
LF 12-33	-44.9	-140	0.016
CC 13-34	-43.6	-134	0.012
CC 33-3	-41.4	-134	0.037
CC 3-RD	-40.8, -40.9* ²	-133, -134* ²	0.023
CC 6-RD2	-41.2	-133	0.024
Busch 14-15	-46.2	-149	0.000
CC 23-22	-45.3	-149	0.017
CC 43-22	-45.0	-146	0.015
CC 44-21	-47.9	-143	0.013
CC 41-28	-49.3	-150	0.000
CC 43-27	-48.8	-142	0.021
CZ 31-16	-49.4	-147	0.000
CZ 23-15	-52.3, -52.6* ²	-147	0.000
CC 32-32	-47.0	-143	0.070
CZ 12-1	-51.6	-145	0.000
*			
CZ 42-1	-52.4	-169	0.054
CC 13-1	-51.7	-151	0.000
CC 6-RD2	-41.4	-148	0.024
CC 1-RD	-41.2	-147	0.000
CC 4	-42.3	-128	0.032
CC 3-RD	-41.4	-147	0.023
CC 33-3	-42.3	-152	0.037

* Unpublished carbon and hydrogen isotope data (Rice et al.) provided by Northwest Natural Gas, Co. (H. J. Meyer). C₂₊ data from Table 10, this investigation.

*² duplicate gas analysis

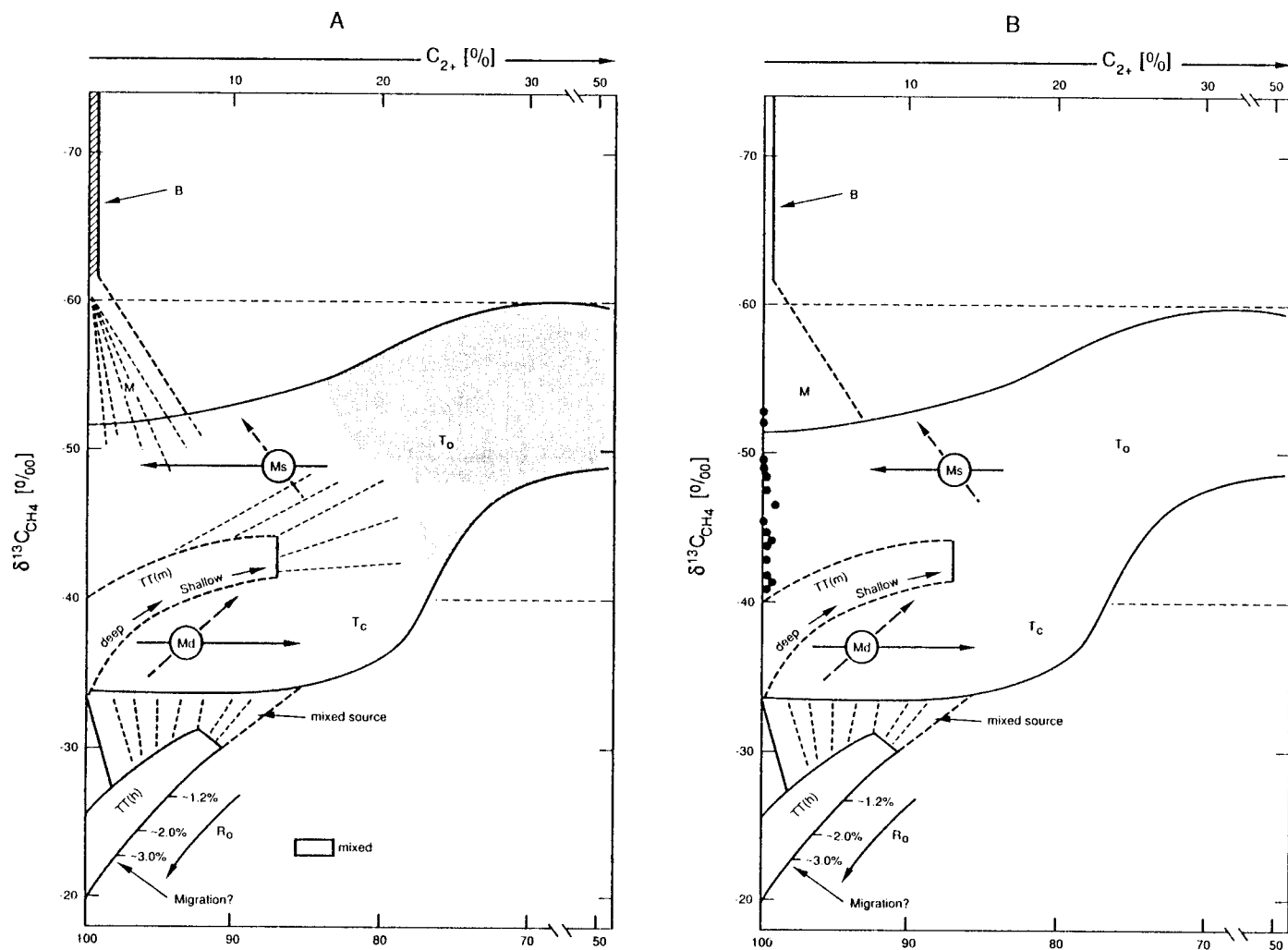


Figure 24. Plot of C_{2+} hydrocarbon concentration in gases in relation to δC^{13} of methane. a) Illustration of genetic fields as adapted from Schoell (1983). b) Compositional variations of Mist gases. Arrows M_s and M_d indicate compositional changes resulting from shallow and deep migration, respectively.

wet gas and/or oil accumulations have never been discovered in the Mist area (H. J. Meyer, personal communication, 1991; D. Wermiel, personal communication, 1991).

An important advancement in the field of natural gas characterization makes use of both the carbon and hydrogen isotopic composition of methane to define genetic origin (Schoell, 1983). These parameters are not only independent of gas compositional changes, but the use of hydrogen isotopes allows better discrimination between associated (condensate or oil) and non-associated (dry thermal) gases (Schoell, 1983). Figures 25a and 25b illustrate the natural gas genetic fields defined by $\delta^{13}\text{C}$ and δD isotopic correlations, as adopted from Schoell (1983), and where the Mist gases plot within these fields, respectively. Two genetic types of gas (mixed and thermogenic) are distinguished for Mist based on isotopic composition.

- 1). Mixed gases (M) at Mist are characterized by $\delta^{13}\text{C}$ values of their methane between -43.6 and -52.6‰ and δD values between -134 and -169‰. A much greater proportion of the Mist gases are characterized as "mixed" using $\delta^{13}\text{C}$ versus δD , in contrast to the $\delta^{13}\text{C}$ versus C_{2+} plot. Furthermore, two groups of "mixed" gas can be distinguished from Figure 25b. The first group (designated #1) is isotopically light with respect to carbon (-51.6 to -52.6‰). With the exception of the sample from well CZ 42-1 ($\delta\text{D} = -169$), this group is also characterized by a small δD range (-145 to -151‰). The second group of mixed gases (#2 in Figure 25b) covers a broader $\delta^{13}\text{C}$ range (-43.6 to -49.4‰) but has a δD distribution (-134 to -150‰) similar to group #1. This

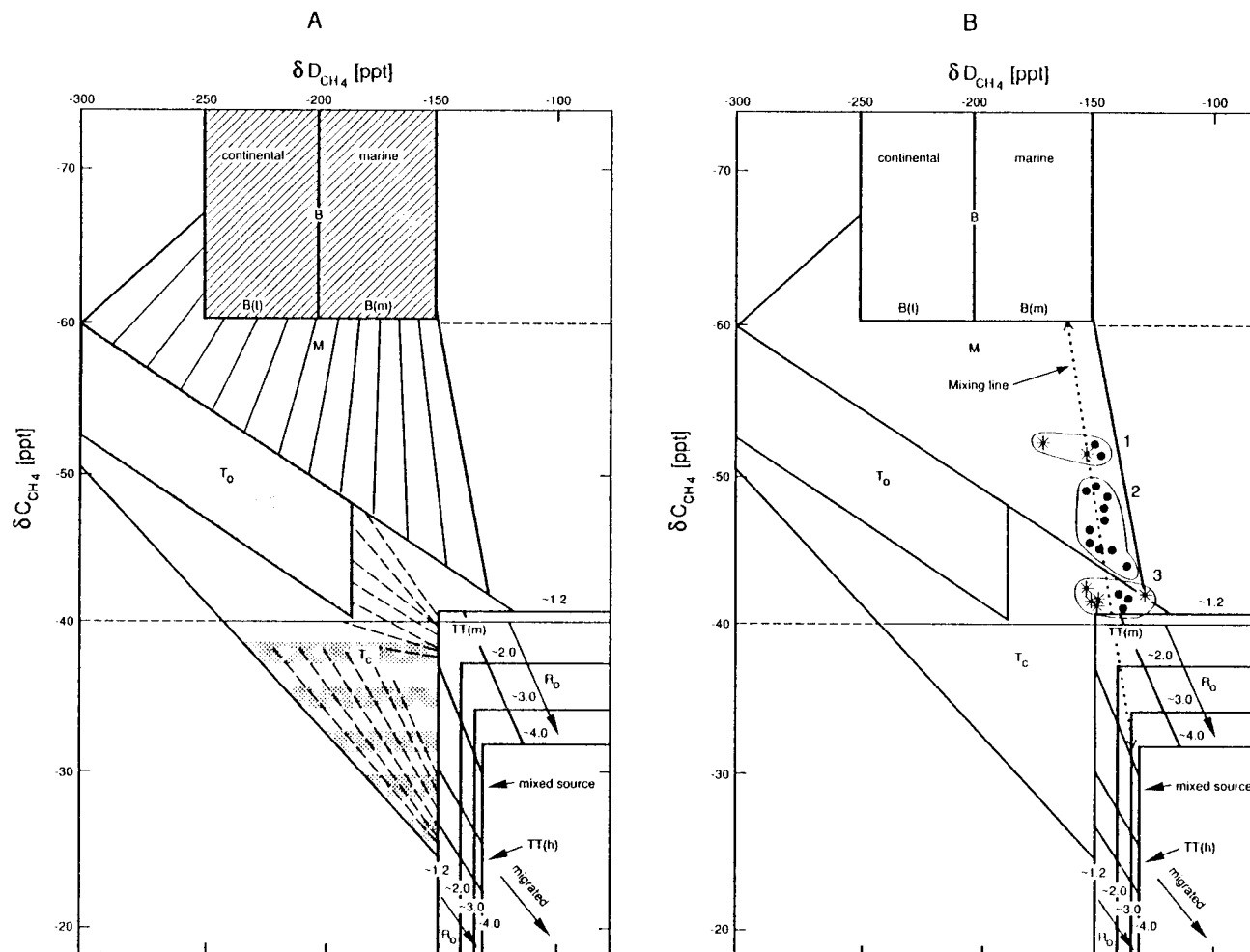


Figure 25. Variation of δD and $\delta^{13}C$ in methane of natural gases. a) Illustration of genetic fields as adapted from Schoell (1983). b) Isotopic variations of Mist gases (* = unpublished isotopic data, Rice et al.; • = isotopic data from samples collected as part of this study - see Table 11).

investigator suggests that both groups of "mixed" gases have been derived from mixing biogenic (B) and non-associated thermogenic (TT) gas, with the differences in isotopic composition due to mixing of different proportions of the two types of end member gases.

- 2). Thermogenic gases at Mist are genetically characterized as condensate associated gases (T_c) (gas group #3, Fig. 25b), according to Schoell's (1983) classification scheme. This investigator suggests that although the gases are thermally derived, they are in fact non-associated "dry" thermogenic gases (TT) which have the isotopic signature of a condensate associated gas (T_c) due to minor mixing with a biogenic component. This interpretation is based on the following evidence:
 - a). Source rocks in the deeper parts of the North Willamette Basin are mature enough to generate non-associated dry thermogenic gas ($R_o = 1.64\%$, Exxon GPE Fed. Com. #1 well - >10,000, 3048 m). It is generally agreed that the point where dry gas generation commences corresponds to vitrinite reflectance values greater than 1.2% (Schoell, 1983).
 - b). Mist gases are essentially devoid of C_{2+} hydrocarbons. Although secondary processes can account for this compositional signature, it must be remembered that condensate or oil associated gases have relatively high C_{2+} concentrations (2-10+%) compared to non-associated gases

(Schoell, 1980). It would be difficult to support a hypothesis that suggested stripping (removal) of essentially the total volume of C_{2+} hydrocarbons which would be found in a condensate-type environment, without their presence being noted elsewhere in the field. Furthermore, neither wet gas nor condensates have been documented in the Mist area with the exception of a few gas shows on mud logs (H. J. Meyer, personal communication, 1991; D. Wermiel, personal communication, 1991).

- c) The presence of genetically "mixed" gas in the field provides supportive evidence for this alternative explanation. Mixing a small amount of isotopically light biogenic gas with isotopically heavier non-associated thermogenic gas (TT_m or $TT_m - TT_h$ mixture) would result in an isotopic composition plotting just outside the non-associated field and in the lower corner of the condensate associated gas field (as shown by gas group #3 - Fig. 25b).

As mentioned earlier, secondary processes (migration, mixing) can alter both the original isotopic and compositional genetic signature of a gas. These various processes and resulting compositional variations have been evaluated by Schoell (1983). Secondary processes which are important with respect to Mist are migration and mixing.

Migration results in a depletion of the C_{2+} component of natural gases through a process of stripping or segregation along the migration path (Coleman et al., 1977; Schoell, 1983; Silverman, 1971). The arrows M_s in Figure 24 illustrate the expected change in both C_{2+} and $\delta^{13}C$ composition as a result of shallow migration. The solid horizontal arrow indicates the change expected only with migration, while the dashed arrow represents the expected change due to mixing of different genetic types of gas resulting from migration. Because isotopically the Mist gases are characterized as mixed or thermogenic, yet compositionally are similar to biogenic gases, a process such as migration with stripping must be operative which causes the loss of heavier gaseous hydrocarbons.

Mixing gases of different origin will result in changes to both the C_{2+} concentration and isotopic composition. Mixing non-associated (TT) thermogenic gas (with relatively low C_{2+}) with biogenic (B) gas, coupled with the affects of migration, could result in a natural gas dominated by methane. On the other hand, gases resulting from mixing associated thermogenic gas (T) and biogenic gas (B) almost always retain a noticeable C_{2+} component, although it may be much lower than the original associated end member concentration (Schoell, 1983; Mattavelli et al., 1983). Mixing also results in gases with isotopic compositions between the contributing end members (Schoell, 1983). At Mist a linear change from gas group 1 to 3 is evident for both $\delta^{13}C$ and δD with increased mixing (see Fig. 25b).

Because both biogenic and thermogenic gases contribute to the commercial viability of the Mist gas field, it is of interest to estimate the degree of mixing for each of the three gas groups identified in Figure 25b. This information can then be used to assess the relative importance of each genetic process to natural gas generation in the Mist field. $\delta^{13}\text{C}$ compositions were used for mixing calculations with the assumption that changes to the isotopic composition of the gas resulted primarily from mixing processes. A starting biogenic $\delta^{13}\text{C}$ end member composition of -67‰ was used. Because no pure biogenic gas has been identified at Mist, this value was determined by averaging $\delta^{13}\text{C}$ compositions of published biogenic gases from similar age gas fields (Schoell, 1980). For the thermogenic end member a $\delta^{13}\text{C}$ of -32‰ was used for the mixing calculations. This value was arrived at based on the following evidence:

- 1). Measured $\delta^{13}\text{C}$ values for kerogens and coals from this investigation average -26.2‰ for 15 samples (see Appendix B.3). This provides a lower limit for $\delta^{13}\text{C}$ values of thermogenic methane.
- 2). Experimental pyrolysis investigations indicate that methane cracked from kerogen and/or coal is initially depleted in ^{13}C relative to the starting material. With increasing maturation of the source material methane becomes progressively enriched in ^{13}C (Sackett et al., 1970; Sackett, 1978; Chung and Sackett, 1979). This increasing ^{13}C enrichment has also been observed in natural systems (Stahl, 1977; Stahl and Carey, 1975).

- 3) Equations for estimating $\delta^{13}\text{C}_{\text{CH}_4}$ based on source maturity have been developed for various types of source rocks (e.g., $\delta^{13}\text{C} = 14.8\log R_o - 41\text{‰}$ for marine organic matter; $\delta^{13}\text{C} = 8.6\log R_o - 28\text{‰}$ for terrestrial organic matter) (Schoell, 1980). Using an R_o of 1.64% (maximum average observed in this investigation), marine organic matter would yield methane with an initial $\delta^{13}\text{C}$ of -38‰ , whereas terrestrial organic matter would generate methane with a $\delta^{13}\text{C}$ of -26‰ . Because Mist source rocks contain a mixed marine-terrestrial organic matter assemblage, the above values were averaged yielding a $\delta^{13}\text{C}$ of -32‰ . This initial thermogenic end member value would fall in the mixed marine-terrestrial source field of Figure 25b. Additionally, there is good agreement between this calculated initial value and the initial $\delta^{13}\text{C}$ value obtained from drawing a best fit line through the observed isotopic values to the mixed source field on Figure 25b.

Results of mixing calculations are presented in Table 12. For the individual gases in each gas group, the mixing proportions of biogenic versus thermogenic gas have been averaged and are presented in Figure 26. It is obvious that a major portion of the gas produced from wells in gas groups 1 and 2 has been derived from microbially mediated processes (biogenic gas). On the other hand, gases in group 3 have been derived predominantly from thermal processes with only a 27% (average) biogenic contribution.

Table 12. Calculated mixing proportions of biogenic and thermogenic gas in the identified gas groups at Mist.

Gas Group and Well Name	Biogenic Gas (%)	Thermogenic Gas (%)
<u>Group 1 - Mixed:</u>		
CZ 23-15	58.3	41.7
CZ 12-1	56.0	44.0
CZ 42-1	58.1	41.9
CC 13-1	56.3	43.7
<u>Group 2 - Mixed:</u>		
CC 32-32	42.8	57.2
CZ 31-16	49.7	50.3
CC 43-27	48.0	52.0
CC 41-28	49.4	50.6
CC 44-21	45.4	54.6
CC 43-22	37.1	62.9
CC 23-22	38.0	62.0
Busch 14-15	40.6	59.4
LF 12-33	36.9	63.1
CC 13-34	33.1	66.9
<u>Group 3 - Thermogenic:</u>		
CC 3	25.3	74.7
CC 6-RD2	26.3	73.7
CC 33-3	28.2	71.8
CC 4	29.4	70.6
CC 1-RD	26.4	73.6

Mixing proportions were calculated using the following equations:

$$(X)(-67\text{‰}) + (Y)(-32\text{‰}) = Z \quad \text{and} \quad X + Y = 1$$

where X = % biogenic contribution

Y = % thermogenic contribution

Z = $\delta^{13}\text{C}$ composition of the specific sample

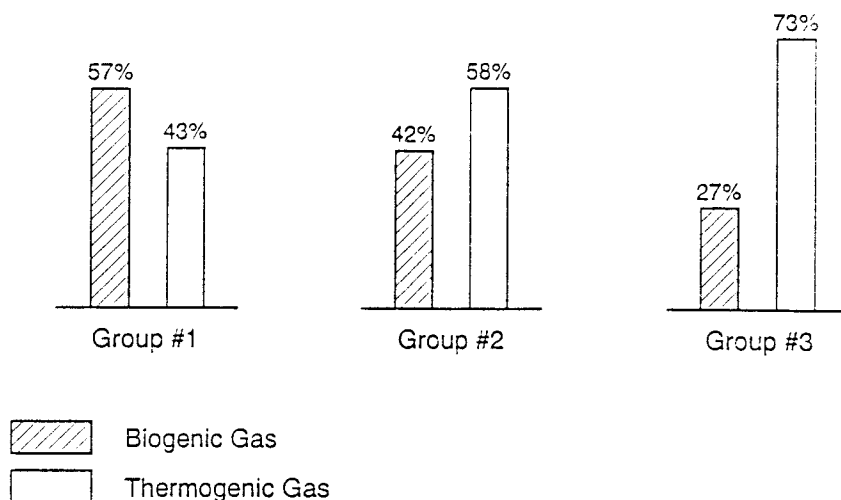


Figure 26. Histograms showing average mixing proportions of the three gas groups at Mist.

The interpretation that Mist gases contain a major proportion of biogenically derived methane, genetically manifested as mixed gas, is a marked deviation from existing interpretations (unpublished industry interpretations, H. J. Meyer, written communication, 1987). However, it should be pointed out that some of these interpretations, which characterized the Mist gases as thermogenic, were based on a limited number of samples collected from the same wells/reservoirs (e.g., CC-3, CC-6, etc.) that this investigator classifies as being of thermal origin (see gas group 3, Fig. 25 and Table 12). Other unpublished data (Rice et al.) showed a distinct isotopic variation between wells (see Table 11). The early interpretations either did not cover a sufficient number of wells to notice the variances in isotopic composition or did not recognize the significance of the variations. The importance of the interpretation presented here is that for provinces where gas potential appears

limited, based on source rock geochemistry, may in fact be commercially viable due to biologically mediated processes being operative.

Before leaving the subject of natural gas genetic origin, alternative gas generative mechanisms or sources need to be evaluated. Alternatives which have received sufficient attention to warrant consideration are 1) that thermogenic gas generation has been accelerated by the heat derived from igneous intrusions or magmatic activity, and 2) coal deposits are contributing to or are the sources of the Mist gases.

The heat derived from igneous intrusive bodies (e.g., sills) can have profound effects on the maturity of sedimentary organic matter in the vicinity of the contact zone (Schoell, 1982; Simoneit et al., 1981, 1984; Niem and Niem, 1985). These effects have been documented in the Astoria Basin (see Fig. 14) and given the geologic history of N.W. Oregon it is reasonable to assume that similar events may have occurred in the North Willamette Basin. With regard to igneous intrusions such as sills, most documented cases show that significant thermal influence on the sedimentary organic matter is limited to a relatively short distance away from the contact zone (Simoneit et al., 1981, 1984). However, it has also been reported that the thermal effects of intrusions may extend a fair distance away (up to 1500 ft or 457 m) from the contact zone (Safley, 1989; Niem and Niem, 1985).

On the other hand, the influx of heat derived from igneous activity in general may have helped accelerate the maturation process in N.W. Oregon over and above that of normal burial. As discussed earlier, vitrinite reflectance values for the Hamlet-Yamhill fm. in the North Willamette Basin show a gradual increase down to approximately 9,000 ft (2,743 m). Below this depth organic matter maturity shows a dramatic increase well into the catagenetic stage of hydrocarbon generation. Additionally, the presence of igneous intrusives and volcanic sequences (e.g., Cole Mtn. basalts, Goble Volcanics, and Tillamook Volcanics) in N.W. Oregon, emplaced prior to or contemporaneous with Hamlet-Yamhill and Cowlitz strata, might lend support to such a theory. Indeed, over 3000 ft (900 m) of basalt flows and possible Goble/Cole Mtn. intrusives were encountered in the Exxon GPE Federal well (Niem et al., 1991) above and into Cowlitz sandstone and mudstone strata. The presence of these upper Eocene volcanics in the Exxon GPE Federal well lends support to the possibility of an overall higher geothermal gradient in the deeper parts of the North Willamette Basin. Additionally, Safley (1989) found elevated vitrinite reflectance values (in the oil and dry gas range) in the Hamlet fm. 100's of meters away from an adjacent 300 m thick gabbroic sill in S.W. Clatsop County. An excellent example of a mixed biogenic-thermogenic gas, where the thermogenic component has been derived from igneous intrusive activity, is presented by Schoell (1982, 1983) for the Gulf of California. The resulting mixed gas has an isotopic signature (e.g., $\delta^{13}\text{C} \approx -53$ to -55‰ , and $\delta\text{D} \approx -160$ to -165‰) very similar to that represented by gas group #1 at Mist.

The possibility that coal has sourced at least some of the Mist gas is an intriguing alternative. There is increasing subsurface and surface evidence that coal layers in the Cowlitz deltaic sandstone facies are more abundant and widespread in N.W. Oregon than first thought (Berkman, 1990; Farr, 1989; Niem et al., 1991; A. R. Niem, personal communication, 1991). This alternative is appealing because despite the fact that disseminated sedimentary organic matter in the Mist area is of the right type and maturity to source dry thermogenic gas, it has only limited generative capacity (see Fig. 20-22). Based on the C&W coal samples analyzed for this investigation, as well as data presented by Armentrout and Suek (1985) for coals in S.W. Washington, generative potential is not a limiting factor for coals. The problem that arises is that published geochemical data on coal in the Mist area currently does not exist. The limited data from this investigation show that the coals are immature ($R_o = 0.36\%$) and thus probably not capable of generating significant thermal gas. It is thought that the majority of methane generated in coals begins in the vitrinite reflectance range of 1.3 to 1.4% (Tissot and Welte, 1984). If higher rank deposits exist in the deeper parts of the North Willamette Basin, where vitrinite reflectance values as high as 1.64% have been recorded for type III kerogens, thermal gas generation from coal would certainly be possible. It should be noted that non-marine strata containing coal and carbonaceous mudstone were penetrated in the Cowlitz Formation in the Exxon GPE Federal well (A. R. Niem, personal communication, 1991). Furthermore, Walsh and Lingley (1991) show that lignitic to subbituminous B & C coals exist in the type Cowlitz Fm. in S.W. Washington. They also point out that many coals in the Puget Group from the Puget Basin of western

Washington are higher rank and could be gas sources due to heating by the Oligocene-early Miocene igneous granodiorite plutons of the Washington Cascades.

In addition to the lack of geochemical data on coal deposits is the fact that available natural gas genetic classification schemes do not distinguish between disseminated terrestrial organic matter (type III kerogen) and massive terrestrial organic matter (coal). The ability to make such a distinction is generally based on available geologic and source rock geochemical data. For example, it is generally agreed that natural gases of N.W. Germany are sourced from Carboniferous coal measures (Schoell, 1983; Stahl et al., 1977). However, this interpretation is based to a large extent on the fact that the rank (maturity) of the coal is sufficient to source gas. The isotopic signature of those natural gases was previously thought to be representative of coal-derived gases (e.g., $\delta^{13}\text{C} = -24$ to -30‰ , $\delta\text{D} = -170$ to -120‰) (Schoell, 1980, 1983). However, more recent data from other coal-derived natural gases (e.g., San Juan Basin) show that a wider isotopic range is possible (Schoell, 1983).

Source rock maturation data from this investigation (e.g., Exxon GPE Federal well) show that disseminated sedimentary organic matter in the North Willamette Basin is capable of generating dry thermogenic gas. It is also possible that coals in the Mist area could have contributed to the gas accumulations. However, a systematic geologic and geochemical evaluation of the coals is needed to provide concrete evidence for this hypothesis.

What must be remembered about both alternatives is that they only have potential application to thermogenic gas generation. Whether the mechanism or source of thermogenic gas at Mist is disseminated organic matter in the mudstones and sandstones, coal deposits, or that both have been influenced by igneous processes does not minimize the importance of the interpreted biogenic gas contribution to the field.

Migration Considerations

There is compelling evidence for gas migration at Mist. Mixed gas with a predominant thermogenic component has accumulated in some of the shallow Cowlitz sandstone (C&W) reservoirs near the Nehalem arch where organic matter in the surrounding mudstones is immature and incapable of generating this type of gas (see Fig. 27, gas group 3). Based on source rock maturation data from this investigation, mature source rocks capable of generating thermogenic gas are located approximately 10-15 miles (16-24 km) east and southeast of these reservoirs. Figure 27 illustrates the distribution of gas groups 1, 2, and 3 in the Mist area, potential migration paths of the thermogenic gas, and the general location of mature source rocks (e.g., designated by the Exxon GPE Federal Commission #1 well). Biogenic gas (gas group 1) is most abundant in the northeastern and southeastern most parts of the field. Thermogenic gas (gas group 3) is most abundant in the center of the field and approximately equal mixtures of biogenic and thermogenic gas are found in reservoirs in the northwestern and southwestern parts of the field.

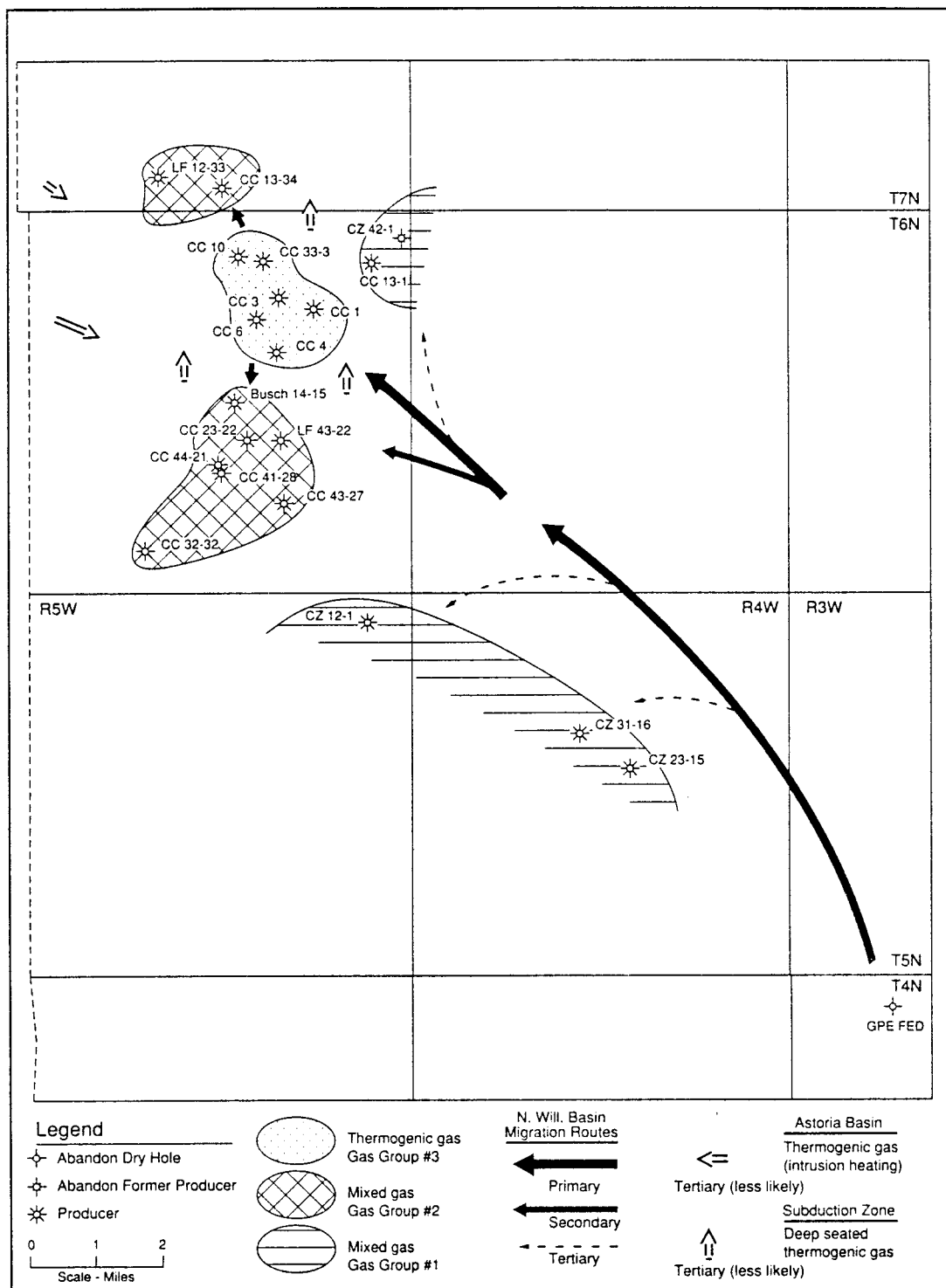


Figure 27. Distribution of gas groups in the Mist field and potential gas migration routes.

When considering the distribution of gas types with respect to mature source areas it is obvious that preferential migration routes exist. This is supported by the fact that producing wells/reservoirs closest to mature source strata have the lowest percentage of thermogenic gas (e.g., only 42% for well CZ 23-15, see Table 12, Fig. 27). On the other hand, thermogenic gas accounts for approximately 73% of the gas in reservoirs tapped by wells such as CC 3, CC 6, CC 33-3, and CC 1 (see Fig. 27).

The data suggest that along the primary migration route (see Fig. 27) a fairly direct, unimpeded pathway exists for migration to reservoirs now containing predominantly thermogenic gas. It is interesting to note that between the area of mature source strata and the reservoirs of gas group #3, directly along the depicted primary route, approximately 26 dry wells and only 4 producing wells have been drilled (Oregon Department of Geology and Mineral Industries, 1991).

Secondary and even tertiary migration routes (see Fig. 27) are also postulated to account for various degrees of mixing, especially in light of the relative proximity of gas group 1 to mature source areas. It is possible that migration along the secondary and tertiary routes was restricted or impeded due to formational properties (localized variations in porosity and permeability) as well as fault-controlled mechanisms.

Niem et al. (1990, 1991) show that the Mist gas field is located on the east flank of the Nehalem arch and that a large NW-SE trending graben cuts obliquely across the arch, extending possibly from the Exxon GPE Federal well to the center of

the field (to gas group 3). The graben represents a fault migration pathway in the Cowlitz sandstone for thermogenic gases, either in solution or as a separate gas phase, to the center of the field. The timing of the faulting is not clear, but many faults cut the Cowlitz C&W sandstone and Cowlitz mudstone and are terminated by the late Eocene unconformity of the overlying Keasey Fm. (Refugian) as suggested by seismic and well data (Alger, 1985; Bruer et al., 1984). Many normal faults were reactivated during the late Miocene as oblique-slip, right and left lateral conjugate faults. It may have been that biogenic gas was formed in the broad Nehalem anticlinal fold soon after burial of the Hamlet and Cowlitz strata in a compressional stress regime. The Nehalem arch was forming and biogenic methane would have been widespread throughout the North Willamette and Astoria Basins, with subsequent migration towards the highest part of the Eocene arch. Then during a period of late Eocene extension the NW-SE trending Nehalem or Boomer Graben was formed, perhaps simultaneously with thermal heating by sills and dikes and a higher geothermal heat gradient associated with the Goble Volcanics encountered in the Exxon well. Such thermal events, along with simple basin subsidence and burial, could have given rise to the production of thermogenic gas which then migrated up the graben to the northwest. Alternatively, Armentrout and Suek (1985) suggested that simple sediment basin accumulation and downwarping would have put the Hamlet-Yamhill fm. in the hydrocarbon generation window about 33 Ma. Thus migration of generated gas could have occurred in Oligocene time. Yet another alternative is that middle Miocene "invasive" intrusions of Columbia River Basalt in the Astoria Basin could be a heat source for thermogenic gas generation at Mist

(Niem and Niem, 1985). This gas would have migrated from the northwest to the southeast (see Fig. 27), but a lack of Cowlitz sandstone in this basin precludes much of a migration path.

Recently, Niem et al. (1990, 1991) show in offshore seismic profiles that highly deformed upper Eocene to Miocene accreted strata were underplated in thrust faults beneath the offshore Astoria Basin only several kilometers off Astoria and Cannon Beach, Oregon. These subducted deep-marine strata are exposed along the west side of the Olympic Peninsula where they consist of highly deformed thrust faulted melange mudstone and sandstone and broken formation mudstone and sandstone (Hoh melange and broken formation, and Ozette melange and broken formation of Snively and Kvenvolden, 1989). These onshore strata, particularly near thrust faults, are thermally mature and give rise to thermogenic gas seeps and oil seeps (probably sourced in the middle to upper Eocene Ozette melange) along the central and northwest Washington coast (Kvenvolden et al., 1989). Snively and Kvenvolden (1989), and Snively (1987) suggest that the underplated melange and broken formation could give rise to the thermogenic gas seeps observed in the overlying forearc or marginal basin strata via deep seated faults. Snively (personal communication to A. R. Niem, 1990, 1991) suggests that a similar mechanism could apply for the thermogenic gases in the Mist field via deep seated Nehalem Graben faults cutting down through the Tillamook Volcanics and Siletz River Volcanics to the presumed underthrust upper Eocene to Miocene melange and broken formation below. This is a third avenue of migration (from directly below the field).

However, when comparing the isotopic composition of these subduction zone thermogenic gases with Mist data, there are very noticeable differences (compare Table 13 with Table 11) in isotopic character. Kvenvolden et al. (1989) suggested, as is proposed for Mist, that the lack of C_{2+} hydrocarbons in these seeps is due to stripping of the higher molecular weight hydrocarbons during migration. The carbon isotopic data presented for the Garfield and Sol Duc gas seeps are characteristic of thermogenic gas (isotopically much heavier than Mist). It is also unlikely that subduction zone gas could have migrated up faults through several kilometers of Siletz River Volcanics and Tillamook Volcanics. The deeply buried Yamhill mudstones below the Tillamook Volcanics could also be a gas source (Wells et al., 1983). However, no maturation data is presently available on this unit although it appears to be immature (A. R. Niem, personal communication, 1991).

Table 13. Analyses of hydrocarbon gases from natural gas seeps, Olympic Peninsula, Washington (From Kvenvolden et al., 1989).

Gas Seep	CH ₄ (%)	C ₂₊ (%)	δ ¹³ C _{CH₄} (‰)	δD (‰)
Garfield gas mound	99.9+	.0069	-34.5	-177
	99.9+	.0073	-34.8	-196
Sol Duc Hot Springs gas seep	99.9+	.051	-36.5	-174

It was initially thought that evidence for gas migration at Mist might be substantiated by evaluating stable isotope fractionation. However, outside of a small

number of cases where fractionation appears to have resulted from migration, this process is not believed to occur to an appreciable extent (Schoell, 1983, 1984b; Fuex, 1980; Stahl et al., 1977). In addition, isotopic changes resulting from mixing of different genetic gases at Mist serves to mask any fractionation changes that might have occurred as a result of the migration process.

NITROGEN

Observed Spatial Trend of Methane and Nitrogen

Variances in reservoir gas composition due to changing methane and nitrogen concentrations are a definite concern with respect to the continued economic viability and exploration focus at Mist. Current exploration efforts are directed toward the east and southeast away from the main Mist field. Reservoir gas compositions show a general systematic change in the same direction. In a general west to east direction gas compositions show a decrease in methane concentration (98 to 49%) and a corresponding increase in the "contaminant" nitrogen concentration. Figure 28 illustrates this relationship.

Several hypotheses have been suggested in an attempt to explain the observed spatial trend (H. J. Meyer, personal communication, 1986, 1991). Source rock geochemical data suggest that the most likely source of at least some of the thermogenic gas is from the deeper parts of the North Willamette Basin, with subsequent migration updip to the Mist field reservoirs to the northwest (see Fig. 27). Assuming this holds true, then one or both of the following scenarios may be valid in explaining the observed trend.

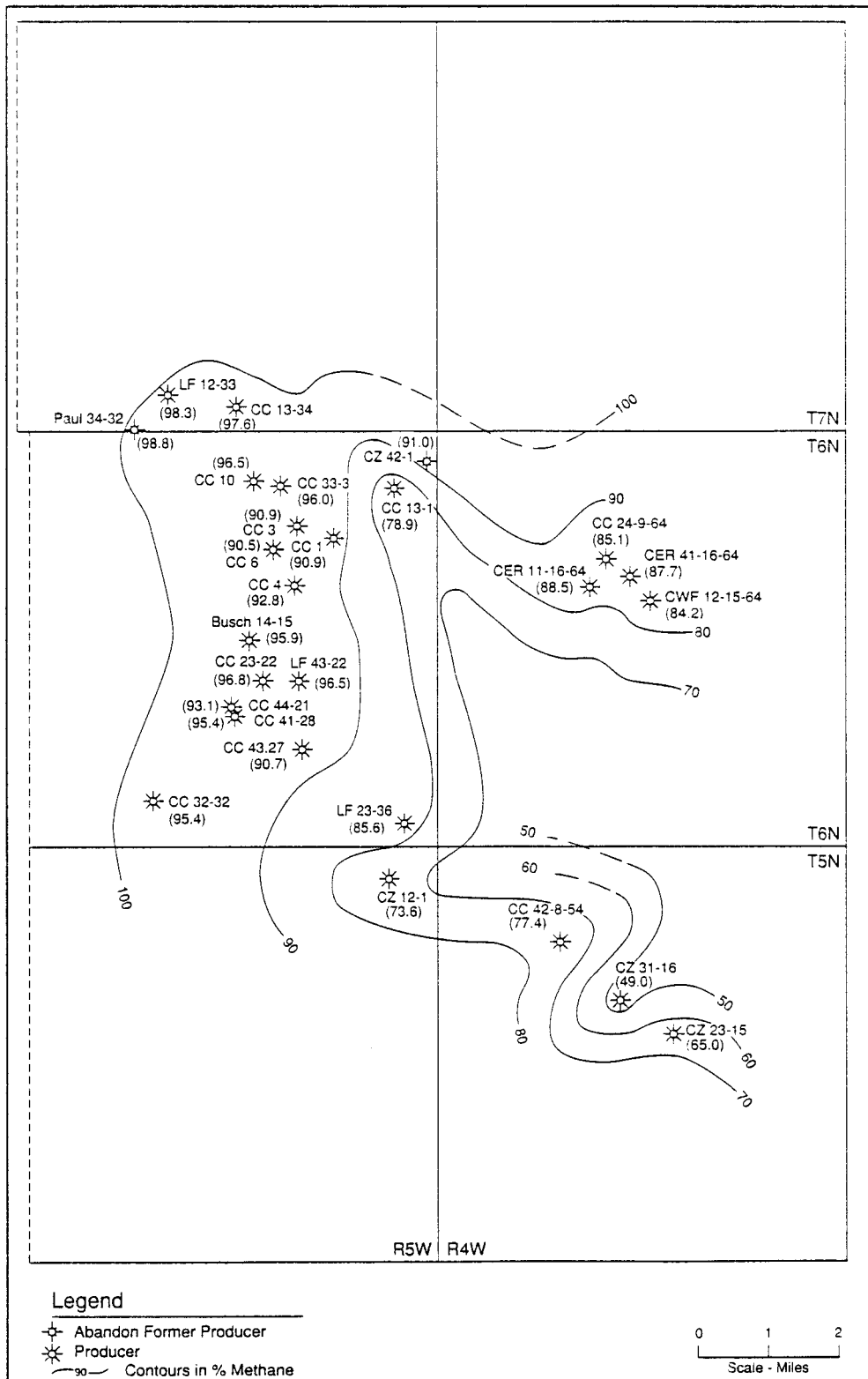


Figure 28. Contour map showing methane concentration (% methane) variability of reservoir gas.

1. Nitrogen has also been generated with methane in the deeper parts of the North Willamette Basin and has migrated updip in much the same manner as the methane.
2. Nitrogen has been generated over the whole area (e.g., in the Mist field and basinward) (H. J. Meyer, personal communication, 1986). Migration, if it has occurred, has been much shorter in distance than in (1) and has resulted in more of a "pooling effect".

From the observed spatial trend of methane and nitrogen concentrations it is obvious that whatever the mechanism or source of nitrogen, both generation and greatest accumulation have occurred east and southeast of the Mist field (e.g., in T5N, R4W and T6N, R4W - Fig. 28). Whether this also corresponds to generation in the deeper parts of the North Willamette Basin (e.g., both vertical and lateral migration) depends upon the mechanism invoked for generation (see following section on source evaluation).

Source Evaluation

Nitrogen generally constitutes a minor component (1 to <10%) in most natural gases, and there is some evidence from both experimental studies and natural systems which suggests that it is generated along with methane and other hydrocarbon gases during thermal maturation of sedimentary organic matter (Jenden et al., 1988; Stahl

et al., 1977; Klein and Juntgen, 1972). However, there are numerous examples of natural gases in the literature where nitrogen constitutes a major component of the gas (e.g., Sacramento basin - up to 87% N₂, N.W. German coal-derived gases - up to 82% N₂, Dutch natural gas - up to 15% N₂, etc.) (Jenden and Kaplan, 1989; Jenden et al., 1988; Stahl et al., 1977; Bokhoven and Theeuwes, 1966). Additionally, in a survey of over 12,000 natural gases the U.S. Bureau of Mines (1983) found that 10% of U.S. gases contained $\geq 25\%$ nitrogen.

Despite the fact that nitrogen can be a significant, if not economically limiting component in many natural gases, no systematic published study has been carried out in an attempt to elucidate its origin or source(s). Experimental work by Klein and Juntgen (1972) and Rohrback et al. (1983) has shown that nitrogen is released during pyrolysis of sedimentary organic matter. Activation energies required for nitrogen generation range from 40 to 70 kcal mol⁻¹ (Klein and Juntgen, 1972). This might support the suggestion that overmature organic matter may yield a greater proportion of nitrogen to methane than less mature organic matter (Lutz et al., 1975; Tissot and Welte, 1984). Additional evidence suggesting that sedimentary organic matter is a principal source of nitrogen in natural gas comes from both analyzed nitrogen concentrations of various rock types and the correlation of organic geochemical parameters with nitrogen concentration (e.g., vitrinite reflectance, fixed carbon content of coal, $\delta^{13}\text{C}_{\text{CH}_4}$) (Deines, 1980; Stahl et al., 1977; Lutz et al., 1975; Tissot and Welte, 1984). Fine-grained sedimentary rocks and coals contain an order of magnitude, or more, nitrogen than other rock types (Baur and Wlotzka, 1972; Faure,

1986). Also, atomic C/N ratios in kerogen and coal are found to increase with increasing organic matter maturation (Tissot and Welte, 1984; Waples, 1977).

However, because of the pervasiveness of nitrogen in most natural systems (e.g., geosphere, atmosphere, etc.), there are other potentially significant sources of nitrogen that must be considered. Metamorphic and igneous (generally silicic types) rocks have been cited as potential nitrogen sources (Baur and Wlotzka, 1972; Beebe and Curtis, 1968; Haendel et al., 1986). Nitrogen in metamorphic rocks occurs as ammonium bound within silicate minerals (e.g., micas, K-feldspar, plagioclase) (Stevenson, 1959, 1962; Haendel et al., 1986; Honma and Itihara, 1981). With increasing metamorphic grade nitrogen content in the rock shows a fairly systematic decrease (Haendel et al., 1986). The same general trend was also noted in areas of contact metamorphism, where nitrogen concentration decreases toward the contact zone (Haendel et al., 1986). Although igneous rocks contain less nitrogen than metamorphic rocks (Baur & Wlotzka, 1972; Faure, 1986), they still represent a potential source of nitrogen. In some gas-producing regions the concentration of nitrogen increases with proximity to basement rocks (Headlee, 1962; Beebe and Curtis, 1968). Perhaps more important is the role of igneous processes in mediating volatile degassing of the mantle. It has been estimated that the mantle contains an order of magnitude more nitrogen than the crust, atmosphere, and hydrosphere combined (Jenden et al., 1988; Baur and Wlotzka, 1972; Krauskopf, 1959; Mason, 1952). One last source of nitrogen that should always be evaluated when considering high-nitrogen natural gases is the possibility that atmospheric nitrogen has been

either trapped or introduced into the formation (e.g., paleo air, meteoric water), or introduced during the sample collection process (e.g., sample contamination).

The preceding discussion is intended to illustrate that a wide variety of sources may potentially contribute nitrogen to natural gas deposits. In most cases, a number of these sources can be eliminated from consideration based on regional or site-specific geologic information. Additionally, parameters such as N_2/Ar , $^3He/^4He$, and $\delta^{15}N$ may be used to further constrain the number of potential sources.

The source(s) of nitrogen in the natural gases at Mist can be evaluated on the basis of the geology of N.W. Oregon and by comparing nitrogen parameter measurements for Mist gases (Table 14) with those of other sources (Table 15). For this investigation gas samples from 15 wells were collected by this investigator during the Fall of 1986 and subsequently submitted to Coastal Science Laboratories, Inc. in Austin, Texas for $^{15}N/^{14}N$ isotopic analysis. The results of these analyses are presented in Table 14 along with available N_2 and N_2/Ar data. As discussed earlier, nitrogen concentrations in Mist gases range from approximately 1 to 51% (see Table 10). Low-nitrogen and high-thermogenic methane gas mixtures are found in the western part of the field near the Nehalem arch. High-nitrogen and high-biogenic methane gas mixtures are found east and southeast of the Mist field proper. This distribution corresponds to lower nitrogen concentrations at the northwestern margin of the North Willamette Basin, with higher concentrations basinward (see Fig. 28).

Table 14. $\delta^{15}\text{N}$, N_2 and N_2/Ar measurements for Mist gases.

Well Name	$\delta^{15}\text{N}^{\text{A}}$ (‰)	N_2^{B} (%)	$\text{N}_2/\text{Ar}^{\text{C}}$
LF 12-33	-0.1	1.7	----
CC 13-34	-0.1	2.4	----
CC 33-3	+0.1	4.0	----
CC 3-RD	-3.4	9.0	1014
CC 6-RD2	-2.4, -2.7	6.9	----
Busch 14-15	-0.6	4.1	----
CC 23-22	+1.5	3.2	----
CC 43-22	----	3.5	----
CC 44-21	-4.5, -4.6	6.9	----
CC 41-28	+0.9	4.6	----
CC 43-27	-3.0	9.3	----
CZ 31-16	+0.7	51.0	----
CZ 23-15	-1.1	35.0	----
CC 32-32	-0.5, -0.7	4.4	----
CZ 12-1	-0.7, -0.7	26.4	----
CC 4	----	7.2	433
CC 10	----	3.5	468
CC 1	----	9.1	1001

^A Samples collected as part of this investigation. Analysis by Coastal Science Laboratories, Inc., Austin, Texas (Feb.-Mar. 1987). Accuracy = $\pm 0.2\text{‰}$

^B Data provided by W. T. Amies, Northwest Natural Gas, Co., Portland, Oregon. Also see Table 10 - this report.

^C Unpublished data - provided by H. J. Meyer, Northwest Natural Gas, Co., Portland, Oregon.

Wells CC-4 and CC-10 were "shut-in" at the time of N_2/Ar analysis.

Table 15. N_2/Ar , $\delta^{15}N$, and N_2 values for various nitrogen sources.

NITROGEN SOURCE	N_2/Ar^A	$\delta^{15}N^B$ (‰)	N_2^C (ppm)	REFERENCE
Atmosphere	40-80 40-120	---- ----	---- ----	Jenden et al. (1988) Mason (1952)
Igneous Rocks	----	-10 to +15, avg. +5	----	^B Baur & Wlotzka (1972) Sakai et al. (1984)
• submarine basalt glass	----	avg. +0.2		Becker (1977)
• basalts & ultramafics	----	+17	14-30	^C Baur & Wlotzka (1972)
Volcanic Gases	40-300	----	----	^A Matsuo et al. (1978)
• Island Arc (Japan, New Zealand)	40-2600	----	----	
• Hawaiian Isl.	<(40-300)	----	----	
Mantle	est. 12	est. +1.3	10%	^A Matsuo et al. (1978) ^B Wetzel & Winkler (1979) ^C Krauskopf (1959)
Sedimentary Rocks				
• marine sediments	----	avg. +6-8	1772	^B Wada et al. (1975)
• shale	----	----	600	^C Baur & Wlotzka (1972)
• sandstone	----	----	120	
Sedimentary Organic Matter	----	-3 to +13	----	Stiehl & Lehmann (1980) Sweeney et al. (1978)
Natural Gas	Variable	-15 to +18	Up to 90% by volume	^B Hoering & Moore (1958) Muller et al. (1976) Stahl et al. (1977) ^C Baur & Wlotzka (1972)
Coal	----	-2.5 to +6.3 +0.3 to +3.7	2000-30,000	^B Dreschler & Stiehl (1977) Stiehl & Lehmann (1980) ^C Baur & Wlotzka (1972)
Humic Acid	----	0 to +3	----	Sweeney et al. (1978)

From a geologic point of view a metamorphic source of nitrogen can be ruled out due to the absence of metamorphic rocks in the Mist area (Alger, 1985; Niem et al., 1990, 1991; Bruer et al., 1984). Thermal contact metamorphic type effects resulting from igneous or magmatic activity can however be considered as a possible heat source component in discussions of potential nitrogen generation during thermal maturation of sedimentary organic matter. Atmospheric nitrogen can also be eliminated from consideration on the basis of N_2/Ar measurements (H. J. Meyer, written communication, 1987). Atmospheric N_2/Ar ratios fall in the range of the 40-120 (Jenden et al., 1988; Mason, 1952), whereas values for Mist gases fall in the range of 400 to >1000.

Whether or not an igneous or mantle source can be ruled out on the basis of N_2/Ar ratios is questionable. While most volcanic gases have N_2/Ar ratios between 40 and 300, lower values have been measured for the Hawaiian islands and ratios as high as 2600 have been recorded in island arc settings (e.g., New Zealand and Japan) (Jenden et al., 1988; Matsuo et al., 1978). Low N_2/Ar ratios from the Hawaiian islands may reflect a deep mantle source, for which Matsuo et al. (1978) estimated a ratio of approximately 12. Evidence supporting a mantle source for the Hawaiian islands comes from the fact that $^3He/^4He$ ratios in Hawaiian basalts and basaltic glass are elevated (5 to 30 times the atmospheric value, $R_A = 1.4 \times 10^{-6}$) with respect to $^3He/^4He$ measurements recorded for crustal sources ($\approx 0.02 R_A$) (Poreda et al., 1986; Jenden et al., 1988; Lupton, 1983; Craig and Lupton, 1976). The island arc N_2/Ar

ratios may actually reflect a nitrogen contribution from sedimentary organic matter in the crust (Jenden et al., 1988).

With respect to nitrogen source and N_2/Ar data, the Mist area is somewhat similar to the island arc system. Northwest Oregon has been characterized by igneous and magmatic activity as well as moderate sediment accumulation (Niem and Niem, 1985; Wells et al., 1984; Rarey, 1986; Mumford, 1988). The Goble Volcanics and Cole Mtn. Volcanics in Clatsop County and in the Exxon well in Columbia County have calc-alkaline affinities to the Western Cascades (Rarey, 1986; Mumford, 1988). Additionally, N_2/Ar ratios calculated for Mist gases are in the same general range as those observed in island arcs.

A nitrogen source from sedimentary organic matter is possible using the same maturation mechanism proposed for the generation of thermogenic methane gas at Mist -- maturation by burial, accelerated by the heat derived from igneous intrusive and extrusive activity either directly or, more likely, due to a resultant higher geothermal gradient. This is supported by the following evidence:

- 1). Elevated N_2/Ar ratios preclude an atmospheric nitrogen source.

Furthermore, the highest N_2/Ar ratios observed in the Mist gases (e.g., >1000) were calculated from gas analyses from wells interpreted by this investigator as tapping predominantly thermogenic gas reservoirs (e.g., CC-3, CC-6).

- 2). $\delta^{15}\text{N}$ data fall in the general range observed for sedimentary organic matter and coal deposits (compare Table 14 with Table 15). The depletion of ^{15}N in some of the samples may be the result of preferential fractionation of ^{14}N over ^{15}N during maturation and nitrogen release. Alternatively, $\delta^{15}\text{N}$ data may be a reflection of the isotopic ratio of the precursor material (Rigby and Batts, 1986).

- 3). Igneous rocks generally have $\delta^{15}\text{N}$ values that are positive (average $\sim +4.2\text{‰}$), although negative values have also been recorded (Wetzel and Winkler, 1979; Sakai et al., 1984). The Mist gases are depleted by 2.7 to 8.7‰ with respect to the average $\delta^{15}\text{N}$ in igneous rocks (Mist gases have a $\delta^{15}\text{N}$ range from -4.5 to +1.5‰). Although possibly accelerating the maturation and generation process, igneous activity does not appear to be contributing nitrogen to the system. In other words, igneous processes may be part of the maturation mechanism but are not direct sources of nitrogen.

- 4). $^3\text{He}/^4\text{He}$ ratios from Mist gases (G. J. Stormberg unpublished data) range from 0.64 to 0.75 R_A suggesting a mantle component in the gases. This is not meant to imply that the mantle is sourcing the nitrogen of the Mist field, but rather provides a source of heat for accelerating organic matter maturation (Poreda et al., 1988).

Although the above evidence suggests that thermally mature sedimentary organic matter is the source of nitrogen in the Mist gases, it is obvious that the nitrogen data are not very diagnostic with respect to source selection. It is assumed that N_2/Ar ratios are representative of all Mist gases. Unfortunately, Ar is not routinely analyzed for during gas composition analysis. As a result, no N_2/Ar ratios are available for reservoirs producing genetically mixed gas with a significant biogenic component. The thermogenic gases for which N_2/Ar data was available are low-nitrogen gases (e.g., nitrogen constitutes a minor component; <10%). Furthermore, the distribution of $\delta^{15}N$ values is fairly random and does not provide a diagnostic indicator of either source or migration as was the case with $\delta^{13}C$ values for the methane gas component. There is some evidence from other natural gas deposits which suggests that natural gas $\delta^{15}N$ values increase with increasing source rock maturity (Stahl et al., 1977). However, this trend was not seen at Mist where both $\delta^{15}N$ -enriched and $\delta^{15}N$ -depleted isotopic ratios are found in all three of the identified gas groups.

It is obvious that additional work needs to be carried out if the question of nitrogen variability in the Mist reservoirs is to be understood fully. H. J. Meyer (personal communication, 1986, 1991) suggested that increased nitrogen concentrations in reservoirs southeast and northeast of the main Mist field may be due to differential diffusion between nitrogen and methane. This alternative assumes 1) that both nitrogen (in the form of ammonia) and methane are derived from the thermal maturation of sedimentary organic matter and/or coal by deep burial and the

thermal effects of igneous (intrusive) activity, and 2) dissolved nitrogen (as soluble ammonia) is expelled from the source rock and migrates soon after generation, while methane initially remains adsorbed on the coal and kerogen. It is thought that the ammonia reacts during migration to form much of the nitrogen (N_2) gas, which subsequently accumulates in available reservoirs. With increasing thermal stress adsorbed methane is released and because of its greater diffusion rate, overtakes migrating nitrogen (N_2) to accumulate in reservoirs in the northwest part of the field.

A second alternative, favored by this investigator, is that nitrogen gas is derived from both microbial and thermal processes using a mechanism similar to that proposed for the generation of the hydrocarbon gas component. At Mist, high-nitrogen gases are found in association with reservoirs containing the greatest percentage of biogenic gas (compare Fig. 27 with Fig. 28). In microbiological systems, once an anaerobic environment is established, microorganisms utilize (in decreasing order of preference) nitrate, sulfate, and carbon dioxide as electron acceptors (Mechalas, 1974; D. L. Stoner, INEL, personal communication, 1991). The order of utilization follows depth and the successively decreasing availability of the preceding electron acceptor (Fenchel and Blackburn, 1979). If the nitrogen gas is partly microbial in origin, then the following scenario might explain the methane-nitrogen variability in the Mist field:

- Nitrate respiration resulting in the generation of N_2 would commence with the development of an anaerobic environment. Because of greater sediment

deposition and thickness near the depocenter of the North Willamette Basin, it is postulated that nitrate respiration would initially begin east and southeast of the Mist field (at the leading edge of basin subsidence and burial). An environment conducive to nitrate respiration would be gradually developed in an east to west direction toward the Nehalem arch. Nitrogen gas generation would be greatest east and southeast of the Mist field with subsequent migration and diffusion to the nearest available reservoirs. With continued burial and eventual depletion of the nitrate pool, first sulfate reduction, then CO_2 reduction would be initiated. As with NO_3^- reduction, microbial reduction of CO_2 to CH_4 (methanogenesis) would be initiated east and southeast of the Nehalem arch with subsequent accumulation in available reservoirs already containing nitrogen gas. With further burial and the effects of igneous activity (intrusives, extrusives, magma sources) on sedimentary organic matter maturation, thermogenic methane would be generated along with a thermally derived nitrogen gas component. This thermogenic gas may have followed a different and longer migration route (e.g., up the forming Nehalem Graben) to the northwest part of the field; first filling or topping off any remaining space in the lower reservoirs, and then migrating via faults to topographically higher reservoirs (e.g., near the Nehalem arch). This alternative scenario would account for 1) high-nitrogen concentrations in reservoirs also containing a predominant biogenic gas component, 2) subordinate concentrations of thermogenic gas in reservoirs closest to mature source rocks, and 3) the

presence of genetically mixed (biogenic and thermogenic) natural gas in all reservoirs in the field.

By a process of elimination, sedimentary organic matter appears to be the leading candidate as the source of nitrogen in the Mist gases. However, the problem of nitrogen variability in the field will require further investigation in order to be completely understood. Information on nitrogen availability (concentration and type) in the source rocks, additional N_2/Ar data, as well as $\delta^{15}N$ data from potential source rocks would be useful to help define the source and mechanism of nitrogen gas generation.

SUMMARY AND CONCLUSIONS

A study has been performed to evaluate the oil and gas potential of middle to upper Eocene source rocks in the Mist area of northwest Oregon and to determine the genetic origin of natural gas in the Mist gas field. The source rock evaluation included an assessment of organic richness, organic matter quality, maturity, and generative potential on subsurface mudstone samples from the Hamlet fm. in the Astoria Basin, and from the Hamlet-Yamhill and Cowlitz formations in the Mist field and the North Willamette Basin to the southeast. Two coal samples from the deltaic C&W sandstone unit of the Cowlitz Fm. (Mist area) were also evaluated as a part of this study. Although the mudstone samples have relatively low average organic carbon contents ($<1.0\%$), both TOC and rock-eval pyrolysis data indicate that the Hamlet, Hamlet-Yamhill, and Cowlitz formations all represent fair source rock units with some gas potential, but with little or no potential for generating oil. As expected, the coal samples are organic-rich ($>41\%$ TOC).

The organic matter in the mudstones from all three formations is interpreted as being predominantly type III gas-prone kerogen, which is consistent with interpretations from previous studies. With the exception of one coal sample from the C&W sandstone, all samples are characterized by low hydrogen- and high oxygen-index values. This suggests deposition of terrestrial derived organic matter in an oxidizing environment and/or the presence of low hydrocarbon-yielding residual organic matter. The coal sample from an outcrop of the C&W sandstone shows

higher hydrogen- and lower oxygen-index values suggesting moderately good source rock potential. Despite the predominance of type III kerogen, data from pyrolysis-GC, gas chromatography, and visual kerogen assessment suggest that the sedimentary organic matter in these potential source rocks is of mixed marine-terrestrial origin. Small but obvious differences in the amount of marine versus terrestrial organic matter input to the system are evident. Hamlet bathyal slope mudstones from the Astoria Basin appear to have a slightly greater marine organic matter component than the Cowlitz and Hamlet-Yamhill prodelta mudstones from the North Willamette Basin. The observed variation is probably a reflection of proximity to the Eocene coastline at the time of sediment deposition.

Although organic richness and organic matter quality data suggest that all three mudstone units and the coals in the C&W sandstone could be potential sources of natural gas for the Mist field, the organic-rich coals probably represent the best potential candidates from an organic matter quantity and quality perspective. However, the organic matter maturation data presented in this investigation indicate that Hamlet-Yamhill mudstones are the only source rocks of sufficient maturity to source thermogenic natural gas. Vitrinite reflectance data indicate that all three formations are immature to moderately mature ($R_o \leq 0.72\%$) with respect to peak gas generation to a depth of approximately 9000 ft (2743 m). The coals have experienced the least maturation (max. $R_o \leq 0.36\%$) of all the samples analyzed. Below 9000 ft (2743 m) the Hamlet-Yamhill kerogens show a dramatic increase in maturation level (1.07% to 1.64%), well into the catagenetic stage of hydrocarbon

generation. Igneous activity (e.g., intrusive events) has been suggested as a possible cause for the increase in maturity seen for the Hamlet-Yamhill mudstones below 9000 ft (2743 m). The pyrolytic effect of intrusions (e.g., sills) on sedimentary organic matter has been documented in the Astoria Basin and in other areas. Possible sills and dikes associated with the eruption of the thick Goble Volcanics could be a yet undocumented heat source and may explain the abrupt increase of R_o in the Hamlet-Yamhill samples in the deep Exxon GPE Federal well. Thus, a likely maturation mechanism is that below about 9000 ft (2743 m) the combined effects of both burial and higher geothermal gradients from past igneous activity have resulted in the maturation of the Hamlet-Yamhill kerogens to a quantitatively important degree. Based on the proposed maturation mechanism, other source rock units (especially organic-rich coals) in the deeper parts of the North Willamette Basin (\geq 9000-10,000 ft or 2743-3048 m) may also be mature enough to source thermogenic gas. However, deep exploratory drilling near the depocenter of the North Willamette Basin (downdip from the 11,287 ft deep Exxon GPE Federal Commission #1 well) may be necessary to provide evidence to support this hypothesis. Furthermore, there is evidence that organic-rich coal deposits are more abundant in the North Willamette Basin than previously thought. Although source rocks heated by Eocene and Miocene basaltic intrusions in the Astoria Basin are not proposed as a major source of gas for the Mist field, offshore (Astoria Basin) generation and accumulation of hydrocarbons should not be precluded from future exploration considerations. Deep seated subduction gas generated in the presumed underplated Eocene-Miocene

melange and broken formation, and/or the Yamhill Fm. beneath the Eocene volcanics, are yet other but less likely sources of thermogenic gas.

Gas composition and stable isotope data were used to help determine the genetic origin of the natural gas and nitrogen at Mist. The gases are dominated by two compounds - CH_4 and N_2 , in highly variable amounts. The hydrocarbon fraction of the gases is essentially pure methane (>99.93%), and is characterized by $\delta^{13}\text{C}_{\text{CH}_4}$ values between -53 and -40‰ and $\delta\text{D}_{\text{CH}_4}$ values between -169 and -128‰. Nitrogen constitutes more than 99% of the nonhydrocarbon fraction. $\delta^{15}\text{N}$ values range from -4.6 to +1.5‰. Methane-nitrogen reservoir concentrations vary from 98.8 - 1.2% to 49 - 51%, respectively. Low-nitrogen gases are confined to the western edge of the North Willamette Basin near the Nehalem arch. High-nitrogen gases are found east and southeast of the arch.

Results from previous studies suggested that the natural gas in the Mist field was thermally derived. C_{2+} and $\delta^{13}\text{C}$ data from this investigation also suggest that most of the Mist gas was generated as a result of thermal maturation of organic matter, but in association with condensate formation. Secondary processes such as mixing and migration are thought to account for this genetic signature by removal of the thermogenic C_{2+} component during migration, and mixing of $\delta^{13}\text{C}$ ratios from the biogenic and thermogenic end member gases. On the other hand, δD and $\delta^{13}\text{C}$ data indicate that the majority of the Mist gas is a genetically "Mixed" gas, consisting of varying proportions of both thermogenic and biogenic components. In fact, carbon

and hydrogen isotopic data indicate that three gas groups, representing different mixing proportions of thermogenic and biogenic gas, may be indentifiable in the Mist field. Gases with a dominant biogenic component are found east and southeast of the Nehalem arch in the general direction of the North Willamette Basin depocenter. Gases with a dominant thermogenic component are located close to the crest of the Nehalem arch, approximately 20 km northwest and updip from identified mature source rocks in the North Willamette Basin. A third gas group of intermediate mixing proportions is also found near the Nehalem arch. Based on the distribution of the gas groups with respect to the location of thermally mature source rocks, it is apparent that generation and accumulation of the methane has occurred in stages. Generation of biogenic gas probably occurred early in the development of the North Willamette Basin (e.g., late Eocene), followed by maturation of sedimentary organic matter and generation of thermogenic gas. Relatively long distance migration is indicated for the thermogenic gas component.

Nitrogen data are not very diagnostic in terms of identifying the source of nitrogen in the Mist gases. An atmospheric source of nitrogen can be ruled out on the basis of elevated N_2/Ar ratios (400-1000) found in the gases. A metamorphic or igneous source is also not favored based on geologic considerations and $\delta^{15}N$ values, respectively. Sedimentary organic matter is proposed as the source of nitrogen based on the fact that $\delta^{15}N$ data are generally consistent with values reported for sedimentary organic matter. One generation mechanism suggested by other investigators is that both the methane and nitrogen are thermally derived. With this

mechanism, the variability of reservoir gas nitrogen concentrations in the field is thought to be due to early nitrogen release (as soluble ammonia) with migration to available reservoirs east and southeast of the main Mist field. The methane, initially adsorbed onto the coal or kerogen, would be expelled from the source rock later than nitrogen. However, because of its greater diffusivity, methane would soon overtake the nitrogen with subsequent migration to topographically higher reservoirs near the Nehalem arch. An alternative generation mechanism, favored by this investigator, is that nitrogen was generated by both microbial and thermal processes (similar to the proposed generation mechanism for the hydrocarbon gas component). In this hypothesis, the formation of N_2 by nitrate respiration would have commenced during early burial (late Eocene) and, along with biogenic methane, would have migrated to the nearest available reservoirs east and southeast of the main Mist field. Subsequent deep burial and igneous activity would have resulted in the generation of thermogenic methane and nitrogen. The thermogenic component would have migrated via the Nehalem Graben to topographically higher reservoirs near the Nehalem arch, with some contribution to the reservoirs already containing biogenic methane and nitrogen. However, based on available data it is not possible to definitively identify either the source of nitrogen or the mechanism of nitrogen gas generation.

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APPENDICES

APPENDIX A

Location of Wells Used in this Study

<u>Company</u>	<u>Well Name</u>	<u>Location</u>
<hr/> Clatsop County <hr/>		
Oregon Natural Gas Development Corp.	Johnson 33-33	SE 1/4 sec. 33, T.8N., R.8W.
Oregon Natural Gas Development Corp.	Patton 32-9	sec. 9, T.7N., R.8W.
Standard Oil Co. Of California	Hoagland No. 1	sec. 11, T.7N., R.10W.
Diamond Shamrock Corp.	Boise Cascade 11-14	sec. 14, T.7N., R.7W.
Diamond Shamrock Corp.	Clatsop County 33-11	sec. 11, T.6N., R.6W.
<hr/> Columbia County <hr/>		
Reichhold Energy Corp.	Longview Fiber 12-33	NW 1/4 sec. 33, T.7N., R.5W.
ARCO	Busch 14-15	SW 1/4 sec. 15, T.6N., R. 5W.
ARCO	Columbia County 23-22	SW 1/4 sec. 22, T.6N., R.5W.
ARCO	Longview Fiber 23-36	SW 1/4 sec. 36, T.6N., R.5W.
ARCO	Columbia County 43-22	SE 1/4 sec. 22, T.6N., R.5W.
ARCO	Columbia County 43-27	SE 1/4 sec. 27, T.6N., R.5W.
Northwest Natural Gas Co.	Columbia County 3 R.D.	NE 1/4 sec. 10, T.6N., R.5W.
Reichhold Energy Corp.	Paul 34-32	SE 1/4 sec. 32, T.7N., R.5W.

ARCO	Columbia County 4	NE 1/4 sec. 15, T.6N., R.5W.
Northwest Natural Gas Co.	Columbia County 1 R.D.	NW 1/4 sec. 11, T.6N., R.5W.
Northwest Natural Gas Co.	Columbia County 6 R.D. 2	SW 1/4 sec. 10, T.6N., R.5W.
Northwest Natural Gas Co.	Columbia County 10	SW 1/4 sec. 3, T.6N., R.5W.
Northwest Natural Gas Co.	Columbia County 33-3	SE 1/4 sec. 3, T.6N., R.5W.
Reichhold Energy Corp.	Crown Zellerbach 42-1	NE 1/4 sec. 1, T.6N., R.5W.
ARCO	Columbia County 13-1, R.D.	SW 1/4 sec. 1, T.6N., R.5W.
ARCO	Columbia County 13-34	SW 1/4 sec. 34, T.7N., R.5W.
ARCO	Columbia County 44-21	SE 1/4 sec. 21, T.6N., R.5W.
ARCO	Columbia County 32-32	NE 1/4 sec. 32, T.6N., R.5W.
ARCO	Crown Zellerbach 12-1 (CFI 12-1)	NW 1/4 sec. 1, T.5N., R.5W.
ARCO	Crown Zellerbach 31-16 (CFI 31-16)	NE 1/4 sec. 16, T.5N., R.4W.
Tenneco	Columbia County 41-28	NE 1/4 sec. 28, T.6N., R.5W.
ARCO	Longview Fiber 23-25	SW 1/4 sec. 25, T.6N., R.5W.
ARCO	Crown Zellerbach 23-15 (CFI 23-15)	SW 1/4 sec. 15, T.5N., R.4W.
Reichhold Energy Corp.	Columbia County 43-5	SE 1/4 sec. 5, T.6N., R.5W.
ARCO	Banzer 34-16	SE 1/4 sec. 16, T.6N., R.5W.

Reichhold Energy Corp.	Columbia County 33-8	SE 1/4 sec.8, T.6N., R.5W.
ARCO	Columbia County 22-27	NW 1/4 sec. 27, T.6N., R.5W.
American Quasar Petroleum Co.	Longview Fiber 25-33	SE 1/4 sec. 25, T.6N., R.5W.
Reichhold Energy Corp.	Crown Zellerbach 32-26	NE 1/4 sec. 26, T.5N., R.4W.
Reichhold Energy Corp.	Crown Zellerbach 34-26	SE 1/4 sec. 26, T.5N., R.4W.
Reichhold Energy Corp.	Crown Zellerbach 4	NW 1/4 sec. 36, T.5N., R.4W.
Reichhold Energy Corp.	Crown Zellerbach 2	NW 1/4 sec. 8, T.4N., R.3W.
Exxon Corp.	G.P.E. Federal Com #1	sec. 3, T.4N., R.3W.
American Quasar Petroleum Co.	Investment Management 34-21	NW 1/4 sec. 34, T.6N., R.4W.
ARCO	CFI 41-4 Cav. Forest Ind.	NE 1/4 sec. 4, T.5N., R.4W.
ARCO	Columbia County 42-8	NE 1/4 sec. 8, T.5N., R.4W.
ARCO	Columbia County 24-9	SW 1/4 sec. 9, T.6N., R.4W.
ARCO	CER 41-16 Cav. Energy Res.	NE 1/4 sec. 16, T.6N., R.4W.
ARCO	CFW 12-15	NW 1/4 sec. 15, T.6N., R.4W.
Nehama and Weagant Energy Co.	CER 11-16 Cav. Energy Res.	NW 1/4 sec. 16, T.6N., R.4W.

APPENDIX B

Additional Source Rock Analytical Data

Source Rock Sample Reference Data

<u>Sample Number</u>	<u>Sample Type</u>	<u>Well Name</u>	<u>Depth Interval</u>	<u>Formation</u>
86-806	cuttings	Johnson 33-33	8600-8750	Hamlet
86-807	cuttings	Johnson 33-33	8870-8960	Hamlet
86-808	cuttings	Patton 32-9	7170-7260	Hamlet
86-809	cuttings	Patton 32-9	7860-7950	Hamlet
86-810	cuttings	Exxon GPE Fed. #1	7900-7920	Cowlitz
86-811	cuttings	Exxon GPE Fed. #1	10250-10270	Yamhill
86-812	cuttings	Exxon GPE Fed. #1	10760-10780	Yamhill
86-813	cuttings	CC 33-3	2000-2270	Cowlitz
86-814	cuttings	CZ 32-26	3370-3520	Cowlitz
86-815	cuttings	CZ 32-26	4570-4720	Yamhill
86-816	cuttings	CZ 4	4010-4130	Cowlitz
86-817	cuttings	CZ 4	5360-5420	Cowlitz
86-818	cuttings	IM 34-21	1260-1350	Cowlitz
86-819	cuttings	IM 34-21	2880-3030	Yamhill
86-820	outcrop coal	NA	0	C&W
86-821	sidewall core, coal	CFI 41-4	1917	C&W

CC = Columbia County

CZ = Crown Zellerbach

IM = Investment Management

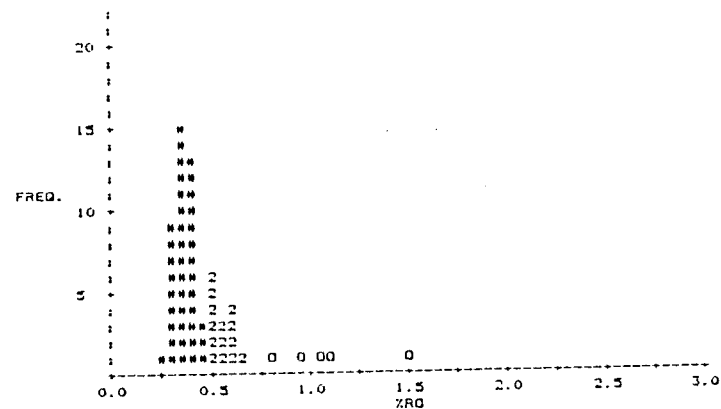
C&W = Clark and Wilson of the upper Cowlitz Fm.

APPENDIX B.1

Vitrinite Reflectance Plots

DESCRIPTION:..JOHNSON 33-33 MIST OREGON
 COMMENT:.....SPL. NO. 86R0806
 MEAN DEPTH:.. B600

TOTAL POPULATION STATISTICS
 COUNT: 60 MIN: .299 MAX: 1.520 MEAN: .490 STD.DEV.: .216



NO.	RANGE	COUNT	POPULATION GROUPS		MEAN	STD.DEV.
			MIN	MAX		
1 ***	.200- .500	41	.299	.496	.386	.043
2	.500- .700	14	.500	.691	.574	.051

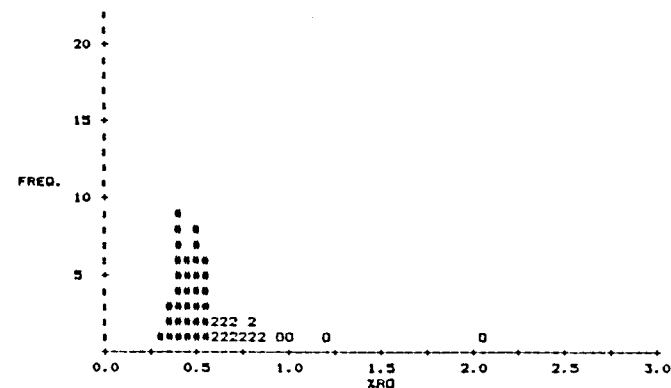
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..JOHNSON 33-33 MIST OREGON
 COMMENT:.....SPL. NO. 86R0806
 MEAN DEPTH:.. B600

1	.299	25	.400	51	.608
2	.309	27	.400	52	.612
3	.323	28	.401	53	.612
4	.326	29	.406	54	.642
5	.339	30	.406	55	.690
6	.343	31	.407	56	.819
7	.344	32	.418	57	.990
8	.346	33	.420	58	1.072
9	.346	34	.420	59	1.104
10	.346	35	.421	60	1.520
11	.350	36	.421		
12	.353	37	.424		
13	.353	38	.428		
14	.367	39	.475		
15	.373	40	.477		
16	.377	41	.495		
17	.378	42	.500		
18	.386	43	.519		
19	.386	44	.529		
20	.388	45	.534		
21	.388	46	.547		
22	.391	47	.548		
23	.394	48	.558		
24	.397	49	.561		
25	.397	50	.564		

DESCRIPTION:..JOHNSON 33-33 MIST OREGON
 COMMENT:.....SPL. NO. 86R0807
 MEAN DEPTH:.. B870

TOTAL POPULATION STATISTICS
 COUNT: 47 MIN: .334 MAX: 2.078 MEAN: .602 STD.DEV.: .284



NO.	RANGE	COUNT	POPULATION GROUPS		MEAN	STD.DEV.
			MIN	MAX		
1 ***	.250- .600	33	.334	.578	.475	.066
2	.600- .900	10	.610	.860	.730	.083

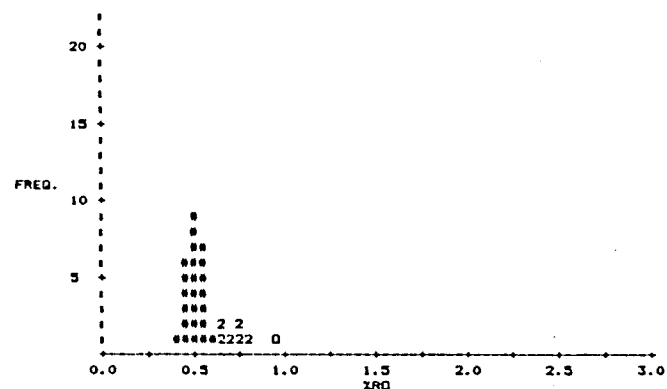
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..JOHNSON 33-33 MIST OREGON
 COMMENT:.....SPL. NO. 86R0807
 MEAN DEPTH:.. B870

1	.334	26	.541		
2	.367	27	.549		
3	.383	28	.552		
4	.398	29	.556		
5	.400	30	.558		
6	.402	31	.558		
7	.409	32	.565		
8	.409	33	.577		
9	.415	34	.610		
10	.440	35	.621		
11	.443	36	.670		
12	.444	37	.674		
13	.447	38	.703		
14	.456	39	.735		
15	.456	40	.794		
16	.460	41	.807		
17	.465	42	.817		
18	.479	43	.860		
19	.489	44	.964		
20	.500	45	1.007		
21	.506	46	1.241		
22	.510	47	2.077		
23	.528				
24	.531				
25	.540				

DESCRIPTION:..PATTON 32-9 MIST OREGON
COMMENT:.....86R0808
MEAN DEPTH:.. 7170

TOTAL POPULATION STATISTICS
COUNT: 31 MIN: .411 MAX: .960 MEAN: .583 STD.DEV.: .120



NO.	RANGE	COUNT	POPULATION GROUPS		MEAN	STD.DEV.
			MIN	MAX		
1 ***	.400-.650	24	.411	.603	.527	.048
2	.650-.900	6	.672	.816	.744	.049

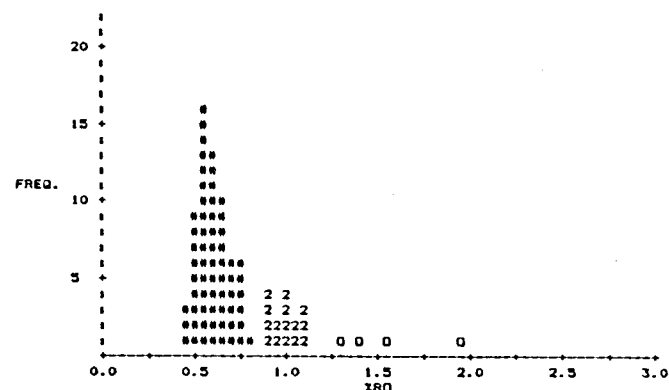
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..PATTON 32-9 MIST OREGON
COMMENT:.....86R0808
MEAN DEPTH:.. 7170

1	.411	26	.692
2	.461	27	.747
3	.463	28	.752
4	.464	29	.783
5	.472	30	.815
6	.491	31	.959
7	.492		
8	.500		
9	.513		
10	.520		
11	.524		
12	.526		
13	.537		
14	.541		
15	.542		
16	.544		
17	.551		
18	.566		
19	.569		
20	.569		
21	.576		
22	.593		
23	.598		
24	.603		
25	.671		

DESCRIPTION:..PATTON 32-9 MIST OREGON
COMMENT:.....86R0809
MEAN DEPTH:.. 7860

TOTAL POPULATION STATISTICS
COUNT: 83 MIN: .472 MAX: 1.953 MEAN: .743 STD.DEV.: .258



NO.	RANGE	COUNT	POPULATION GROUPS		MEAN	STD.DEV.
			MIN	MAX		
1 ***	.400-.850	64	.472	.812	.626	.083
2	.850-1.200	15	.907	1.128	1.021	.070

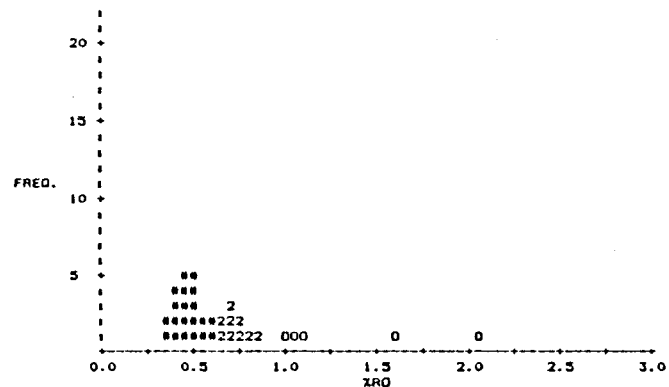
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..PATTON 32-9 MIST OREGON
COMMENT:.....86R0809
MEAN DEPTH:.. 7860

1	.471	26	.597	51	.691	76	1.073
2	.475	27	.597	52	.707	77	1.113
3	.482	28	.598	53	.710	78	1.117
4	.512	29	.600	54	.724	79	1.127
5	.514	30	.601	55	.726	80	1.319
6	.514	31	.604	56	.734	81	1.438
7	.520	32	.607	57	.734	82	1.567
8	.528	33	.610	58	.758	83	1.954
9	.533	34	.617	59	.763		
10	.540	35	.622	60	.776		
11	.540	36	.625	61	.782		
12	.542	37	.625	62	.791		
13	.552	38	.629	63	.793		
14	.559	39	.638	64	.811		
15	.563	40	.639	65	.906		
16	.577	41	.640	66	.926		
17	.583	42	.650	67	.927		
18	.583	43	.652	68	.940		
19	.587	44	.652	69	.990		
20	.587	45	.659	70	.999		
21	.589	46	.664	71	1.008		
22	.590	47	.664	72	1.029		
23	.590	48	.670	73	1.047		
24	.590	49	.677	74	1.049		
25	.594	50	.686	75	1.050		

DESCRIPTION:..REICHOLO CC 33-3 MIST OREGON
 COMMENT:.....B6R0813
 MEAN DEPTH:.. 2000

TOTAL POPULATION STATISTICS
 COUNT: 34 MIN: .370 MAX: 2.060 MEAN: .694 STD.DEV.: .351



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.350- .650	20		.370	.647	.493	.075
2	.650- .900	9		.678	.852	.760	.053

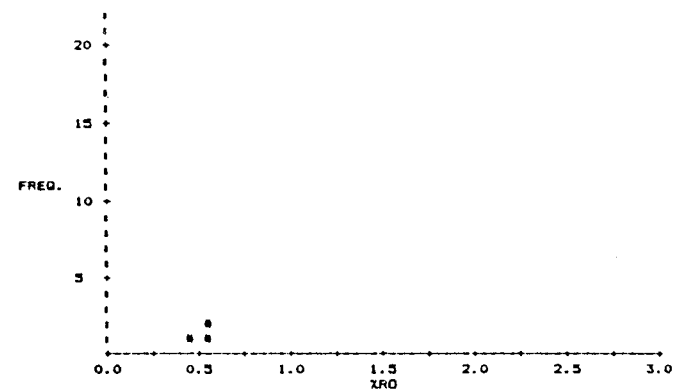
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..REICHOLO CC 33-3 MIST OREGON
 COMMENT:.....B6R0813
 MEAN DEPTH:.. 2000

1	.370	26	.774
2	.384	27	.794
3	.413	28	.821
4	.421	29	.851
5	.421	30	1.022
6	.434	31	1.058
7	.457	32	1.118
8	.462	33	1.646
9	.470	34	2.059
10	.472		
11	.491		
12	.507		
13	.521		
14	.521		
15	.532		
16	.538		
17	.581		
18	.584		
19	.623		
20	.646		
21	.678		
22	.698		
23	.739		
24	.739		
25	.739		

DESCRIPTION:..EXXON GPE FEDERAL NO.1 MIST OREGON
 COMMENT:.....B6R0810
 MEAN DEPTH:.. 7900

TOTAL POPULATION STATISTICS
 COUNT: 3 MIN: .481 MAX: .599 MEAN: .559 STD.DEV.: .053



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.400- .600	3		.481	.599	.559	.053

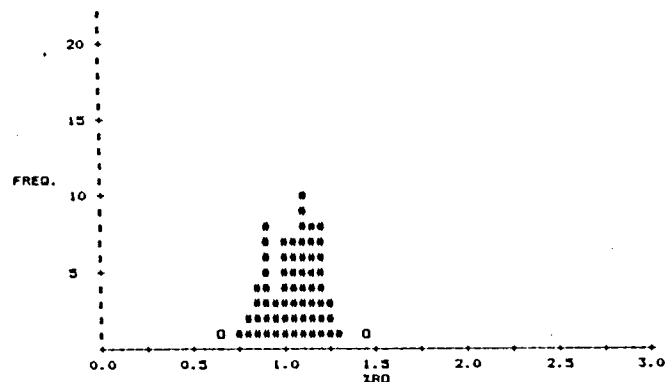
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..EXXON GPE FEDERAL NO.1 MIST OREGON
 COMMENT:.....B6R0810
 MEAN DEPTH:.. 7900

1	.481
2	.596
3	.598

DESCRIPTION:..EXXON GPE FEDERAL NO.1 MIST OREGON
 COMMENT:.....86R0811
 MEAN DEPTH:.... 10250

TOTAL POPULATION STATISTICS
 COUNT: 44 MIN: .479 MAX: 1.461 MEAN: 1.072 STD.DEV.: .144



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.700-1.400	62		.789	1.324	1.072	.128

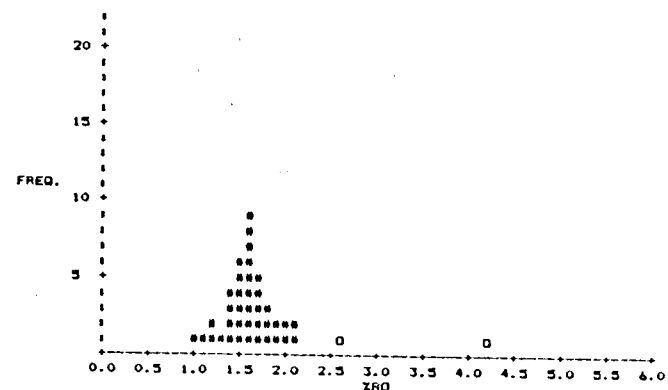
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..EXXON GPE FEDERAL NO.1 MIST OREGON
 COMMENT:.....86R0811
 MEAN DEPTH:.... 10250

1	.478	26	1.047	51	1.199
2	.789	27	1.050	52	1.200
3	.808	28	1.053	53	1.200
4	.821	29	1.067	54	1.207
5	.887	30	1.080	55	1.210
6	.887	31	1.087	56	1.214
7	.888	32	1.091	57	1.215
8	.889	33	1.099	58	1.221
9	.906	34	1.103	59	1.231
10	.912	35	1.113	60	1.255
11	.915	36	1.113	61	1.262
12	.922	37	1.115	62	1.264
13	.923	38	1.119	63	1.323
14	.924	39	1.127	64	1.460
15	.929	40	1.130		
16	.936	41	1.134		
17	.968	42	1.134		
18	.969	43	1.147		
19	.997	44	1.161		
20	1.003	45	1.165		
21	1.015	46	1.169		
22	1.021	47	1.169		
23	1.040	48	1.171		
24	1.043	49	1.186		
25	1.046	50	1.189		

DESCRIPTION:..EXXON GPE FEDERAL NO.1 MIST OREGON
 COMMENT:.....86R0812
 MEAN DEPTH:.... 10760

TOTAL POPULATION STATISTICS
 COUNT: 40 MIN: 1.020 MAX: 4.214 MEAN: 1.732 STD.DEV.: .498



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.900-2.200	38		1.020	2.198	1.643	.263

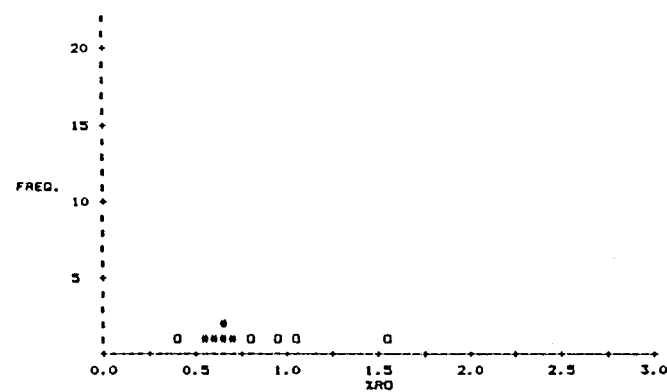
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..EXXON GPE FEDERAL NO.1 MIST OREGON
 COMMENT:.....86R0812
 MEAN DEPTH:.... 10760

1	1.020	26	1.720		
2	1.133	27	1.726		
3	1.211	28	1.763		
4	1.286	29	1.795		
5	1.329	30	1.802		
6	1.405	31	1.841		
7	1.432	32	1.851		
8	1.448	33	1.934		
9	1.480	34	1.966		
10	1.501	35	2.038		
11	1.523	36	2.088		
12	1.532	37	2.198		
13	1.547	38	2.198		
14	1.576	39	2.645		
15	1.578	40	4.213		
16	1.602				
17	1.615				
18	1.617				
19	1.618				
20	1.641				
21	1.650				
22	1.674				
23	1.674				
24	1.678				
25	1.710				

DESCRIPTION:..REICHOID CZ 32-26 MIST OREGON
 COMMENT:.....86R0814
 MEAN DEPTH:.. 3370

TOTAL POPULATION STATISTICS
 COUNT: 10 MIN: .406 MAX: 1.561 MEAN: .813 STD.DEV.: .308



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.500- .750	5		.593	.735	.656	.047

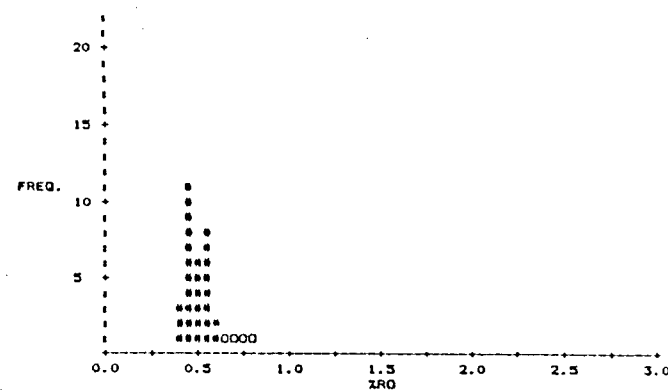
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..REICHOID CZ 32-26 MIST OREGON
 COMMENT:.....86R0814
 MEAN DEPTH:.. 3370

1 .406
 2 .592
 3 .631
 4 .655
 5 .668
 6 .735
 7 .843
 8 .955
 9 1.076
 10 1.561

DESCRIPTION:..REICHOID CZ 32-26 MIST OREGON
 COMMENT:.....86R0815
 MEAN DEPTH:.. 4570

TOTAL POPULATION STATISTICS
 COUNT: 34 MIN: .413 MAX: .819 MEAN: .544 STD.DEV.: .092



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.350- .650	30		.413	.641	.518	.058

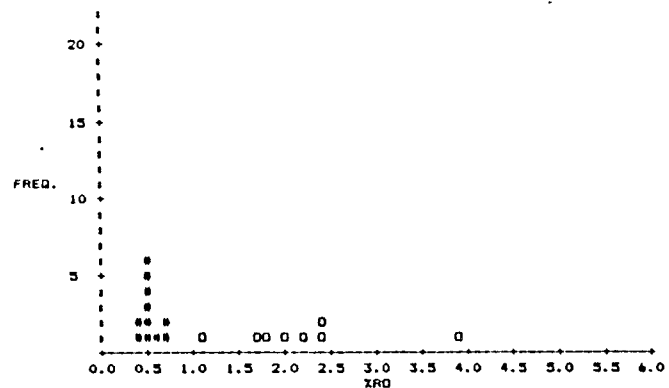
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..REICHOID CZ 32-26 MIST OREGON
 COMMENT:.....86R0815
 MEAN DEPTH:.. 4570

1	.413	26	.574
2	.428	27	.582
3	.431	28	.585
4	.454	29	.623
5	.458	30	.641
6	.460	31	.656
7	.465	32	.700
8	.472	33	.779
9	.477	34	.819
10	.481		
11	.482		
12	.491		
13	.491		
14	.492		
15	.512		
16	.515		
17	.535		
18	.544		
19	.545		
20	.548		
21	.551		
22	.564		
23	.565		
24	.566		
25	.569		

DESCRIPTION:..REICHOID C14 MIST OREGON
 COMMENT:.....86R0816
 MEAN DEPTH:.... 4010

TOTAL POPULATION STATISTICS
 COUNT: 19 MIN: .491 MAX: 3.987 MEAN: 1.279 STD.DEV.: .963



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.300- .800	11		.491	.732	.581	.083

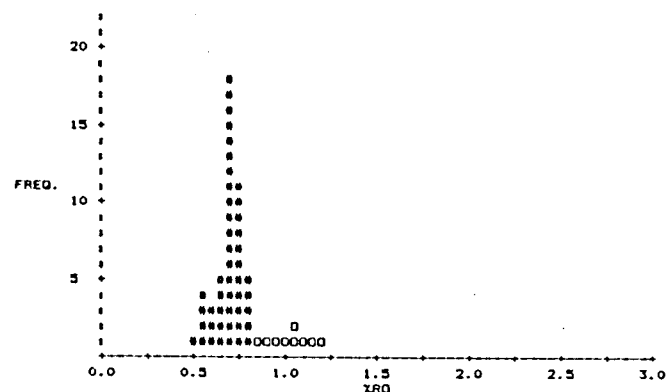
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..REICHOID C14 MIST OREGON
 COMMENT:.....86R0816
 MEAN DEPTH:.... 4010

1	.490
2	.499
3	.501
4	.520
5	.548
6	.561
7	.582
8	.583
9	.614
10	.734
11	.751
12	1.136
13	1.782
14	1.811
15	2.023
16	2.264
17	2.452
18	2.455
19	3.987

DESCRIPTION:..REICHOID C14 MIST OREGON
 COMMENT:.....86R0817
 MEAN DEPTH:.... 5360

TOTAL POPULATION STATISTICS
 COUNT: 56 MIN: .510 MAX: 1.212 MEAN: .772 STD.DEV.: .146



NO.	RANGE	COUNT	POPULATION GROUPS	MIN	MAX	MEAN	STD.DEV.
1 ***	.400- .850	47		.510	.823	.718	.071

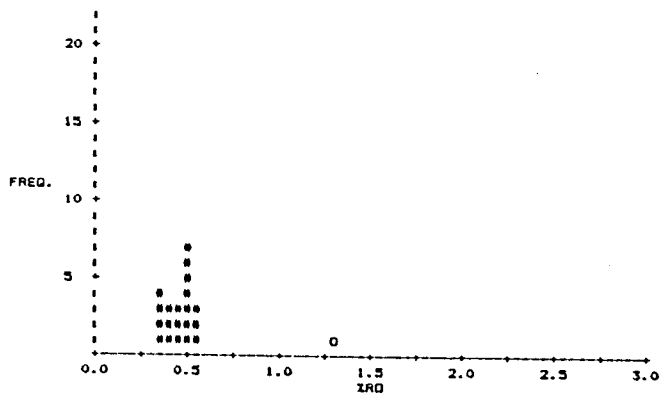
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..REICHOID C14 MIST OREGON
 COMMENT:.....86R0817
 MEAN DEPTH:.... 5360

1	.510	26	.736	51	1.033
2	.588	27	.738	52	1.083
3	.588	28	.742	53	1.086
4	.594	29	.744	54	1.130
5	.596	30	.748	55	1.190
6	.601	31	.748	56	1.211
7	.614	32	.750		
8	.614	33	.751		
9	.660	34	.756		
10	.667	35	.763		
11	.672	36	.770		
12	.685	37	.772		
13	.688	38	.778		
14	.700	39	.784		
15	.707	40	.787		
16	.710	41	.793		
17	.711	42	.795		
18	.714	43	.800		
19	.716	44	.803		
20	.719	45	.803		
21	.726	46	.819		
22	.726	47	.825		
23	.732	48	.877		
24	.733	49	.909		
25	.733	50	.959		

DESCRIPTION:..AMERICAN QUASAR 34-21 MIST OREGON
 COMMENT:.....86R0818
 MEAN DEPTH:.... 1260

TOTAL POPULATION STATISTICS
 COUNT: 21 MIN: .357 MAX: 1.334 MEAN: .518 STD.DEV.: .197



NO.	RANGE	COUNT	MIN	MAX	MEAN	STD.DEV.
1 ***	.300- .600	20	.357	.599	.478	.076

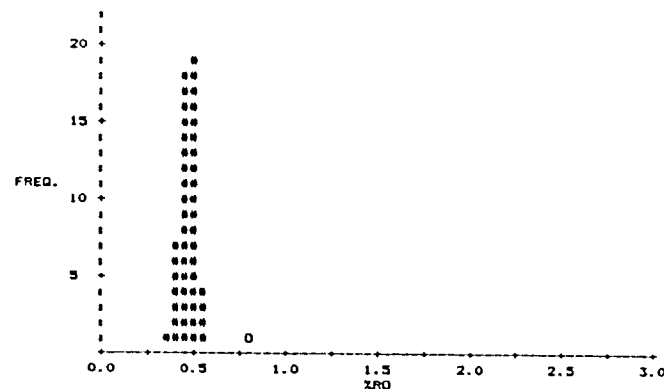
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..AMERICAN QUASAR 34-21 MIST OREGON
 COMMENT:.....86R0818
 MEAN DEPTH:.... 1260

1 .356
 2 .358
 3 .377
 4 .383
 5 .401
 6 .411
 7 .422
 8 .450
 9 .455
 10 .494
 11 .504
 12 .518
 13 .519
 14 .523
 15 .539
 16 .543
 17 .549
 18 .560
 19 .586
 20 .599
 21 1.333

DESCRIPTION:..AMERICAN QUASAR 34-21 MIST OREGON
 COMMENT:.....86R0819
 MEAN DEPTH:.... 2880

TOTAL POPULATION STATISTICS
 COUNT: 50 MIN: .393 MAX: .803 MEAN: .499 STD.DEV.: .041



NO.	RANGE	COUNT	MIN	MAX	MEAN	STD.DEV.
1 ***	.350- .600	49	.393	.596	.492	.044

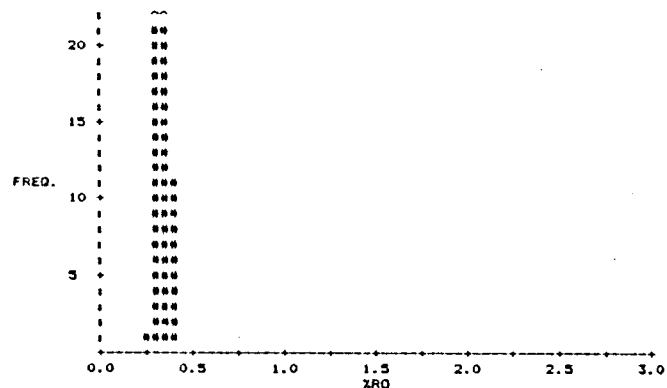
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..AMERICAN QUASAR 34-21 MIST OREGON
 COMMENT:.....86R0819
 MEAN DEPTH:.... 2880

1	.392	26	.498
2	.413	27	.503
3	.418	28	.503
4	.420	29	.505
5	.429	30	.508
6	.444	31	.514
7	.444	32	.518
8	.444	33	.518
9	.451	34	.522
10	.452	35	.523
11	.461	36	.525
12	.462	37	.525
13	.462	38	.529
14	.462	39	.532
15	.464	40	.533
16	.465	41	.533
17	.468	42	.535
18	.469	43	.536
19	.469	44	.547
20	.475	45	.549
21	.476	46	.550
22	.477	47	.551
23	.483	48	.565
24	.489	49	.596
25	.494	50	.802

DESCRIPTION:..AAT 15/4 COAL OREGON
 COMMENT:.....86R0820
 MEAN DEPTH:.. 0

TOTAL POPULATION STATISTICS
 COUNT: 60 MIN: .296 MAX: .435 MEAN: .363 STD.DEV.: .034



NO.	RANGE	COUNT	MIN	MAX	MEAN	STD.DEV.
1 ***	.250- .450	60	.296	.435	.363	.034

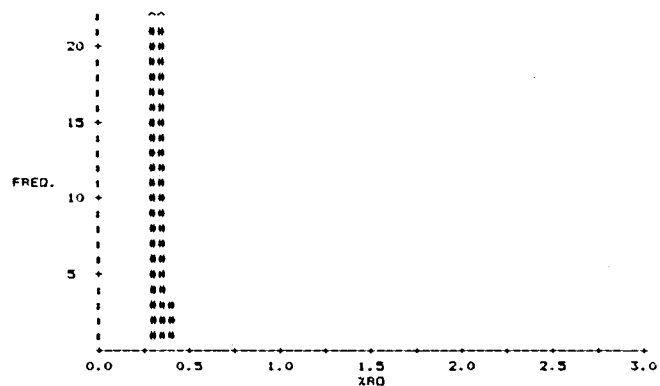
*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..AAT 15/4 COAL OREGON
 COMMENT:.....86R0820
 MEAN DEPTH:.. 0

1	.295	26	.355	51	.403
2	.307	27	.356	52	.406
3	.314	28	.356	53	.406
4	.314	29	.356	54	.409
5	.316	30	.359	55	.416
6	.322	31	.361	56	.422
7	.322	32	.362	57	.422
8	.323	33	.364	58	.428
9	.325	34	.367	59	.430
10	.329	35	.368	60	.435
11	.330	36	.368		
12	.330	37	.369		
13	.333	38	.371		
14	.335	39	.372		
15	.336	40	.375		
16	.338	41	.380		
17	.358	42	.381		
18	.339	43	.385		
19	.339	44	.387		
20	.340	45	.388		
21	.342	46	.388		
22	.343	47	.391		
23	.343	48	.391		
24	.348	49	.396		
25	.352	50	.403		

DESCRIPTION:..CF1 41-4 MIST OREGON
 COMMENT:.....86R0821
 MEAN DEPTH:.. 0

TOTAL POPULATION STATISTICS
 COUNT: 100 MIN: .318 MAX: .438 MEAN: .357 STD.DEV.: .019



NO.	RANGE	COUNT	MIN	MAX	MEAN	STD.DEV.
1 ***	.300- .450	100	.318	.438	.357	.019

*** DENOTES INDIGENOUS POPULATION

DESCRIPTION:..CF1 41-4 MIST OREGON
 COMMENT:.....86R0821
 MEAN DEPTH:.. 0

1	.318	26	.341	51	.356	76	.367
2	.323	27	.344	52	.356	77	.367
3	.326	28	.344	53	.356	78	.369
4	.326	29	.344	54	.357	79	.369
5	.326	30	.344	55	.357	80	.369
6	.329	31	.344	56	.357	81	.370
7	.332	32	.345	57	.359	82	.370
8	.332	33	.345	58	.359	83	.372
9	.334	34	.347	59	.359	84	.372
10	.335	35	.347	60	.360	85	.376
11	.335	36	.347	61	.360	86	.376
12	.337	37	.348	62	.360	87	.376
13	.337	38	.348	63	.360	88	.379
14	.337	39	.348	64	.360	89	.379
15	.337	40	.348	65	.361	90	.379
16	.337	41	.350	66	.361	91	.381
17	.338	42	.351	67	.361	92	.381
18	.340	43	.351	68	.363	93	.382
19	.340	44	.351	69	.363	94	.386
20	.340	45	.353	70	.363	95	.391
21	.340	46	.353	71	.364	96	.391
22	.340	47	.354	72	.364	97	.392
23	.341	48	.354	73	.366	98	.400
24	.341	49	.354	74	.367	99	.405
25	.341	50	.354	75	.367	100	.438

APPENDIX B.2

Bitumen Data - Saturate Fraction

SAMPLE: SAT 86-806/7 <<RA1184>>

	AREA%
NORMAL PARAFFINS	47.600
ISOPRENOIDS	14.786
RESOLVED UNKNOWNNS	37.615

NAME	AREA%	NAME	AREA%
NC12	.063	NC22	1.357
IP13	.019	NC23	1.030
IP14	.063	NC24	.869
NC13	.594	NC25	.880
IP15	.359	NC26	.725
NC14	2.930	NC27	.731
IP16	1.756	NC28	.740
NC15	6.423	NC29	1.408
NC16	7.300	NC30	.590
IP18	3.274	NC31	1.057
NC17	6.897	NC32	.584
IP19	6.595	NC33	.287
NC18	4.961	NC34	.249
IP20	2.720	NC35	.112
NC19	3.352	NC36	.043
NC20	2.393	NC37	.046
NC21	1.960	NC38	.016

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-806/7 <<RA1184>>

RATIOS:

PRISTANE/PHYTANE=	2.424
NC17/IP19=	1.046
NC18/IP20=	1.824
NC18/NC19=	1.480

CPI= 1.377

NORMALIZATION--> NC17, IP19, NC21

NC17=	44.637
IP19=	42.680
NC21=	12.683

SAMPLE: SAT 86-808/9 <<RA1185>>

	AREAZ
NORMAL PARAFFINS	42.301
ISOPRENOIDS	14.950
RESOLVED UNKNOWNNS	42.749

NAME	AREAZ	NAME	AREAZ
NC11	.042	NC22	1.919
NC12	.303	NC23	1.958
IP13	.122	NC24	1.769
IP14	.266	NC25	1.396
NC13	1.031	NC26	1.539
IP15	.716	NC27	1.605
NC14	2.073	NC28	1.586
IP16	1.750	NC29	2.999
NC15	3.174	NC30	1.165
NC16	3.324	NC31	1.904
IP18	2.273	NC32	1.023
NC17	3.273	NC33	.700
IP19	7.638	NC34	.438
NC18	2.625	NC35	.190
IP20	2.185	NC36	.078
NC19	1.959	NC37	.102
NC20	1.645	NC38	.045
NC21	1.935		0.000

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-808/9 <<RA1185>>

RATIOS:

PRISTANE/PHYTANE=	3.496
NC17/IP19=	.428
NC18/IP20=	1.201
NC13/NC19=	1.340

CPI= 1.435

NORMALIZATION--> NC17,IP19,NC21

NC17=	25.475
IP19=	59.458
NC21=	13.066

SAMPLE: SAT 86-810 <<RA1186>>

	AREA%
NORMAL PARAFFINS	43.710
ISOPRENOIDS	7.458
RESOLVED UNKNOWNNS	48.833

NAME	AREA%	NAME	AREA%
NC12	.026	NC22	3.182
IP13	.014	NC23	3.166
IP14	.010	NC24	2.594
NC13	.072	NC25	1.981
IP15	.023	NC26	1.274
NC14	.241	NC27	.718
IP16	.216	NC28	.712
NC15	2.036	NC29	.950
NC16	4.506	NC30	.460
IP18	1.738	NC31	.576
NC17	5.836	NC32	.282
IP19	2.728	NC33	.246
NC18	4.871	NC34	.812
IP20	2.728	NC35	.242
NC19	3.321	NC36	.074
NC20	2.554	NC37	.125
NC21	2.834	NC38	.016

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-810 <<RA1186>>

RATIOS:

PRISTANE/PHYTANE=	1.000
NC17/IP19=	2.139
NC18/IP20=	1.785
NC18/NC19=	1.467

CPI= 1.052

NORMALIZATION--> NC17,IP19,NC21

NC17=	51.198
IP19=	23.936
NC21=	24.366

SAMPLE: SA 86-811/12 <<RA1187>>

	AREAZ
NORMAL PARAFFINS	64.313
ISOPRENOIDS	9.158
RESOLVED UNKNOWNNS	26.529

NAME	AREAZ	NAME	AREAZ
NC11	.154	NC23	3.935
NC12	.459	NC24	3.988
IP13	.185	NC25	4.050
IP14	.403	NC26	3.776
NC13	1.307	NC27	3.618
IP15	.590	NC28	3.067
NC14	2.774	NC29	2.881
IP16	1.526	NC30	1.768
NC15	4.056	NC31	1.452
NC16	3.868	NC32	.731
IP18	1.623	NC33	.511
NC17	3.819	NC34	.328
IP19	3.654	NC35	.179
NC18	3.375	NC36	.094
IP20	1.177	NC37	.076
NC19	3.114	NC38	.047
NC20	3.197	NC39	.036
NC21	3.603	NC40	.024
NC22	4.011	NC41	.016

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SA 86-811/12 <<RA1187>>

RATIOS:

PRISTANE/PHYTANE=	3.105
NC17/IP19=	1.043
NC18/IP20=	2.868
NC19/NC19=	1.034

CPI= 1.116

NORMALIZATION--> NC17,IP19,NC21

NC17=	34.482
IP19=	32.993
NC21=	32.526

SAMPLE: SAT 86-813 <<RA1165>>

	AREA%
NORMAL PARAFFINS	45.741
ISOPRENOIDS	9.341
RESOLVED UNKNOWNNS	44.918

NAME	AREA%	NAME	AREA%
NC14	.148	NC24	1.070
IP16	.246	NC25	.959
NC15	2.759	NC26	.622
NC16	7.143	NC27	.592
IP18	2.412	NC28	.372
NC17	8.453	NC29	1.157
IP19	3.725	NC30	.245
NC18	6.443	NC31	.855
IP20	2.958	NC32	.123
NC19	4.769	NC33	.118
NC20	3.002	NC34	.040
NC21	2.675	NC35	.122
NC22	2.368	NC36	.012
NC23	1.675	NC37	.019

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-813 <<RA1165>>

RATIOS:

PRISTANE/PHYTANE=	1.259
NC17/IP19=	2.269
NC18/IP20=	2.178
NC18/NC19=	1.351

CPI= 2.069

NORMALIZATION--> NC17, IP19, NC21

NC17=	56.913
IP19=	25.080
NC21=	18.007

SAMPLE: SAT 86-814 <<RA1166>>

	AREA%
NORMAL PARAFFINS	46.842
ISOPRENOIDS	11.387
RESOLVED UNKNOWNNS	41.271

NAME	AREA%	NAME	AREA%
NC14	.054	NC24	.314
IP16	.100	NC25	.623
NC15	1.217	NC26	.462
NC16	5.486	NC27	.298
IP18	2.335	NC28	.271
NC17	9.486	NC29	.399
IP19	5.113	NC30	.227
NC18	9.264	NC31	.304
IP20	4.340	NC32	.199
NC19	6.739	NC33	.188
NC20	4.188	NC34	.112
NC21	3.142	NC35	.092
NC22	1.955	NC36	.008
NC23	1.310	NC37	.014

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-814 <<RA1166>>

RATIOS:

PRISTANE/PHYTANE=	1.178
NC17/IP19=	1.855
NC19/IP20=	2.135
NC19/NC19=	1.375

CPI= 1.166

NORMALIZATION--> NC17, IP19, NC21

NC17=	53.471
IP19=	79.818
NC21=	17.712

SAMPLE: SAT 86-815 <<RA1167>>

	AREAZ
NORMAL PARAFFINS	42.613
ISOPRENIDS	11.252
RESOLVED UNKNOWNNS	46.135

NAME	AREAZ	NAME	AREAZ
NC14	.123	NC24	1.399
IP16	.305	NC25	1.110
NC15	2.240	NC26	.821
NC16	5.569	NC27	.688
IP18	2.497	NC28	.548
NC17	7.092	NC29	1.060
IP19	4.813	NC30	.341
NC18	6.236	NC31	.806
IP20	3.636	NC32	.122
NC19	4.392	NC33	.073
NC20	2.983	NC34	.046
NC21	2.657	NC35	.228
NC22	2.217	NC36	.041
NC23	1.790	NC37	.028

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-815 <<RA1167>>

RATIOS:

PRISTANE/PHYTANE=	1.324
NC17/IP19=	1.473
NC18/IP20=	1.715
NC18/NC19=	1.420

CPI= 1.573

NORMALIZATION--> NC17,IP19,NC21

NC17=	48.699
IP19=	33.054
NC21=	18.246

SAMPLE: SAT 86-816 <<RA1168>>

	AREA%
NORMAL PARAFFINS	43.115
ISOPRENOIDS	13.125
RESOLVED UNKNOWN	43.760

NAME	AREA%	NAME	AREA%
IP16	.248	NC23	1.318
NC15	2.155	NC24	.815
NC16	6.343	NC25	.870
IP18	2.926	NC26	.514
NC17	9.860	NC27	.242
IP19	5.841	NC28	.263
NC18	7.304	NC29	.435
IP20	4.111	NC30	.214
NC19	4.787	NC31	.330
NC20	3.489	NC32	.146
NC21	2.987	NC35	.145
NC22	1.898		0.000

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-816 <<RA1168>>

RATIOS:

PRISTANE/PHYTANE=	1.421
NC17/IP19=	1.517
NC18/IP20=	1.777
NC18/NC19=	1.526

CPI= 1.322

NORMALIZATION--> NC17,IP19,NC21

NC17=	50.091
IP19=	33.021
NC21=	16.888

SAMPLE: SAT 86-817 <<RA1169>>

	AREAZ
NORMAL PARAFFINS	45.485
ISOPRENOIDS	11.853
RESOLVED UNKNOWN	42.662

NAME	AREAZ	NAME	AREAZ
IP15	.028	NC24	2.231
NC14	.160	NC25	2.474
IP16	.395	NC26	2.444
NC15	1.348	NC27	2.473
NC16	2.614	NC28	2.256
IP18	2.003	NC29	3.268
NC17	3.501	NC30	1.709
IP19	7.055	NC31	2.284
NC18	3.370	NC32	.982
IP20	2.373	NC33	.761
NC19	3.024	NC34	.683
NC20	2.538	NC35	.189
NC21	2.803	NC36	.073
NC22	2.123	NC37	.028
NC23	2.151		0.000

REQUESTED CALCULATIONS USING AREA PERCENT VALUES FROM:

SAMPLE: SAT 86-817 <<RA1169>>

RATIOS:

PRISTANE/PHYTANE=	2.973
NC17/IP19=	.496
NC18/IP20=	1.420
NC18/NC19=	1.114

CPI= 1.282

NORMALIZATION--> NC17,IP19,NC21

NC17=	26.207
IP19=	52.809
NC21=	20.983

APPENDIX B.3

$\delta^{13}\text{C}$ Isotope Data - Mist Kerogens and Coals

<u>Sample Number</u>	<u>$\delta^{13}\text{C}$ (‰)</u>
86-806	-25.4
86-807	-26.3
86-808	-26.1
86-809	-26.3
86-810	-25.8
86-811	-25.9
86-812	-25.8
86-813	-26.5
86-814	-26.1
86-815	-26.3
86-816	-26.6
86-817	-26.7
86-819	-26.1
86-820	-25.0
86-821	-27.7