Preliminary Evaluation of the Petroleum Potential of the Tertiary Accretionary Terrane, West Side of the Olympic Peninsula, Washington

A. Geology and Hydrocarbon Potential
B. Comparison of Molecular Markers in Oil and Rock Extracts
C. Composition of Natural Gases in Seeps, Outcrops, and a Test Well

U.S. GEOLOGICAL SURVEY BULLETIN 1892

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

PRELIMINARY EVALUATION OF THE PETROLEUM POTENTIAL OF THE TERTIARY ACCRETIONARY TERRANE, WEST SIDE OF THE OLYMPIC PENINSULA, WASHINGTON

Frontispiece. Petroglyphs by the Makah Indians cut in graywacke sandstone of the Hoh melange and broken formation.

Preliminary Evaluation of the Petroleum Potential of the Tertiary Accretionary Terrane, West Side of the Olympic Peninsula, Washington

A. Geology and Hydrocarbon Potential

By PARKE D. SNAVELY, JR. and KEITH A. KVENVOLDEN

B. Comparison of Molecular Markers in Oil and Rock Extracts

By KEITH A. KVENVOLDEN, JOHN B. RAPP, FRANCES D. HOSTETTLER, and PARKE D. SNAVELY, JR.

C. Composition of Natural Gases in Seeps, Outcrops, and a Test Well

By KEITH A. KVENVOLDEN, MARGARET GOLAN-BAC, and PARKE D. SNAVELY, JR.

This volume is published as chapters A, B, and C.
These chapters are not available separately

U.S. GEOLOGICAL SURVEY BULLETIN 1892

DEPARTMENT OF THE INTERIOR
MANUEL LUJAN, Jr., Secretary

U.S. GEOLOGICAL SURVEY
Dallas L. Peck, Director

March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1989

For sale by the
Books and Open-File Reports Section
U.S. Geological Survey
Federal Center, Box 25425
Denver, CO 80225

Library of Congress Cataloging-in-Publication Data

Preliminary evaluation of the petroleum potential of the Tertiary Accretionary
Terrane, west side of the Olympic Peninsula, Washington.
p. cm. — (U.S. Geological Survey bulletin ; 1892)
Includes bibliographies.
Supt. of Docs. no. : I 19.3:1892A–C
Contents: Geology and hydrocarbon potential / by Parke D. Snavely, Jr.
and Keith A. Kvenvolden — Comparison of molecular markers in oil and rock
extracts / by Keith A. Kvenvolden . . . [et al.] — Composition of natural gases
in seeps, outcrops, and a test well / by Ketih A. Kvenvolden, Margaret Golan-Bac, and Parke D. Snavely.
1. Petroleum—Geology—Washington (State)—Olympic Peninsula.
2. Geology, Stratigraphic—Tertiary. 3. Geology—Washington (State)—Olympic
Peninsula. I. Snavely, Parke Detweiler, 1919– . II. Series.
QE75.B9 no. 1892 557.3 s—dc20 89-600169
[TN870.5] [553 .2'8'0979794] CIP

CONTENTS

[Letters designate chapters]

Chapter A

Geology and Hydrocarbon Potential

By PARKE D. SNAVELY, JR., and KEITH A. KVENVOLDEN

U.S. GEOLOGICAL SURVEY BULLETIN 1892

PRELIMINARY EVALUATION OF THE PETROLEUM POTENTIAL OF THE TERTIARY ACCRETIONARY TERRANE, WEST SIDE OF THE OLYMPIC PENINSULA, WASHINGTON

CONTENTS

PLATE
[In pocket]

FIGURES

TABLES

Geology and Hydrocarbon Potential

By Parke D. Snavely, JR. *and* Keith A. Kvenvolden

Abstract

Convergence between Pacific and North American plates during late Eocene and late middle Miocene times produced two principal terranes of melange and broken formation on the continental margin of Washington and Oregon. The only onshore exposures of the melanges are along the west side of the Olympic Peninsula, where they have been transported eastward during subduction-accretion tectonics. Seismic-reflection profiles and exploration drilling indicate that these structurally complex rocks are widespread on the Washington inner continental shelf and are inferred to be present on the outer shelf of Oregon. Along the west coast of the Olympic Peninsula, the terrane that formed during the late Eocene convergence is informally referred to as the Ozette melange and broken formation. The accretionary terrane that formed in late middle Miocene time is informally named the Hoh melange and broken formation. Both of these tectonic melanges were included in the Hoh rock assemblage.

Regional reconnaissance geologic studies, together with the collection of samples for organic geochemical analyses, were conducted by the authors in the Eocene to upper middle Miocene accretionary terranes along the west side of the Olympic Peninsula to appraise the hydrocarbon potential of these structurally complex rocks. About 150 samples, chiefly from biostratigraphically dated strata, were collected from widespread localities and analyzed for vitrinite reflectance and source-rock characteristics. These analyses indicate that most of the sedimentary rocks in the Ozette and Hoh melanges and broken formations are marginally mature and have a low content of type III organic matter; therefore, they are gas prone rather than oil prone.

Organic geochemical analyses, using molecular markers, indicate that the oil in fractured reservoirs of middle Miocene Hoh rocks in the Sunshine Mining Co. Medina No. 1 well is related to oil extracted from microseeps in the middle Eocene siltstone (smell muds) of the Ozette melange that crops out in places along the coast as far as 140 km north of the well. Therefore, the thermogenic gas and oil of seeps along the west side of the Olympic Peninsula are considered to have been generated in the Ozette melange and broken formation and to have migrated into younger strata, such as the middle Miocene Hoh rocks penetrated in the Medina No. 1 well.

INTRODUCTION

The complex tectonic and stratigraphic history of the thick accretionary terrane that forms the core of the Olympic Peninsula within the horseshoe-shaped rim of lower to middle Eocene tholeiitic basalt of the Crescent Formation (fig. 1) is only broadly understood. This terrane, which is informally referred to as the Olympic core rocks (Tabor and Cady, 1978a), was subjected to episodic interactions between the oceanic plates and the North American plate; these interactions included subduction and perhaps obduction and rifting along the continental margin (Tabor and Cady, 1978a; Snavely, 1987). Our understanding of the geologic framework of the Olympic Peninsula coastal area, that is, the western core rocks, is based principally upon mapping by Koch (1968), Stewart (1970), Rau (1975, 1979), and Snavely and others (1986), regional studies by Tabor and Cady (1978b), and reconnaissance studies by P. D. Snavely, Jr. (unpub. data, 1984 and 1985). Attempts by these workers to unravel the structural complexities and evolution of these Tertiary broken formations and melanges were handicapped by (1) lack of continuous outcrops required to establish a detailed stratigraphic and tectonic framework, (2) the paucity of microfossils needed to provide precise biostratigraphic control, (3) a lack of knowledge as to the source areas and depositional patterns of terrigenous detritus interbedded in the bathyal argillaceous deposits, and (4) lack of exposures or subsurface data in coastal areas that are widely covered by glacial outwash.

In contrast, the homoclinal Tertiary sequence that overlies the Crescent Formation, the so-called peripheral rocks (fig. 1), is well understood, and the structure, stratigraphy, source areas, environments of deposition, and biostratigraphy are documented in a number of maps and reports (Brown and others, 1960; Gower, 1960; Rau, 1964; Snavely and others, 1978, 1980a, 1986).

Snavely (1987) published an interpretation of the Tertiary evolution of the continental margin of Oregon and Washington, based upon an analysis of the onshore and offshore geology as interpreted from widely spaced seismic-reflection profiles and subsurface data from 10

Manuscript approved for publication, April 20, 1989.

exploration wells drilled in the mid-1960's. The report suggests that the tectonic framework of the Olympic Peninsula was not only molded by episodes of convergence between the oceanic plates and the Olympic Mountains and Coast Range terranes, but was further complicated by north-directed transpressional forces. These transpressional forces presumably resulted from the buttress effect of the Vancouver Island pre-Tertiary block against a northward-moving Olympic terrane driven by intermittent coupling with a northward-moving Pacific plate. These northward directed forces have subducted Eocene core rocks beneath the Crescent basalts along the Crescent thrust fault on the northwest flank of the Olympic Mountains (Snavely and Wagner, 1981; Tabor, 1983; Snavely, 1983, 1987; Snavely and others, 1986). Recent seismic-reflection and seismic-refraction studies by Canadian workers, as part of their LITHOPROBE program (for example, Clowes and others, 1987), have shown that Olympic core rocks have been subducted northward and underplate Paleozoic and Mesozoic rocks and the lower Eocene basalt on Vancouver Island.

Despite these limiting geologic factors, we have attempted to group the broken formations and melanges into broad time- and rock-stratigraphic units, or microterranes (fig. 2; pl. 1). On the basis of limited reconnaissance studies in the western core rocks, we have attempted to

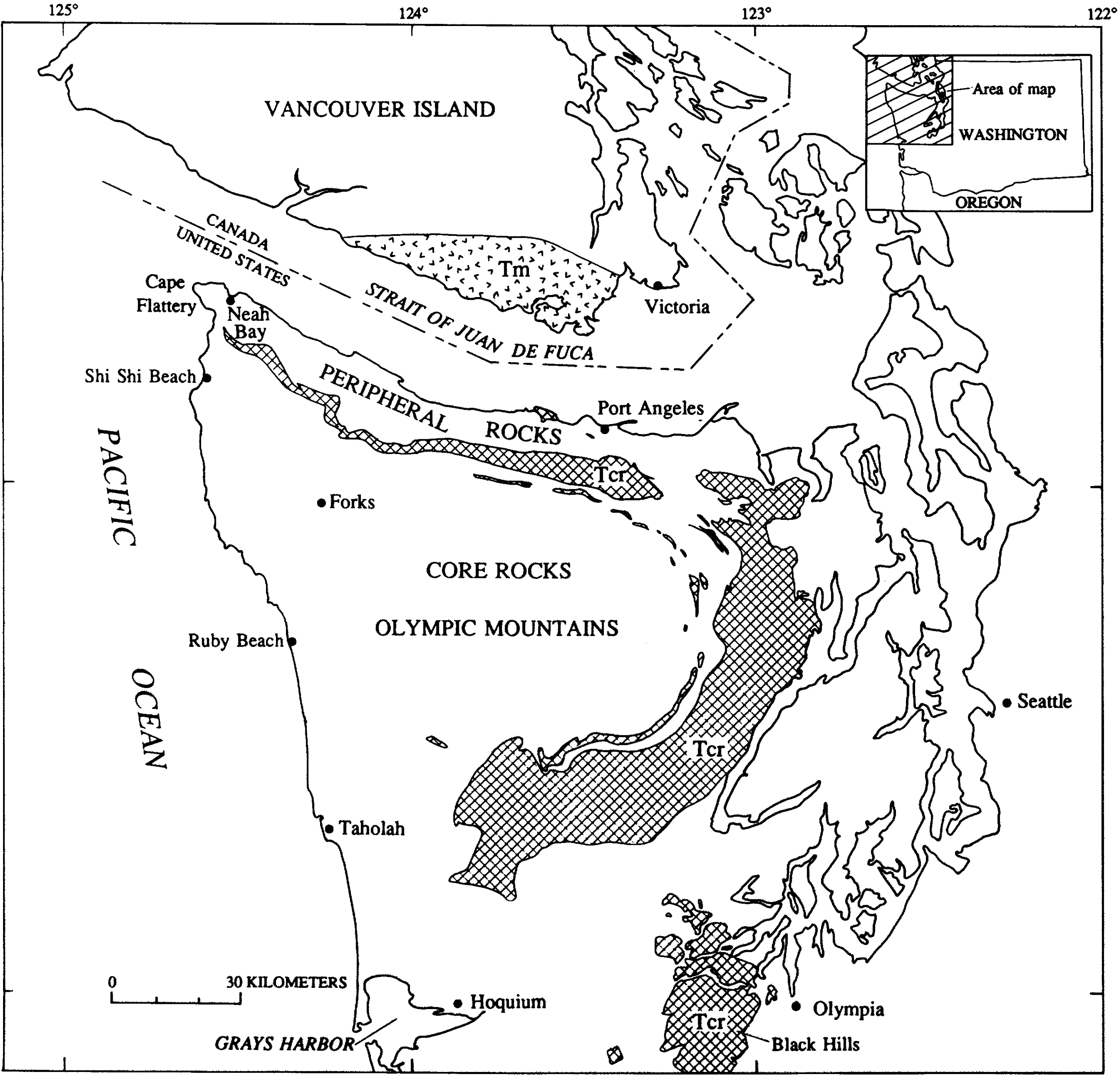

Figure 1. Distribution of core and peripheral rocks in relation to lower and middle Eocene submarine basalt of the Crescent Formation (Tcr) on Olympic Peninsula and lower Eocene Metchosin Volcanics (Tm) on Vancouver Island, British Columbia.

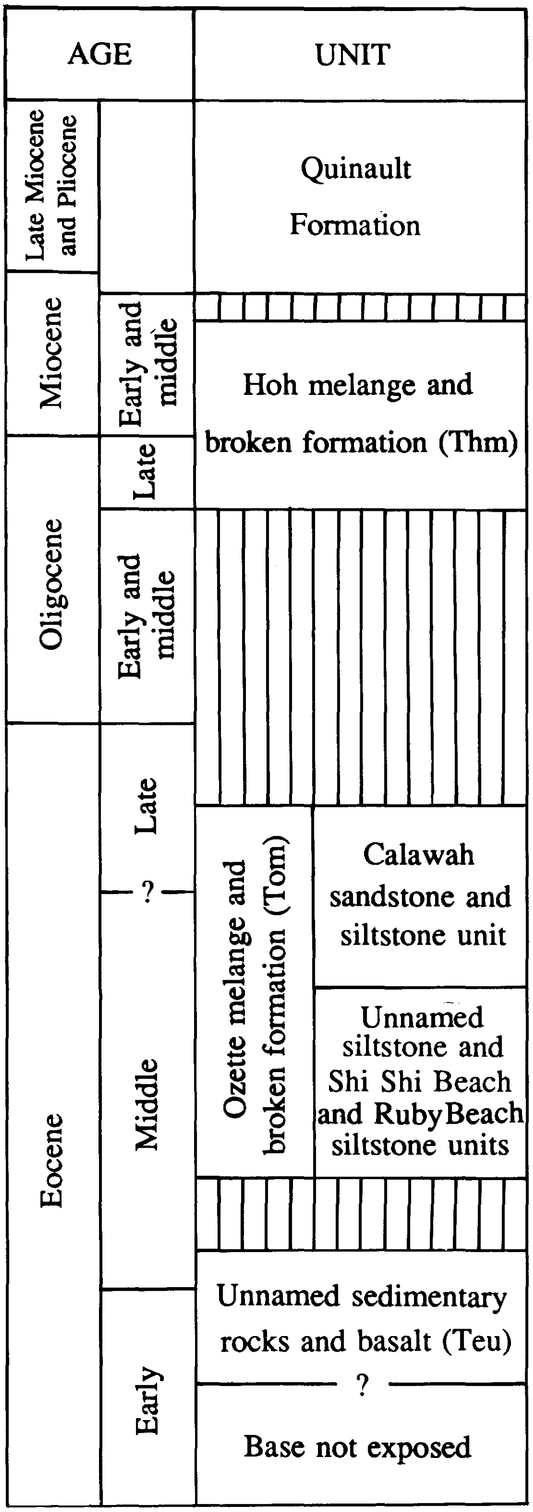

Figure 2. Generalized composite section showing stratigraphic relation of Ozette and Hoh melanges and broken formations as used in this report. Missing strata of latest Eocene and early and middle Oligocene ages may have been subducted during late Oligocene. Unit symbols refer to plate 1.

differentiate two major terranes of melange and broken formation: the Eocene Ozette melange and the late Oligocene to middle Miocene Hoh melange. Some of the structural and stratigraphic boundaries mapped by earlier workers and compiled by Tabor and Cady (1978b) have been revised to broadly outline these two melange terranes. Undoubtedly, our reinterpretation of the mapping of earlier workers will be modified when new detailed geologic mapping, subsurface information, and seismic-refraction data become available for the complex western Olympic accretionary terranes.

Stratally disrupted rock sequences in the western core rocks (Tabor and Cady, 1978a), which range in age from early(?) Eocene to late middle Miocene,[1] are inferred to record two major periods of more head-on convergence between Pacific oceanic plates and the North American plate (Snavely, 1987). The earliest major period of convergence recorded in the Olympic accretionary terrane is interpreted to be of late Eocene (Narizian) age, as in several places less deformed strata of latest Eocene (Refugian) age unconformably overlie middle Eocene melange. Also, a pronounced unconformity that may be related to this tectonic episode is present within late Eocene strata of the peripheral rocks, between the Hoko River Formation (Narizian Stage) and the overlying Makah Formation (late Narizian and Zemorrian Stages; Snavely and others, 1980a, 1986). A regional unconformity on the Oregon and Washington continental shelf (Snavely and others, 1980b; Snavely, 1987) further supports a major period of plate interaction prior to the deposition of strata of latest Eocene (Refugian) age. The youngest plate interaction recorded in the Olympic accretionary wedge occurred in late middle Miocene time, as only moderately deformed strata of late Miocene and Pliocene age unconformably overlie Eocene and middle Miocene melange and broken formations.

The melange and broken formation that formed during the late Eocene episode of convergence include the following units (fig. 2): (1) An unnamed lower(?) and lower middle Eocene sequence of sandstone and siltstone that includes minor basalt flows and gabbro sills (unit Tur of Tabor and Cady, 1978b), (2) an unnamed middle Eocene siltstone that includes hydrocarbon-rich melange at Shi Shi Beach (Petroleum Creek block of Snavely and others, 1986) and at Ruby Beach, and (3) a middle and upper Eocene sequence of thick- to medium-bedded micaceous turbidite sandstone with minor siltstone and coaly interbeds (unit Two of Tabor and Cady, 1978b, and the Ozette Lake-

---

[1] Most of the allochthonous Sooes terrane (unit TJs, pl. 1) and the terrane south of the Crescent fault and north of the Calawah fault (unit Tcc, pl. 1) of Snavely and others (1986) are not assigned to the Ozette melange and broken formation. The Petroleum Creek block (Snavely and others, 1986) included in the Sooes terrane is here considered to be in the lower plate of this allochthonous terrane and represents part of the Ozette melange and broken formation of this report.

Calawah Ridge block of Snavely and others, 1986), herein informally referred to as the Calawah sandstone and siltstone. The latter two units comprise the Ozette melange and broken formation (Tom) of this report (fig. 2).

The youngest melange and broken formation, informally named the Hoh melange and broken formation (Thm), formed during the late middle Miocene convergence and consists of thin-bedded siltstone and sandstone with thick interbeds of sandstone and minor conglomerate of late Oligocene to late middle Miocene age (Rau, 1975).

These four units are composed chiefly of stratally disrupted sequences and broken formation separated by tectonic boundaries that in places are marked by zones of melange. Broken formations form long linear packets that include relatively intact to highly disrupted strata. Faults form most of the boundaries between units, and strata have been stacked by both subduction and obduction processes. Tectonic blocks in the melange units are commonly sandstone and lesser amounts of basalt, both of which are locally derived. Exotic materials such as blueschist and eclogite are absent. The total thickness of the lower Eocene to middle Miocene Olympic accretionary wedge, as inferred from gravity models, may be as much as 15 to 20 km (MacLeod and others, 1977).

The structural relations between strata assigned to the Ozette and Hoh melanges and broken formations in this report are unclear as these two units were not differentiated by Rau (1979) in his mapping between the Bogachiel and Hoh Rivers. However, on the basis of sparse foraminiferal data (Rau, 1979; written commun., 1983–1985), strata of both middle and late Eocene and late Oligocene to middle Miocene age occur in this melange, which Rau (1975) assigned to his Hoh rock assemblage. Reconnaissance studies by Snavely (1984, 1985) suggest that sheared Calawah sandstone underlies the broad folds mapped by Rau (1979) in strata of late Oligocene to middle Miocene age, the Hoh melange of the present report. For example, along the west side of the Minter Creek syncline only moderately deformed upper Oligocene strata overlie sheared and broken micaceous Calawah sandstone; however, the precise contact is not exposed.

Geologic mapping east of Point of the Arches (Snavely and others, 1986) indicates that strata correlative with the Calawah sandstone underplates strata as young as late Eocene. Also, geologic interpretations of seismic-reflection profiles on the inner continental shelf, together with subsurface data from Pan Am well P–0141, suggest that an older sandstone sequence that may correlate with the Ozette melange underlies strata assigned to the upper Oligocene to middle Miocene Hoh melange. Therefore, a speculative tectonic model, in which the Ozette melange underplates the Hoh melange, was used in modifying Rau's mapping between the Bogachiel and Hoh Rivers (pl. 1).

The geology near the coast is complicated by a major northward-trending and westward-dipping thrust fault (or faults) that juxtaposes thick-bedded Oligocene sandstone and conglomerate eastward over Eocene rocks from Ozette Island southward as far as Ruby Beach (pl. 1; Snavely and others, 1986; P.D. Snavely, Jr., unpub. mapping, 1984, 1985). South of Ruby Beach, this fault most likely is offset seaward onto the shelf by the Hoh River fault. It is inferred to continue southward on the shelf, and to intersect the coast between the seacliffs and Hogsback and Little Hogsback. Here, sheared well-indurated siltstone, sandstone, and basalt breccia and pillow lava that form the Hogsback and Little Hogsback are juxtaposed with siltstone and sandstone of the Hoh melange along a high-angle reverse fault. The high vitrinite values (R_o=1.06–1.98 percent) in the Hoh melange adjacent to the fault probably are due to frictional heat generated by movement along this fault, as lower R_o values (average 0.66 percent) occur in areas distant from major faults.

ACKNOWLEDGMENTS

Funding for regional reconnaissance geologic studies and the collection of samples for organic geochemical analyses were supported by the U.S. Department of Energy, Deep Subduction Gas Program, under Interagency Agreement No. DE–A121–83–MC20422. Rock-Eval pyrolysis and vitrinite analyses were made by Clark Geological Services. The authors gratefully acknowledge the (Washington Department of Natural Resources) biostratigraphic data on surface and subsurface samples contributed by Weldon Rau, Washington Division of Geology and Earth Resources. Permission granted by the Olympic National Park and the Quinault Tribal Council to conduct field studies on their lands also is appreciated. Mr. Larry Workman, Environmental Geologist, Quinault Tribal Council, deserves special thanks for his able assistance to us and our colleagues during field studies on the reservation.

In particular, we wish to thank Rowland Tabor, U.S. Geological Survey, for sharing his broad knowledge of the Olympic Mountains and for providing samples of core rocks for assessment of their thermal maturity. Technical reviews by Holly Wagner, U.S. Geological Survey, and Kenneth Peters, Chevron Oil Field Research Company, improved the quality of the manuscript as did a review of an earlier manuscript by Rowland Tabor. We appreciate Diane Minasian's careful preparation of the maps and figures and Juanita Mascardo's skillful typing of the text.

STRATIGRAPHIC FRAMEWORK OF THE WESTERN OLYMPIC CORE ROCKS

Unnamed Lower(?) and Middle Eocene Sedimentary Rocks and Basalt

The oldest unit in the Olympic accretionary terrane is an unnamed sequence of lower(?) and middle Eocene micaceous, feldspathic thick-bedded to massive sandstone and medium-bedded sandstone and siltstone—with minor conglomerate beds, thin flows of pillow basalt, and sills of gabbro—and rare red limestone and tuff beds. This unnamed sequence, which is shown as unit Teu (fig. 2; pl. 1), correlates with unit Tur on the map of Tabor and Cady (1978b). These rocks may have been deposited in a marginal basin that existed west of the lower Eocene ridge basalt that composes the lower part of the Crescent Formation; alternatively, rocks assigned to unit Teu may be a lateral facies of the upper part of the Crescent Formation, which is composed of alkalic basalt flows and breccia with minor interbeds of tuff and volcaniclastic rock—a correlation also suggested by Stewart (1970). However, the flows in the unnamed Eocene unit may represent submarine volcanism within the marginal basin rather than flow tongues that extended westward from the main locus of Crescent volcanism. Basalt flows and breccia and gabbro sills in this unnamed unit are commonly chloritized, albitized, and pervasively stained with manganese. Veins of calcite and laumontite, and less commonly quartz, occur throughout the siltstone, sandstone, and basalt.

Sheared and hydrothermally(?) altered basalt breccia, pillow lava, and well-indurated basaltic siltstone and sandstone that form the large sea stacks at Hogsback and Little Hogsback, about 11.2 km north of Taholah (pl. 1), are questionably assigned to unit Teu. Also, basalt tuff-breccia, pillow(?) lava, and massive basalt exposed in two quarries, one 1.5 km and the other 4.7 km north of Taholah, also are assigned to unit Teu. The basalt at the Hogsback and Little Hogsback and in the quarries is correlated with pillow lava and breccia that are well exposed along the west side of Point Grenville, 4.8 km south of Taholah. Siltstone interbeds in these basalts were assigned a middle Eocene age by Rau (1975).

Ozette Melange and Broken Formation

The Ozette melange and broken formation (fig. 2; pl. 1, unit Tom) consists of two lithologic units: an older unnamed middle Eocene siltstone sequence and the middle and upper Eocene Calawah turbidite sandstone. Although not differentiated on the geologic map (pl. 1), the middle Eocene siltstone crops out in places along the coast from Shi Shi Beach southward to Ruby Beach. Most of the area shown on the map (pl. 1) as unit Tom is the Calawah sandstone and siltstone unit.

Unnamed Middle Eocene Siltstone and Shi Shi Beach-Ruby Beach Siltstone

Thin-bedded to laminated concretionary siltstone and interbeds of very fine grained sandstone of middle Eocene age unconformably overlie the unnamed Eocene sedimentary rocks and basalt. The only known exposure of this relation is in a quarry at the north end of Ozette Lake where middle Eocene siltstone overlies more than 20 m of pillow lava and breccia that are assumed to be part of the unnamed lower(?) and middle Eocene unit (Snavely and others, 1986). At Shi Shi Beach this predominantly siltstone unit was assigned to the Petroleum Creek block by Snavely and others (1986). This siltstone unit is considered to correlate with the middle Eocene siltstone that crops out in the seacliffs at Ruby Beach (fig. 3). Both the Shi Shi and Ruby Beach units are intensely sheared along major thrust faults and are referred to as smell muds because of their petroliferous odor. Calcite and laumontite veins are common in the siltstone and sandstone unit as are calcareous concretions as much as 1 m in diameter.

Calawah Sandstone and Siltstone

The middle and upper Eocene Calawah sandstone and siltstone consist of moderately to intensely deformed medium- to thick-bedded micaceous, carbonaceous, lithofeldspathic turbidite sandstone and minor thick interbeds of dark-gray siltstone and medium-bedded sandstone and siltstone (fig. 4). Lenses of pebble conglomerate, beds of siltstone-chip conglomerate, and thin coal seams are present locally. Laumontite and calcite occur as cement in the sandstone, and veins of calcite and shear zones laced with laumontite are common. The Calawah sandstone and siltstone are widely distributed in the northwestern part of the core rocks (Tabor and Cady, 1978b, unit Two; Snavely and others, 1986, unit Tocss) and may be more than 1,000 m thick. Along major thrust faults, polished tectonic blocks of Calawah sandstone occur in melange composed of the underlying middle Eocene siltstone unit.

Figure 3. Seacliff exposure at Ruby Beach of middle Eocene Ozette melange (smell muds) composed of tectonic blocks of graywacke and minor basalt and conglomerate in sheared siltstone matrix. Sample of smell mud was collected in shear zone near center of photograph.

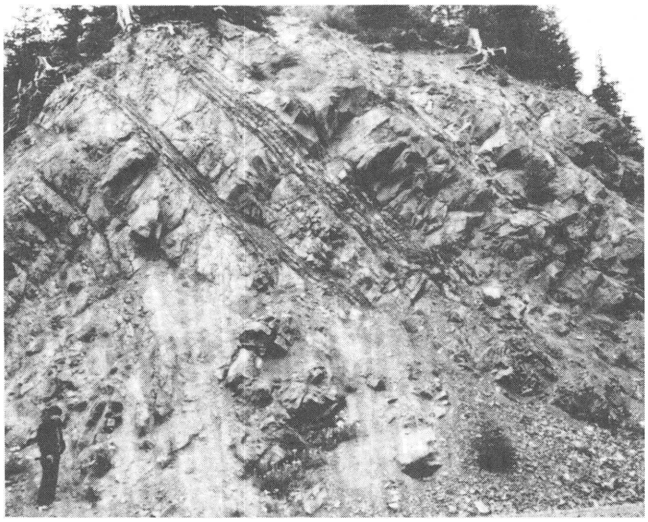

Figure 4. Overturned sequence of graded beds of Calawah micaceous arkosic sandstone and siltstone exposed near Ozette Lake.

Hoh Melange and Broken Formation

In his mapping of the coastal region from the Bogachiel River south to Point Grenville, Rau (1975, 1979) assigned an Eocene to late middle Miocene age to the melange and broken formation sequence of the Hoh rock assemblage. Although he differentiated seven major rock types within the Hoh, and showed the locations and ages for 29 foraminiferal samples, he did not assign ages to his lithologic units. On the basis of Rau's geologic and biostratigraphic studies, together with new foraminiferal collections and reconnaissance geologic studies by P.D. Snavely, Jr., (unpub. data, 1984, 1985) within and adjacent to Rau's map area, most of the coastal rocks included in the Hoh rock assemblage appear to be late Oligocene to late middle Miocene in age. Therefore, on the basis of lithologic and biostratigraphic considerations, we propose that the Hoh rock assemblage of Rau (1975, 1979) be restricted to strata of late Oligocene to late middle Miocene age and be informally referred to as the Hoh melange and broken formation.[2] The older Eocene(?) rocks, which originally were included in Rau's (1975) Hoh rock assemblage, are here assigned to lithologically similar rocks of the Ozette melange and broken formation. Although the contact between these two major accretionary terranes is obscure in most places, it is important to attempt to differentiate these two terranes because they are interpreted to record separate episodes of major plate convergence (Snavely, 1987).

It is difficult, if not impossible, to unravel the detailed stratigraphy of the Hoh melange and broken formation because, in most places, this unit is complexly folded and stacked by imbricate thrusts. The unit constitutes a broken formation interleaved with thick zones of melange (fig. 5A). In places the melange may occur as diapirs that penetrate Hoh and younger strata (fig. 5B). North of the Hoh River and south of Rau's (1979) Goodman Creek fault (pl. 1), Hoh strata crop out in broad synclines and anticlines where their stratigraphic continuity is moderately well preserved (for example, in the Minter Creek syncline, Rau, 1979). Reconnaissance field studies, analysis of wells drilled near the Hoh River, and the interpretation of offshore seismic profiles suggest that the Hoh rocks overlie highly deformed strata that are inferred to be correlative with the Eocene Calawah sandstone and siltstone. Onshore, the precise contact between the Hoh rocks and the Calawah sandstone and siltstone is not exposed, but intense shearing occurs near the contact, as observed along the west side of the Minter Creek syncline and recorded in well logs at a depth of 1,370 m in the Union Oil Co. Milwaukee Land Co. No. 1 well drilled just south of the Hoh River (pl. 1; Rau and McFarland, 1982). These relations suggest that the Calawah sandstone and siltstone underplate the Hoh rocks and that this underthrusting produced the broad detached(?) folds of Hoh strata in the upper plate.

The most complete and relatively undeformed Hoh sequence was drilled in the Milwaukee well, where approximately 1,370 m of strata that range in age from latest Oligocene (Zemorrian) to late middle Miocene (Relizian) were penetrated, as indicated by Rau and McFarland (1982). The lower 90 m of unfossiliferous, thick-bedded sandstone drilled in the Milwaukee well is presumed to be Calawah sandstone; however, no foraminiferal data are available to support this interpretation. Despite the uncertainties as to the age of the sandstone in the lower part of the Milwaukee well, a minimum thickness of about 1,370 m for the Hoh sequence can be established there. The Pan Am well P–0141, drilled on the adjacent continental shelf 16 km southwest of Hoh Head (pl. 1), penetrated about 1,430 m of strata that was assigned an early to middle Miocene age by W.W. Rau (written commun., 1976). As noted in the Milwaukee well, a sandstone unit containing only arenaceous foraminifers was penetrated in the lower part of the P–0141 well between 2,460 and 3,160 m. Although age-diagnostic foraminifers are not present in the lower sandstone interval, vitrinite-reflectance values (R_o=0.97 percent) for kerogen in the sandstone are essentially twice as high as the R_o values for kerogen in the overlying Miocene strata (Brown and Ruth Laboratories, Inc., written commun., 1986), indicating an older age for the sandstone unit that underlies the Hoh rocks. These minimum stratigraphic thicknesses for the Hoh are supported by the thickness of the Hoh sequence exposed on the west flank of the broad Minter Creek syncline, where W.W. Rau (written commun., 1973)

---

[2] The Hoh melange and broken formation as used in this report includes the Browns Point Formation of Glover (1936) and the Elk Ridge block, Mosquito Creek block, and the western part of the Central block of Stewart (1970).

measured about 2,500 m of strata. Based upon this admittedly sparse data, the total thickness of the Hoh sequence is probably at least 2,500 m where it has not been thickened tectonically by folds and thrust faults. This thickness figure is compatible with sections measured in the homoclinally dipping upper Oligocene to upper middle Miocene sequence north of the Crescent Formation (Snavely and others, 1980a, 1986) and with correlative strata penetrated in wells drilled in the deep marginal basin on the Oregon continental shelf (Snavely and others, 1982).

We speculate that the Calawah sandstone and siltstone may underplate the Hoh sequence near the coast and on the adjacent inner continental shelf and that a master shear zone (decollement) separates these two units. In the northwestern part of the Olympic Peninsula, east of Point of the Arches, strata correlative with the Calawah sandstone and siltstone underplate rocks that range in age from pre-Tertiary to latest Eocene (Sooes terrane of Snavely and others, 1986; unit TJs, pl. 1). However, inland along the Clearwater fault the Calawah sandstone apparently is thrust over the Hoh melange, perhaps along a back thrust (duplex) above the major shear zone or decollement (pl. 1).

Subsurface data from the Sunshine Mining Co. and Cascade Natural Gas Rayonier No. 1–A well (Rau and McFarland, 1982), drilled north of Grays Harbor (see inset map, pl. 1), indicate that the middle Miocene rocks are present below strata of late Eocene and Oligocene(?) age. This stratigraphically anomalous relation may be due to underthrusting of the Hoh melange beneath older strata. In their geologic cross section of the continental margin of southwestern Washington, Snavely and Wagner (1982) speculated that the upper Oligocene to upper middle Miocene melange and broken formation may underplate strata as old as the Eocene Crescent Formation in the adjacent Washington Coast Range.

SOURCE ROCK CHARACTERISTICS

Reconnaissance geologic studies and sampling were conducted in the Ozette and Hoh accretionary terranes along the west side of the Olympic Peninsula to evaluate the hydrocarbon potential of these rocks. Samples collected from these melange units include 69 outcrop samples and 28 subsurface samples from test wells drilled near the coast and on the adjacent continental shelf (pl. 1). The samples were collected for organic geochemical measurements including assessment of thermal maturity (tables 1 and 2). In order to provide a regional geochemical framework, 36 samples were collected from rock sequences east and north of the Ozette and Hoh accretionary terranes (pl. 1). These samples include the moderately deformed peripheral rocks in the upper plate of the Crescent thrust fault (table 3); the lower(?) and middle Eocene core rocks (table 4); the Sooes terrane (table 5); and the terrane between the Crescent thrust fault and Calawah fault (table 6). Most of the samples analyzed were from paleontologically dated marine strata that range in age from early Eocene to middle Miocene.

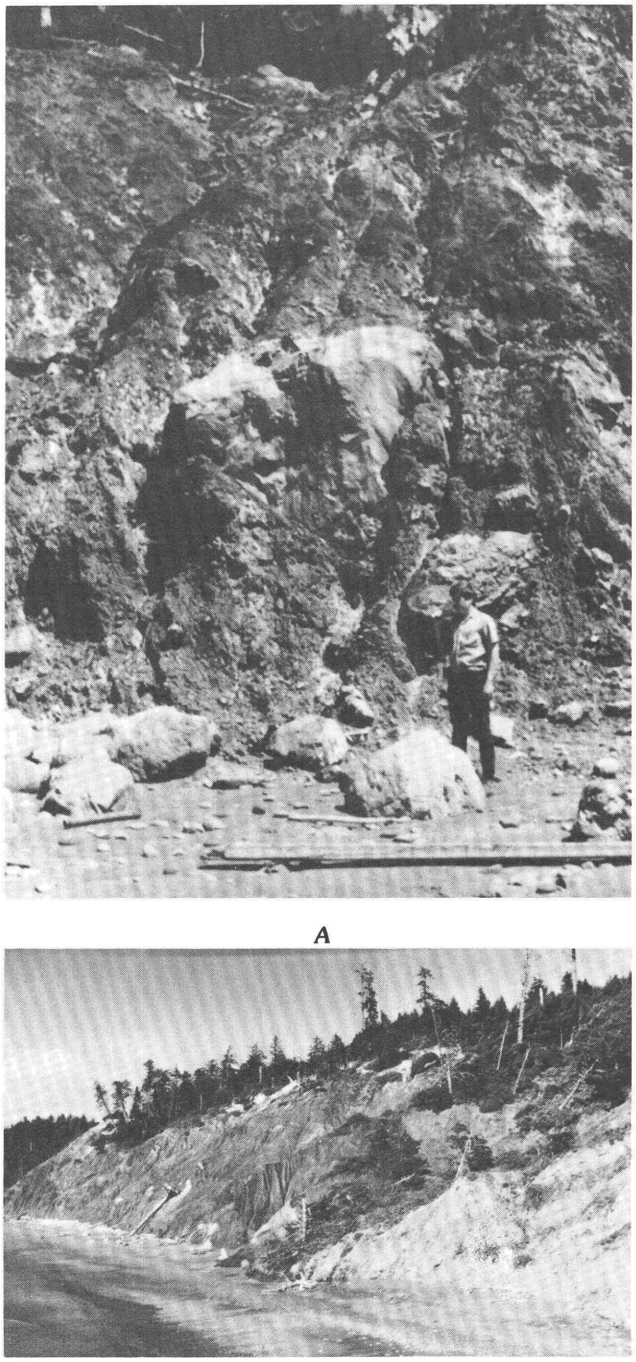

Figure 5. Exposures of Hoh melange on west coast of Olympic Peninsula. *A*, Large polished tectonic blocks of graywacke, as much as 5 m in diameter, encased in sheared middle Miocene siltstone in seacliff near Little Hogsback about 11 km north of Taholah. *B*, Diapir (dark area in center of photograph) penetrating thick-bedded sandstone (light-colored area in lower right of photograph) of the upper Miocene(?) and Pliocene Quinault Formation. Coastal exposure about 60 m high and located about 3.6 km north of Taholah.

Table 1. Vitrinite reflectance, thermal-alteration index, and Rock-Eval analyses of Ozette melange and broken formation (unit Tom on pl. 1)

[R_o, vitrinite reflectance; TAI, thermal-alteration index; T_{max}, temperature of maximum yield of S_2; HI, hydrogen index (mg hydrocarbon/gram TOC); TOC, total organic carbon/gram of rock; S_1, mg hydrocarbon/gram of rock; S_2, mg hydrocarbon/gram of rock; S_3, mg hydrocarbon/gram of rock; S_1+S_2, oil and gas potential; PI, productivity index $S_1/(S_1+S_2)$; --, not determined]

Sample No. (see pl. 1)	R_o(pct)	TAI	Rock-Eval parameters								
			T_{max}	HI	OI	TOC	S_1	S_2	S_3	S_1+S_2	PI
UNNAMED MIDDLE EOCENE SILTSTONE UNIT [Includes Shi Shi Beach (SS) and Ruby Beach (R) units. Shi Shi Beach siltstone included in Petroleum Creek block of Snavely and others (1986)]											
A1 (SS)	--	--	416	138	61	0.88	1.00	1.22	0.53	2.22	0.45
A2 (R)	0.63	2.4-2.6	440	108	10	.49	.08	.53	.05	.61	.13
A3 (R)	.64	2.5	444	98	17	1.20	.20	1.17	.20	1.37	.15
A4 (SS)	.73	2.6	424	37	63	.43	.17	.16	.27	.33	.52
A5	.51	2.5	435	9	27	.44	.04	.04	.12	.08	.50
A6	.61	2.6	442	8	50	.26	.05	.02	.13	.07	.71
A7	.87	2.6	457	43	13	.56	.06	.24	.07	.30	.20
A8	.87	2.8	457	110	7	.83	.16	.91	.06	1.07	.15
A9	.79	2.8	449	102	0	.48	.06	.49	.00	.55	.11
A10	.44	2.4	441	54	8	.26	.04	.14	.02	.18	.22
A11 (R)	.71	2.7	434	227	7	.60	.79	1.36	.04	2.15	.37
A12 (SS)	.49	2.6	406	165	100	.49	.72	.81	.49	1.53	.47
A13 (SS)	.33	2.5	424	92	54	.24	.01	.22	.13	.23	.04
A14 (SS)	.36	2.6	410	151	74	.43	.36	.65	.32	1.01	.36
A15 (SS)	.35	2.1	430	105	50	.22	.01	.23	.11	.24	.04
A16	.54	2.5-2.6	281	61	139	.28	.08	.17	.39	.25	.32
A17	.47	2.4-2.5	435	42	19	.36	.01	.15	.07	.16	.06
CALAWAH SANDSTONE AND SILTSTONE											
A18	0.95	2.8	277	12	287	0.08	0.00	0.01	0.23	0.01	0.00
A19	1.05	--	302	42	71	.07	.01	.03	.05	.04	.25
A20	.58	2.6	424	143	111	.51	.14	.73	.57	.87	.16
A21	.73	2.6	277	75	175	.08	.03	.06	.14	.09	.37
A22	1.11	--	--	--	--	--	--	--	--	--	--
A23	1.67	--	--	--	--	--	--	--	--	--	--
A24	1.29	--	--	--	--	--	--	--	--	--	--
A25	.88	2.6-2.7	273	0	520	.05	.00	.00	.26	.00	.00
A26	.97	3.0	466	24	13	.68	.03	.16	.09	.19	.16
A27	.79	2.8	459	64	12	.81	.04	.52	.10	.56	.07
A28	1.26	3.0	477	49	14	.70	.11	.34	.10	.45	.24
A29	.58	2.6	441	66	15	.41	.02	.27	.06	.29	.07
A30	.72	--	--	--	--	--	--	--	--	--	--
A31	.66	--	--	--	--	--	--	--	--	--	--
A32	.79	--	--	--	--	--	--	--	--	--	--
A33	.75	--	--	--	--	--	--	--	--	--	--
A34	.63	--	--	--	--	--	--	--	--	--	--
A35	1.60	3.0-3.5	535	5	25	1.26	.49	.06	.32	.55	.89

Analytical Techniques

Clark Geological Services[3] analyzed all samples collected during the course of this investigation (tables 1–6). Determinations were made for thermal maturity and kerogen content by reflected and transmitted light and by Rock-Eval pyrolysis with determination of total organic carbon (TOC). Sample processing consisted of the following steps:

1. The samples were first crushed and split for Rock-Eval analysis and kerogen isolation. To isolate the kerogen, each sample was treated with concentrated HCl, HF, and hot HCl. The rock and organic residue were rinsed clean of acids and density separated by 2.0 specific gravity zinc chloride flotation. Plastic resin strew slides were made from a portion of the organic residue and scanned at 100X for determination of kerogen content and thermal-alteration index (TAI).
2. Other portions of the residue were dried at low temperature and suspended in slow-curing plastic resin on petrographic slides. The hardened resin mounts were ground and polished to 0.05 microns for reflectance evaluation. Reflectance measurements were made on as many as one hundred randomly oriented maceral surfaces, using 546 micron incident light on a Zeiss Universal microscope. Vitrinite histograms were prepared that present all reflectance data collected for each sample; for the primary vitrinite population, the reflectance mean was calculated.

---

[3] Clark Geological Services, 43255 Mission Blvd., Suite C, Fremont, California 94539.

Table 2. Vitrinite reflectance, thermal-alteration index, and Rock-Eval analyses of Hoh melange and broken formation (unit Thm on pl. 1)

[See table 1 for symbol explanation]

Sample No. (see pl. 1)	R_o(pct)	TAI	Rock-Eval parameters								
			T_{max}	HI	OI	TOC	S_1	S_2	S_3	S_1+S_2	PI
			SURFACE SAMPLES								
B1	--	--	434	131	10	1.44	0.25	1.88	0.14	2.13	0.12
B2	2.08	--	--	--	--	--	--	--	--	--	--
B3[1]	.54	2.6	430	401	5	4.76	1.41	19.10	.26	20.51	.07
B4	.56	2.5	439	86	14	.91	.02	.78	.13	.80	.03
B5	.83	2.6-2.7	478	39	101	.61	.01	.24	.62	.25	.04
B6	.64	2.5	443	132	17	1.60	--	--	--	--	--
B7	1.50	3.5	459	2	15	.89	.05	.02	.13	.07	.71
B8	1.23	3.0	463	11	11	1.01	.06	.11	.11	.17	.35
B9	1.15	3.1	451	20	36	.64	.02	.13	.23	.15	.13
B10	1.98	3.0-3.5	--	--	16	.74	.05	--	.12	.05	1.00
B11	1.92	3.0-3.5	508	7	17	.69	.04	.05	.12	.09	.44
B12	.50	2.5	438	40	30	.50	.02	.20	.15	.22	.09
B13	.49	2.5	439	81	22	.83	.12	.67	.18	.79	.15
B14	.53	2.6	443	36	26	.50	.03	.18	.13	.21	.14
B15	.62	2.5	441	109	13	.76	.12	.83	.10	.95	.13
B16	.87	2.7-3.3	459	10	11	.98	.34	.97	.11	1.31	.26
B17	1.04	3.0	475	31	41	.29	.04	.09	.12	.13	.31
B18	1.18	2.7-3.3	467	4	12	.49	.09	.02	.06	.11	.82
B19	.76	2.6	439	92	25	.60	.00	.55	.15	.55	.00
B20	.48	2.5	285	50	850	.02	.00	.01	.17	.01	.00
B21	1.77	--	532	16	12	.99	.43	.16	.12	.59	.73
B22	.96	2.8	467	58	1	.80	.19	.46	.01	.65	.29
B23	1.32	--	485	38	13	.47	.05	.18	.06	.23	.22
B24	1.25	--	486	25	20	.69	.04	.17	.14	.21	.19
B25	1.61	--	399	11	33	.81	.01	.09	.27	.10	.10
B26	1.98	--	459	10	21	.73	.00	.07	.15	.07	.00
B27	.87	--	410	34	145	.44	.00	.15	.64	.15	.00
B28	1.06	--	473	88	75	.48	.06	.42	.36	.48	.13
B29	1.12	--	441	40	50	.40	.08	.16	.20	.24	.33
B30	1.08	--	--	--	--	--	--	--	--	--	--
B31	1.71	--	394	10	39	.28	.01	.03	.11	.004	.23
B32	.39	2.4	--	--	--	--	--	--	--	--	--
B33	.58	--	--	--	--	--	--	--	--	--	--
B34	2.05	--	465	8	45	1.04	.00	.08	.47	.08	.00

Well name (see pl. 1)	Well depth (ft)	R_o(pct)	TAI	Rock-Eval parameters								
				T_{max}	HI	OI	TOC	S_1	S_2	S_3	S_1+S_2	PI
				SUBSURFACE SAMPLES								
Union Oil Co.												
Tidelands No. 2	3868-3885	--	2.4-2.5	409	64	88	1.42	0.12	0.91	1.25	1.03	0.12
Tidelands No. 2	4372-4382	--	2.3	460	44	58	.70	.09	.31	.41	.40	.22
Tidelands No. 2	5055-5073	--	--	451	43	30	.81	.07	.35	.25	.42	.17
Union Oil Co. State No. 3												
SWS84-1	4320-4331	--	--	445	137	48	.54	.61	.74	.26	1.35	.46
SWS84-3	5989-6001	--	--	440	95	30	.96	.34	.92	.29	1.26	.27
SWS84-4	6893-6903	--	--	444	97	89	.88	.35	.86	.79	1.21	.29
SWS84-5	7461-7473	--	--	447	119	35	.88	.44	1.05	.31	1.49	.30
SWS84-6	7820-7840	--	--	445	130	38	.42	.27	.55	.16	.82	.33
SWS84-7	8077-8083	--	--	446	147	16	1.39	.40	2.05	.23	2.45	.16
SWS84-8	8475-8490	--	--	446	49	24	1.14	.18	.56	.28	.74	.24
SWS84-9	8916-8936	--	--	448	126	23	1.13	.78	1.43	.27	2.21	.35
Union Oil Co. Rayonier No. 1												
SWS84-10	400-412	0.50	2.5-2.6	435	88	30	.78	.05	.69	.24	.74	.07
SWS84-11	700-713	.55	2.5-2.6	445	255	77	.09	.01	.23	.07	.24	.04
SWS84-12	1000-1007	.61	2.6-2.7	0	0	83	.06	.00	.00	.05	.00	.00
SWS84-13	1450-1456	.52	2.5	442	176	13	1.17	.16	2.07	.16	2.23	.07
SWS84-14	1683-1690	.52	2.5	438	173	18	.82	.10	1.42	.15	1.52	.07
SWS84-15	2150-2152	.59	2.4	437	88	27	.81	.10	.72	.22	.82	.12
SWS84-16	2274-2280	.57	2.4-2.6	440	235	184	.45	.08	1.06	.83	1.14	.07
Sunshine Mining Co. Medina No. 2												
S84-16	5068-5113	.53	2.4	441	62	24	.50	.05	.31	.12	.36	.14
Shell Oil Co.												
P-0150	6408	.66	--	--	--	--	--	--	--	--	--	--
P-0155	6546-6552	.61	--	--	--	--	--	--	--	--	--	--
Union Oil Co. Milwaukee Land Co. No. 1												
S86-3	4445-5383	.51	--	--	--	--	--	--	--	--	--	--
S86-4	4790-5600	.56	--	--	--	--	--	--	--	--	--	--
Sunshine Mining Co. and Cascade Natural Gas Rayonier No. 1-A												
S86-16	2520-2530	1.09	--	--	--	--	--	--	--	--	--	--
S86-17	6380-6390	1.02	--	--	--	--	--	--	--	--	--	--
S86-18	5690	.58	--	--	--	--	--	--	--	--	--	--
S86-20	6380-6410	.60	--	--	--	--	--	--	--	--	--	--
S86-22	6470-6500	.58	--	--	--	--	--	--	--	--	--	--

---

[1] Carbonaceous layer in sandstone; geochemical data not included in averages

Table 3. Vitrinite reflectance, thermal-alteration index, and Rock-Eval analyses of peripheral rocks (unit Tp on pl. 1)

[Localities listed from younger (C1) to older (C7). Samples C5 and C7 are peripheral rocks exposed east of area shown on pl. 1. See table 1 for symbol explanation]

Sample No. (see pl. 1)	R_o(pct)	TAI	Rock-Eval parameters								
			T_{max}	HI	OI	TOC	S_1	S_2	S_3	S_1+S_2	PI
C1	0.42	2.4	428	54	24	0.87	0.02	0.47	0.21	0.49	0.04
C2	.48	2.5	430	61	22	.41	.00	.25	.09	.25	.00
C3	.52	2.5	428	82	2	.45	.04	.37	.01	.41	.10
C4	.61	2.5-2.6	432	52	20	.34	.01	.18	.07	.19	.06
C5	.51	2.5	441	64	14	.44	.04	.28	.06	.32	.00
C6	.53	2.5	436	59	38	.34	.00	.20	.13	.20	.00
C7	1.68	--	--	--	--	--	--	--	--	--	--

Table 4. Vitrinite reflectance, thermal-alteration index, and Rock-Eval analyses of western core rocks (unit Teu on pl. 1)

[See table 1 for symbol explanation]

Sample No. (see pl. 1)	R_o(pct)	TAI	Rock-Eval parameters								
			T_{max}	HI	OI	TOC	S_1	S_2	S_3	S_1+S_2	PI
D1	1.20	--	--	--	--	--	--	--	--	--	--
D2	1.09	--	--	--	--	--	--	--	--	--	--
D3	1.24	--	507	1	59	0.76	0.00	0.01	0.45	0.01	0.00
D4	1.29	3.1	331	8	50	.12	.00	.01	.06	.01	.00
D5	.85	2.7	460	110	45	.58	.04	.64	.26	.68	.06
D6	1.97	--	506	11	39	.94	.00	.10	.37	.10	.00
D7	1.04	--	340	0	92	.25	.00	.00	.23	.00	.00
D8	1.61	--	319	10	50	.90	.02	.09	.45	.11	.18
D9	.83	--	452	86	119	.43	.09	.37	.51	.46	.20
D10	.92	--	473	35	55	.75	.05	.26	.41	.31	.16
D11	.70	2.6-2.7	393	17	596	.24	.00	.04	1.43	.04	.00
D12	.70	2.6-2.7	360	16	51	.43	.04	.07	.22	.11	.36
D13	.92	--	--	--	--	--	--	--	--	--	--

Table 5. Vitrinite reflectance, thermal-alteration index, and Rock-Eval analyses of rocks from the allochthonous Sooes terrane (unit TJs on pl. 1)

[Snavely and others (1986). See table 1 for symbol explanation]

Sample No. (see pl. 1)	R_o(pct)	TAI	Rock-Eval parameters								
			T_{max}	HI	OI	TOC	S_1	S_2	S_3	S_1+S_2	PI
E1	2.29	3.3-3.7	--	--	13	0.70	0.05	--	0.09	0.05	1.00
E2	.33	2.5	442	0	93	.28	.00	0.00	.26	.00	.00
E3	.68	3.0	349	16	63	.19	.00	.03	.12	.03	.00
E4	.56	2.6	428	24	191	.33	.00	.08	.63	.08	.00
E5	.48	2.5	408	24	0	.25	.00	.06	.00	.06	.00
E6	.41	2.5	437	82	90	.39	.01	.32	.35	.33	.03

Table 6. Vitrinite reflectance, thermal-alteration index, and Rock-Eval analyses of rocks from the terrane between Crescent thrust fault and Calawah fault (unit Tcc on pl. 1)

[Snavely and others (1986). See table 1 for symbol explanation]

Sample No. (see pl. 1)	R_o(pct)	TAI	Rock-Eval parameters								
			T_{max}	HI	OI	TOC	S_1	S_2	S_3	S_1+S_2	PI
F1	1.12	3.1	445	12	45	0.33	0.01	0.04	0.15	0.05	0.00
F2	.74	2.8	423	5	65	.20	.00	.01	.13	.01	.00
F3	.78	--	--	--	--	--	--	--	--	--	--
F4	.44	2.4	286	18	54	.28	.00	.05	.15	.05	.00
F5	1.25	--	--	--	--	--	--	--	--	--	--

KEROGEN TYPES

Visual analyses of kerogen type and results from Rock-Eval pyrolysis show that most of the samples contain type III kerogen as indicated on the modified van Krevelen diagram (fig. 6). Samples consist predominantly of indigenous vitrinite and amorphous material with traces of exinite, inertinite, and reworked vitrinite.

TOTAL ORGANIC CARBON

Total organic carbon (TOC) was measured by Rock-Eval on 76 surface and subsurface samples of the middle and upper Eocene Ozette melange and broken formation (table 1) and the upper Oligocene to upper middle Miocene Hoh melange and broken formation (table 2). The values range from 0.02 to 1.60 percent with most values between 0.4 percent and 0.8 percent. Tissot and Welte (1984) state that potential source rock should have TOC values greater than 0.5 percent; thus, a significant part of the strata in these accretionary terranes can be considered potential source beds for petroleum at least from the point of view of TOC values. However, these continental margin sedimentary rocks are relatively low in organic matter and contain type III terrestrial and recycled kerogen, and they are most likely sources of gas rather than oil.

The organic-carbon content of the strata sampled reflect in large part their depositional environment. The turbidite sandstone and siltstone beds in the Calawah sandstone and siltstone (fig. 2) have an average TOC value of 0.47±0.41 percent (table 1); the low values are probably due to rapid sedimentation that diluted the organic content. The Shi Shi Beach and Ruby Beach siltstone (fig. 2), in which the so-called smell muds occur in melange zones, also have surprisingly low TOC values, averaging 0.50±0.26 percent (table 1). These low values may be due to near surface biodegradation of the organic matter, as the seacliff exposures are commonly weathered and water-saturated. In support of this interpretation, a block of sheared and unweathered siltstone in the Shi Shi Beach melange had a TOC value of 1.21 percent. The organic-carbon content of the surface samples of Hoh melange ranges from 0.02 to 1.60 percent with an average of about 0.71±0.33 percent; subsurface Hoh samples average 0.79±0.38 percent (table 2).

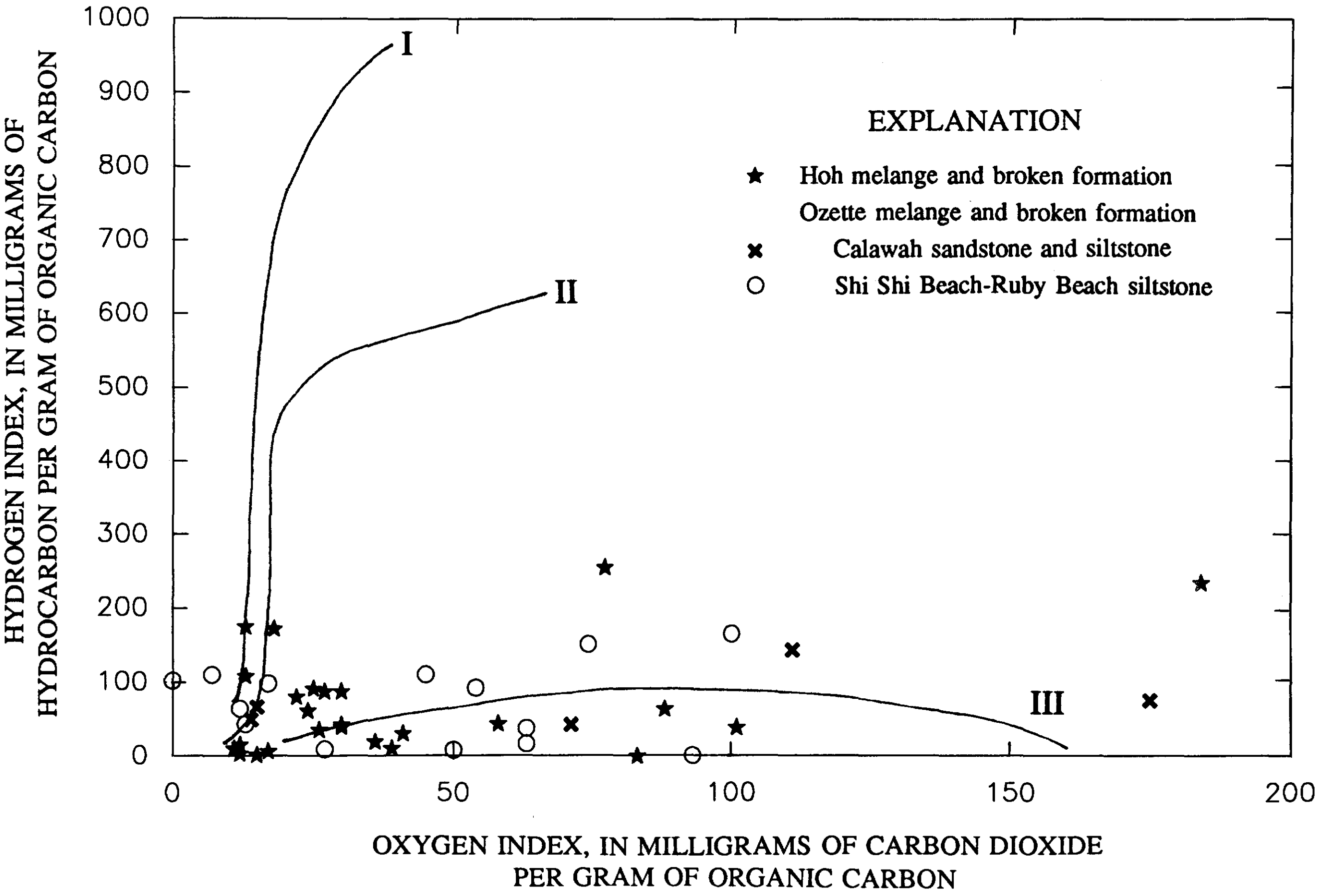

Figure 6. Van Krevelen-type diagram (Tissot and Welte, 1984) showing that organic matter in samples from Ozette and Hoh melanges and broken formations is mostly type III. Type I, algal or oil prone; type II, marine or oil prone; type III, terrestrial or gas prone.

VITRINITE REFLECTANCE (R_o)

An evaluation of the maturation stage for the Ozette and Hoh melanges and broken formations indicates that vitrinite-reflectance (R_o) data are probably the best indicators of the thermal history for most of these type III Tertiary sedimentary rocks. In most cases, the R_o values also provide valuable information on the tectonic setting and account for both time and temperature over the entire maturity range (Dow, 1978). On the basis of the correlation of R_o and temperature established by Price (1983), depth of burial also can be estimated using our calculated gradient of 2.6 °C/100 m (fig. 7). The principal phase of oil and gas generation can be correlated with a random vitrinite-reflectance scale of Dow (1978). If R_o values are considered to be the product of both time and temperature and do not depend upon variation in geothermal gradient or burial history, they are most useful in complex accretionary terranes when burial and erosional histories are difficult to decipher.

Although there is considerable overlap between levels of thermal maturity for the Tertiary sedimentary rocks that crop out in the study area (pl. 1; tables 1–6), certain generalizations can be drawn from vitrinite-reflectance data for 114 surface and subsurface samples collected during this investigation.

1. The moderately deformed peripheral rocks show a general increase in R_o values with increasing stratigraphic age (for example, samples C1–C7 in table 3).
2. For the western core rocks, there is an overall spatial trend of increased thermal maturation from the coast eastward into the eastern core rocks of the Olympic Mountains. There is also a general correlation between R_o values and the distribution of zones of metamorphic minerals outlined on the geologic map of Tabor and Cady (1978b).
3. Due to frictional heating, R_o values in the Ozette and Hoh melanges and broken formations increase abruptly in or adjacent to major faults.
4. The anomalously low R_o values that occur in middle Eocene melanges (microseeps of hydrocarbons) exposed at Shi Shi Beach and Ruby Beach may be attributed to suppression of vitrinite reflectance in these oil-rich sediments—a hypothesis favored with reservation by McCulloh (1979) for a deep test well drilled on the outer continental shelf of southern California off Point Conception. However, our studies show that less deformed middle Eocene strata contain only a trace of oil and correlate with the Shi Shi Beach smell muds; for example, sample A10, table 1, has a low R_o value (0.44 percent), although the PI and T_{max} both indicate a higher level of maturity. Therefore, an alternate

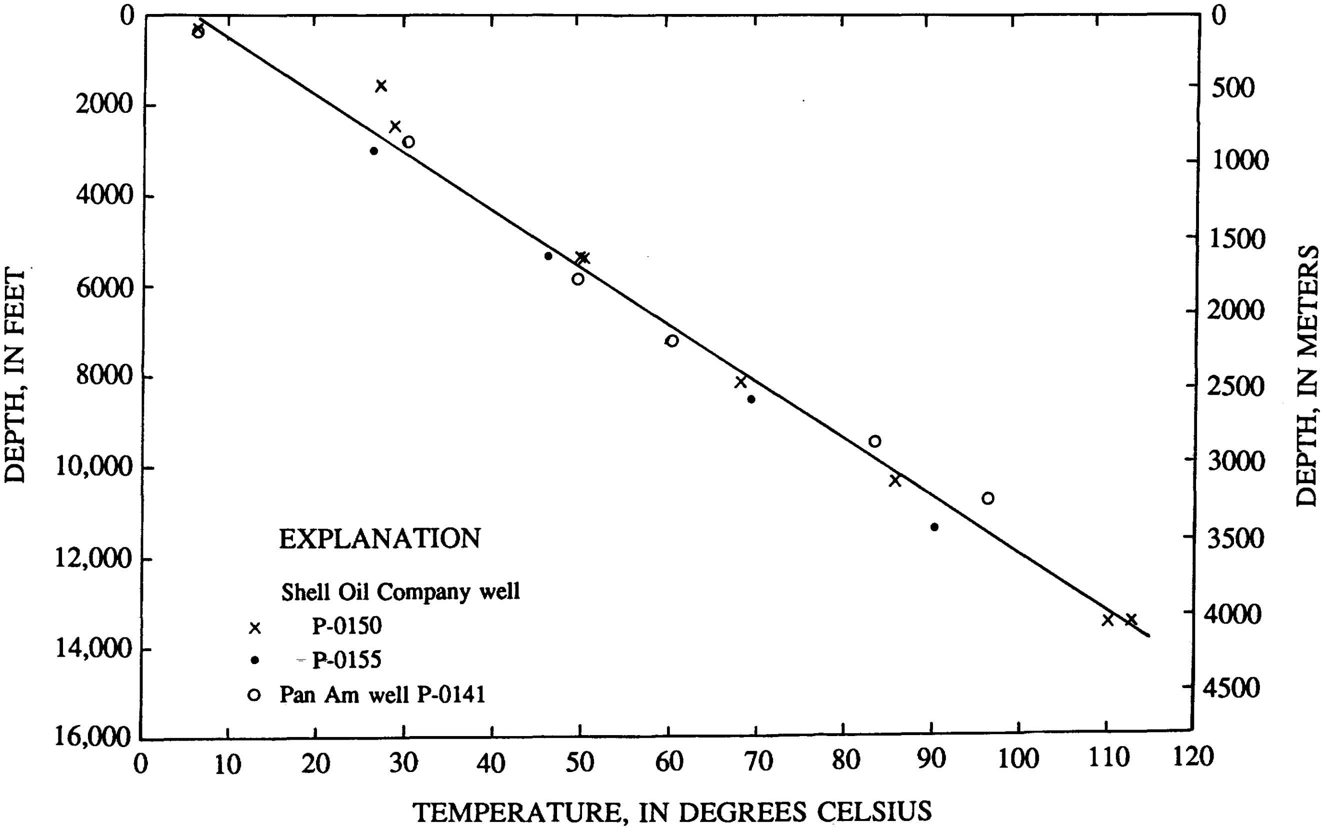

Figure 7. Uncorrected geothermal gradient of 2.60 °C/100 m based on bottom-hole temperatures from wells. Temperature of about 7.5 °C was assigned for sea-floor depth of 100 m (McGary, 1971).

explanation for the low R_o values in these melanges must be considered. One hypothesis that needs to be explored is that high fluid pressures may cause pressure retardation of the vitrinite alteration (McTavish, 1978). As strata below the late Miocene unconformity on the Washington and southern Vancouver Island continental shelves are in an overpressured regime (Shouldice, 1971; Ziegler and Cassell, 1978; Snavely, 1987), perhaps the middle Eocene siltstones in the Ozette melange were overpressured, thus lowering their thermal conductivity. A satisfactory explanation for the occurrence of anomalously low R_o values in some middle Eocene siltstones of the Ozette melange, however, is not evident from our studies. This is particularly puzzling since most of our vitrinite-reflectance values appear compatible with the stratigraphic and tectonic setting of the strata analyzed.

5. On the basis of our geothermal gradient (fig. 7), a higher geothermal gradient may have existed during middle Miocene time, as explained later.
6. Although it is postulated that the Ozette and Hoh melanges and broken formations were formed during two separate episodes of plate convergence, this polyphase deformation is not readily detectable in the thermal maturity of the two melanges, suggesting that the late Oligocene to late middle Miocene subduction may have been responsible for a thermal overprint on these two accretionary wedges that formed near the deformational front along the continental margin.

R_o Values in Ozette Melange

Unnamed Eocene Siltstone and Shi Shi Beach-Ruby Beach Siltstone

Sixteen siltstone samples from these units have R_o values that range from 0.33 to 0.87 percent with an average value of 0.58±0.18 percent (table 1). On the basis of Price's (1983) plot of vitrinite reflectance values versus burial temperature, these R_o values correspond to a peak paleotemperature range of 42 to 169 °C.

Calawah Sandstone and Siltstone

Vitrinite determinations were made on 18 widely spaced samples of Calawah siltstone, and although overprinted by local structures, they indicate a progressive eastward increase in R_o values from 0.58 percent near the coast to 1.67 percent east of the Clearwater fault (table 1, pl. 1). On the basis of the distribution of low-grade metamorphic minerals in the Calawah siltstone, as shown on the map of Tabor and Cady (1978b, unit Two), one would expect R_o values for the Calawah to continue to increase eastward (pl. 1). On the basis of the method of Price (1983), peak paleotemperatures for the Calawah sandstone and siltstone, as reflected by the R_o values, range from 116 to 255 °C with an average R_o value of 0.95±0.33 percent and a corresponding average temperature of 181 °C. If we apply the present-day geothermal gradient of 2.60 °C/100 m, the Calawah sandstone and siltstone along the coast initially would have been buried to a depth of about 4.5 km, whereas east of the Clearwater fault it would have been subducted to a depth of about 10 km.

R_o Values in Hoh Melange and Broken Formation

Siltstone samples collected from surface exposures of the Hoh melange have a wide range of R_o values that vary from 0.39 to 2.08 percent with an average value of 1.11±0.52 percent (table 2). Using Price's (1983) plots of R_o versus temperature, R_o values for the Hoh melange correspond to a peak paleotemperature range of 63 to 284 °C. Anomalously high values greater than 1.0 percent were measured on samples collected adjacent to faults where frictional heating most likely increased the vitrinite reflectance (for example, samples B25–B28, table 2). For surface samples collected in areas where the Hoh melange is only moderately deformed and distant from major faults, R_o values range from 0.39 to 0.96 percent, averaging about 0.66 percent. R_o values for 17 subsurface samples of Hoh siltstone (table 2) range from 0.50 to 1.09 percent, with an average of 0.63±0.17 percent. Two samples with R_o values greater than 1.0 percent in the Sunshine Mining Co. Rayonier No. 1–A well (see inset map, pl. 1) were in shear zones, and their elevated R_o values undoubtedly are due to frictional heating. If these two samples are rejected, the R_o values have a narrow range from 0.50 to 0.66 percent that indicate peak paleotemperatures of 96 to 133 °C. Although based on admittedly sparse sampling, there is an increase in R_o values for the Hoh melange from the coast east of Destruction Island (samples B5 and B6, pl. 1) toward the Clearwater fault (samples B23–B25, pl. 1 and table 2). This eastward increase (0.64 to 1.61 percent R_o) probably reflects the deeper burial of the Hoh melange beneath the Clearwater back thrust, which superimposes lower(?) and middle Eocene sedimentary rocks and basalt (unit Teu) and the Ozette melange (unit Tom) above the Hoh rocks (pl. 1).

Along the coast between Hogsback and Little Hogsback (pl. 1), the R_o values for the structurally complex Hoh melange are unusually high, as these rocks lie in the lower plate of a major north-trending high-angle fault. R_o values for eight samples collected in the seacliffs range from 1.06 to 1.98 percent, averaging 1.47 percent. These high values are inferred to result from frictional heating along the fault. Alternatively, the structurally complex Hoh rocks in this area may be an uplifted segment (welt) of Hoh melange which originally was within a mega-shear zone immediately above the underplated Ozette melange.

Anomalies in R_o Values Versus Present-Day Geothermal Gradient

Shell Oil Co. P–0150 and P–0155 wells (on the inner shelf off Grays Harbor) and Pan Am P–0141 well (pl. 1) were drilled on diapiric structures having cores composed of Hoh melange (for example, Shell P–0155 well; Snavely and Wagner, 1982). On the basis of the plot of vitrinite-reflectance values versus burial temperature (Price, 1983), R_o values of several core samples from these wells are elevated relative to expected values based on the present-day geothermal gradient (fig. 7). For example, side wall core samples from Shell P–0155 well at a depth of 1,980 m (6,500 ft) have a R_o value of 0.61 percent, and from Shell P–0150 well at a depth of 1,950 m (6,408 ft) have a R_o value of 0.66 percent (table 2). These R_o values correlate with peak paleotemperatures of 122 and 133 °C according to the method of Price (1983). When compared to the present-day geothermal gradient of 2.60 °C/100 m, these paleotemperatures indicate burial depths of 3,170 and 3,460 m, or 1,200 to 1,300 m deeper burial than present. These observations suggest that the overpressured siltstones (Snavely, 1987) have been diapirically uplifted more than 1,000 m. Although part of the Hoh melange in the structures drilled by Shell Oil Co. has been removed by erosion along the base of the late Miocene unconformity, there is no conclusive evidence on seismic profiles to indicate that erosion has removed more than a few hundred meters of middle Miocene and older strata (Snavely and Wagner, 1982). An alternate explanation for the high R_o values for siltstone samples in Shell Oil Company wells P–0150 and P–0155, as compared to the present-day geothermal gradient, may involve cooling of the Tertiary sequence after temperatures were elevated during subduction of the warm upper(?) Miocene Juan de Fuca plate when the spreading center was close to the continental margin, as suggested by plate models of Engebretson and others (1985).

Vitrinite Reflectance (R_o) Versus Rock-Eval Temperature (T_{max})

The temperature at which maximum thermal cracking occurs during Rock-Eval pyrolysis is referred to as T_{max}, and its values increase with maturation. The R_o values are based on indigenous vitrinite, whereas T_{max} values are based on the combined pyrolysis products of all macerals.

The relation between R_o and T_{max} for the Ozette and Hoh melanges and broken formations is plotted on figure 8 along with the expected relation between these two parameters as determined by Dow and O'Connor (1982). Samples of the middle Eocene Shi Shi Beach-Ruby Beach siltstone plot near Dow and O'Connor's (1982) expected line, and values for the upper Oligocene to middle Miocene Hoh melange also fall along this line at R_o values less than 1.4 percent. However, most of the Calawah sandstone and

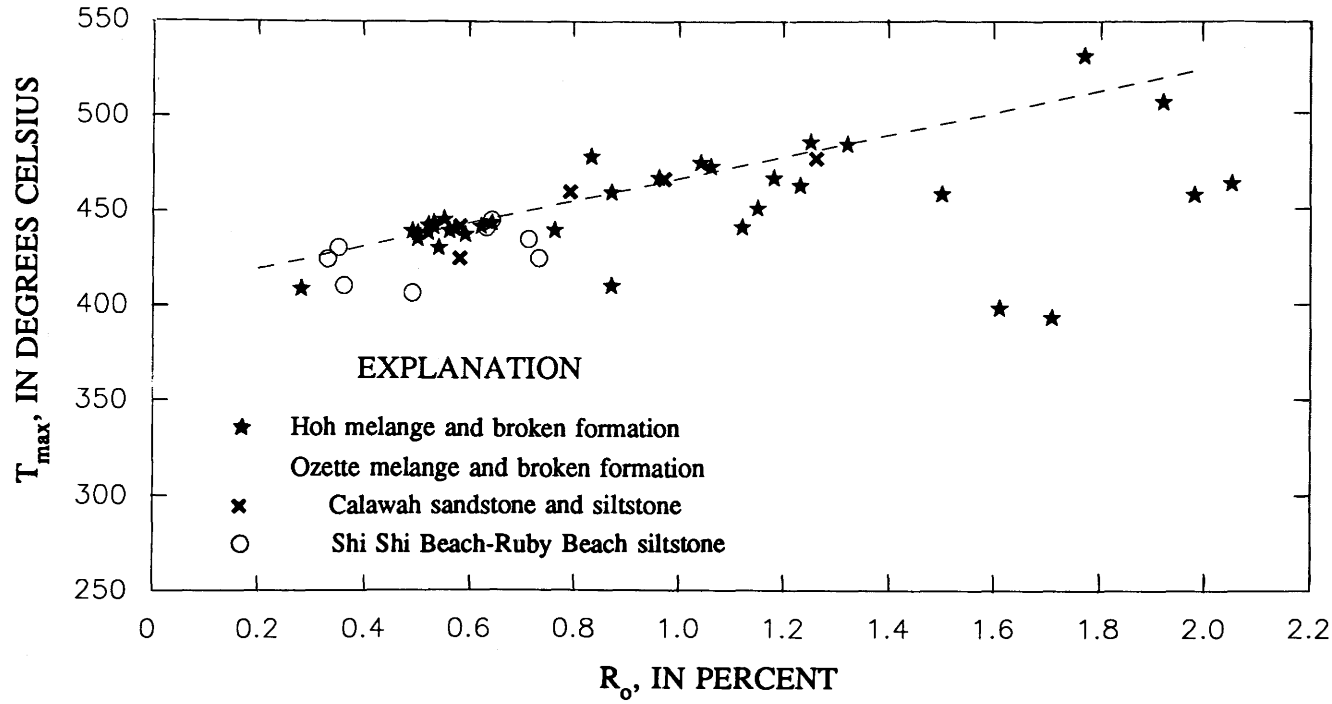

Figure 8. Rock-Eval temperature (T_{max}) versus vitrinite reflectance (R_o) for Ozette and Hoh melanges and broken formations. Dashed line is expected relation as determined by Dow and O'Connor (1982). T_{max} values for samples that have small S_2 peaks (less than 0.2 mg hydrocarbon/g rock) are not shown.

siltstone samples, several Shi Shi Beach-Ruby Beach siltstone samples, and Hoh samples fall well below Dow and O'Connor's (1982) line. These values were rejected because these samples have small S_2 peaks. According to Peters (1986), S_2 peaks of less than 0.2 mg HC/gram of rock give anomalous T_{max} values. The scattered points with R_o values of greater than 1.4 percent are from samples near major faults or from rocks that were deeply buried in the accretionary wedge and suggest that a general linear relation between R_o and T_{max} does not exist where R_o values are exceptionally high.

Vitrinite Reflectance (R_o) Versus Thermal-Alteration Index (TAI)

Thermal-alteration index is measured on a color scale that ranges from 1 to 5, where higher values indicate higher maturity (Staplin, 1969). Inasmuch as vitrinite-reflectance values also are an index of thermal maturity, plots of TAI and R_o values should show a positive correlation. Figure 9 is a plot of the thermal-alteration index versus vitrinite reflectance (R_o) for samples analyzed for the Ozette and Hoh melanges and broken formations. Our data are scattered about the predicted correlation line of Waples (1980) and show the predicted increase in TAI values with higher R_o values. The scatter shown in figure 9 may be due to the presence of reworked material, macerals misidentified as vitrinite, or contamination.

OIL SOURCE ROCKS

Although oil shows are reported in strata as young as late Miocene (Rau and McFarland, 1982), the highest concentrations (including the 12,000 barrels produced from Sunshine Mining Co. Medina No. 1; see inset map, pl. 1) occur in fractured middle Miocene sandstone and siltstone of the Hoh melange and broken formation. The only in situ oil occurs in microseeps in unnamed middle Eocene melanges exposed at Shi Shi Beach and at Ruby Beach. Significantly, the oils from the Shi Shi Beach and Ruby Beach microseeps correlate geochemically with oil from the Jefferson oil seep and the oil produced from Sunshine Mining Co. Medina No. 1 well (see chap. B, this report). The Shi Shi Beach seep is about 140 km north of the Sunshine Mining Co. Medina No. 1 well (pl. 1) indicating that the oil was generated from a mutual, widespread

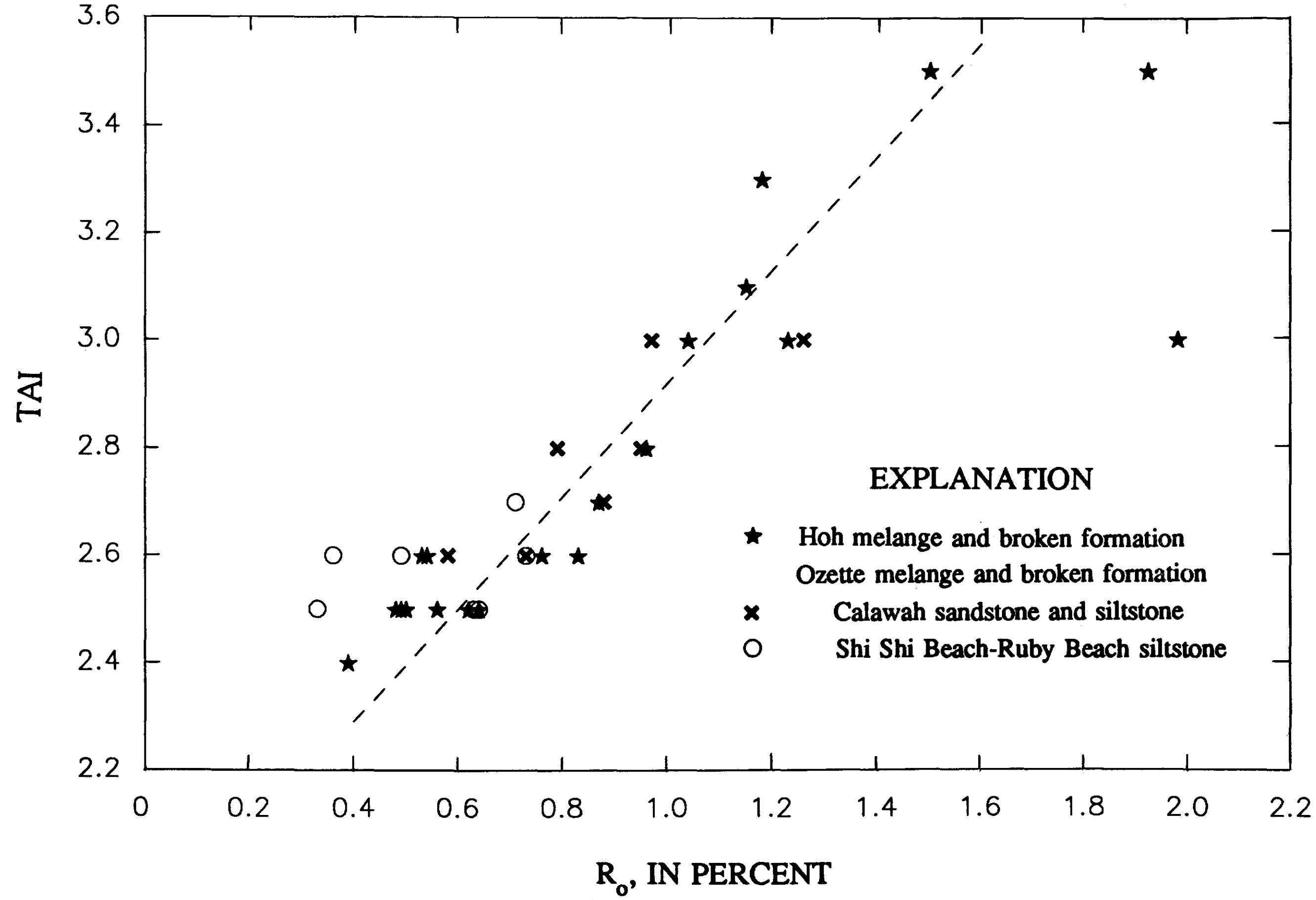

Figure 9. Thermal-alteration index (TAI) versus vitrinite reflectance (R_o) for samples of Ozette and Hoh melanges and broken formations. Dashed line shows predicted correlation line of Waples (1980).

source rock of probable middle Eocene age. The fact that Hoh melange is not present either onshore or offshore in the Shi Shi Beach area (Snavely and others, 1986), supports the interpretation that oil in the Shi Shi Beach microseep could not have been generated from rocks of middle Miocene age.

HYDROCARBON MIGRATION

Numerous shows of oil in test wells are reported in the Hoh rocks that lie immediately below the late Miocene regional unconformity at the base of the Quinault Formation (Rau, 1970; Rau and McFarland, 1982). Approximately 50 exploratory wells have been drilled along the west coast of the Olympic Peninsula, and more than one-half of these wells have reported significant shows of gas and, less commonly, shows of oil. This exploration drilling indicates that the highest concentration of hydrocarbons occurs principally in two widely separated areas near the coast. The northern area is about 2 km north of the mouth of the Hoh River (for example, the Jefferson oil seep); the southern concentration is 2.5 km northwest of Grays Harbor (for example, the Sunshine Mining Co. Medina No. 1 well; see inset map, pl. 1). Whether this bimodal distribution of wells with substantial shows of oil and gas simply reflects drilling activity or is meaningful in terms of hydrocarbon migration pathway is unclear because much of the coastal area is masked by thick deposits of lower and upper Pleistocene glacial outwash.

A general pattern of gas and oil distribution in the middle Eocene to upper middle Miocene melange and broken formations can only be surmised because of limited subsurface data. However, hydrocarbon-bearing pore fluids expelled from an eastward subducted Olympic accretionary prism would be expected to migrate westward and upward, perhaps along major east-dipping thrust faults. Oil appears to have migrated farther westward as oil shows, and minor production occurs in wells drilled near the coast (for example, the Jefferson oil seep and Grays Harbor areas). Gas seeps (for example, the Garfield gas mounds) and shows of gas in numerous wells also occur near the coast; however, gas also occurs farther east in wells drilled in the Forks area and as far east as the Sol Duc Hot Springs gas seep (pl. 1; see chap. C, this report). In the latter area, the source of the gas is probably from lower(?) and middle Eocene core rocks that initially were deeply buried in the accretionary wedge, for these rocks have vitrinite-reflectance values greater than 2.5 percent.

The geologic controls for the concentration of hydrocarbons near the coast are speculated to have been a set of major north-trending, westward-dipping high-angle reverse or thrust faults that generally parallel the coast from near Grays Harbor northward about 130 km to Ozette Island (pl. 1). The hydrocarbon-bearing middle Eocene siltstone at Ruby Beach lies in the lower plate of a high-angle reverse fault that juxtaposes upper Oligocene conglomerate and sandstone and the middle Eocene siltstone. North of the Hoh River, a generally north-trending fault(s) lies just west of the Jefferson oil seep area. The fault intersects the coastline just east of Hoh Head where thick-bedded upper Oligocene turbidite sandstone is in fault contact with Eocene siltstone. Much farther north, just north of the Point of the Arches (pl. 1), upper Eocene and older strata are thrust over the hydrocarbon-bearing middle Eocene melange at Shi Shi Beach (Snavely and others, 1986).

One might speculate, therefore, that a north-south-trending set of faults may have formed a barrier to the westward migration of oil and gas that were generated farther east and were expelled from a progressively more deeply buried part of the accretionary prism. The gas and oil appear to have migrated upward along the coastal fault zones and were concentrated in fault traps or folds in Eocene or middle Miocene rocks, or along the unconformity at the base of upper Miocene strata.

REFERENCES CITED

Brown, R.D., Jr., Gower, H.D., and Snavely, P.D., Jr., 1960, Geology of the Lake Crescent-Port Angeles area, Washington: U.S. Geological Survey Oil and Gas Investigation Map OM-203, scale 1:62,500.

Clowes, R.M., Brandon, M.T., Green, A.G., Yorath, C.J., Sutherland Brown, A., Kanasewich, E.R., and Spencer, C., 1987, Lithoprobe-Southern Vancouver Island—Cenozoic subduction complex imaged by deep seismic reflections: Canadian Journal of Earth Sciences, v. 24, no. 1, p. 31–51.

Dow, W.G., 1978, Petroleum source beds on continental slopes and rises: American Association of Petroleum Geologists Bulletin, v. 62, no. 9, p. 1584–1606.

Dow, W.G., and O'Connor, D.I., 1982, Kerogen maturity and type by reflected light microscopy applied to petroleum exploration, *in* Staplin, F.L. and others, eds., How to assess maturation and paleotemperatures: Society of Economic Paleontologists and Mineralogists, Short Course Number 7, p. 133–157.

Engebretson, D.C., Cox, A., and Gordon, R.G., 1985, Relative motions between oceanic and continental plates in the Pacific basin: Geological Society of America Special Paper 206, 59 p.

Glover, S.L., 1936, Preliminary report on petroleum and natural gas in Washington: Washington Division of Geology Report of Investigations, no. 4, p. 1–24.

Gower, H.D., 1960, Geology of the Pysht Quadrangle, Washington: U.S. Geological Survey Geologic Quadrangle Map GQ–129, scale 1:62,500.

Koch, A.J., 1968, Petrology of the "Hoh Formation" of Tertiary age in the vicinity of the Raft River, western Washington: Seattle, University of Washington, M.S. thesis, 185 p.

MacLeod, N.S., Tiffin, D.L., Snavely, P.D., Jr., and Currie, R.G., 1977, Geologic interpretation of magnetic and gravity anomalies in the Strait of Juan de Fuca, U.S.-Canada: Canadian Journal of Earth Sciences, v. 14, no. 2, p. 223–238.

McCulloh, T.H., 1979, Implications for petroleum appraisal, *in* Cook, H.E., ed., Geologic studies of the Point Conception deep stratigraphic test well OCS–CAL 78–164 No. 1, outer continental shelf, southern California, United States: U.S. Geological Survey Open-File Report 79-1218, p. 26–42.

McGary, N.B., 1971, An atlas of the Columbia River effluent and its distribution at sea: University of Washington Department of Oceanography Special Report Number 47.

McTavish, R.A., 1978, Pressure retardation of vitrinite diagenesis, offshore north-west Europe: Nature, v. 271, p. 648–650.

Peters, K.E., 1986, Guidelines for evaluating petroleum source rock using programmed pyrolysis: American Association of Petroleum Geologists Bulletin, v. 70, no. 3, p. 318–329.

Price, L.C., 1983, Geologic time as a parameter in organic metamorphism and vitrinite reflectance as an absolute paleogeothermometer: Journal of Petroleum Geology, v. 6, no. 1, p. 5–38.

Rau, W.W., 1964, Foraminifera from the northern Olympic Peninsula, Washington: U.S. Geological Survey Professional Paper 374–G, 33 p.

———1970, Foraminifera, stratigraphy and paleoecology of the Quinault Formation, Point Grenville-Raft River coastal area, Washington: Washington Division of Mines and Geology Bulletin, no. 62, 40 p.

———1975, Geologic map of the Destruction Island and Taholah quadrangles, Washington: Washington Division of Geology and Earth Resources Geologic Map GM–13, scale 1:62,500.

———1979, Geologic map in the vicinity of the lower Bogachiel and Hoh River valleys, and the Washington Coast: Washington Division of Geology and Earth Resources Geologic Map GM–24, scale 1:62,500.

Rau, W.W., and McFarland, C.R., 1982, Coastal wells of Washington: Washington Division of Geology and Earth Resources Report of Investigations 26, 4 sheets.

Shouldice, D.H., 1971, Geology of the western Canadian continental shelf: Canadian Petroleum Geology Bulletin, v. 19, no. 2, p. 405–436.

Snavely, P.D., Jr., 1983, Peripheral rocks—Tertiary geology of the northwestern part of the Olympic Peninsula, Washington, *in* Muller, J.E., Snavely, P.D., Jr., and Tabor, R.W., eds., The Tertiary Olympic terrane, southwest Vancouver Island and northwest Washington: Geological Association of Canada, Mineralogical Association of Canada, Canadian Geophysical Union Field Trip Guidebook, Trip 12, 59 p.

———1987, Tertiary geologic framework, neotectonics, and petroleum potential of the Oregon-Washington Continental Margin, *in* Scholl, D.W., Grantz, A., and Vedder, J.G., eds., Geology and resource potential of the continental margin of western North America and adjacent ocean basins—Beaufort Sea to Baja California: Houston, Texas, Circum-Pacific Council for Energy and Mineral Resources, Earth Science Series, Volume 6, p. 305–335.

Snavely, P.D., Jr., MacLeod, N.S., Niem, A.R., and Minasian, D.L., 1986, Geologic map of Cape Flattery area, northwestern Olympic Peninsula Washington: U.S. Geological Survey Open-File Report 86–344B.

Snavely, P.D., Jr., Niem, A.R., MacLeod, N.S., Pearl, J.E., and Rau, W.W., 1980a, Makah Formation—a deep marginal basin sedimentary sequence of late Eocene and Oligocene age in the northwestern Olympic Peninsula, Washington: U.S. Geological Survey Professional Paper 1162–B, 28 p.

Snavely, P.D., Jr., Niem, A.R., and Pearl, J.E., 1978, Twin River Group (upper Eocene to lower Miocene)-Defined: U.S. Geological Survey Bulletin 1457–A, p. A111–A120.

Snavely, P.D., Jr., and Wagner, H.C., 1981, Geologic cross section across the continental margin off Cape Flattery, Washington and Vancouver Island, British Columbia: U.S. Geological Survey Open-File Report 81-0978, 6 p.

———1982, Geologic cross section across the continental margin of southwestern Washington: U.S. Geological Survey Open-File Report 82-459, 10 p.

Snavely, P.D., Jr., Wagner, H.C., and Lander, D.L., 1980b, Geological cross section of the central Oregon continental margin: Geological Society of America Map and Chart Series MC–28J, scale 1:250,000.

Snavely, P.D., Jr., Wagner, H.C., and Rau, W.W., 1982, Sections showing biostratigraphy and correlation of Tertiary rocks penetrated in wells drilled on the southern Oregon continental margin: U.S. Geological Survey Miscellaneous Field Studies Map MF–1482, 1 sheet.

Staplin, F.L., 1969, Sedimentary organic matter, organic metamorphism, and oil and gas occurrence: Canadian Petroleum Geology Bulletin, v. 17, p. 47–66.

Stewart, R.J., 1970, Petrology, metamorphism, and structural relations of graywackes in the western Olympic Peninsula, Washington: Stanford, Stanford University, Ph.D. dissertation, 129 p.

Tabor, R.W., 1983, Eastern core rocks of the Olympic Mountains, Washington, *in* Muller, J.E., Snavely, P.D., Jr., and Tabor, R.W., eds., The Tertiary Olympic terrane, southwest Vancouver Island and northwest Washington: Geological Association of Canada, Mineralogical Association of Canada, Canadian Geophysical Union Field Trip Guidebook, Trip 12, 59 p.

Tabor, R.W., and Cady, W.M., 1978a, The structure of the Olympic Mountains, Washington—analysis of a subduction zone: U.S. Geological Survey Professional Paper 1033, 38 p.

———1978b, Geologic map of the Olympic Peninsula, Washington: U.S. Geological Survey Miscellaneous Investigations Map I–994, scale 1:125,000.

Tissot, B.P., and Welte, D.H., 1984, Petroleum formation and occurrence (2d ed.): Berlin, Springer-Verlag, 699 p.

Waples, Douglas, 1980, Time and temperature in petroleum formation—application of Lopatin's method of petroleum exploration: American Association of Petroleum Geologists Bulletin, v. 64, no. 6, p. 916–926.

Ziegler, D.L., and Cassell, J.K., 1978, A synthesis of OCS well information, offshore Central and Northern California, Oregon, and Washington, *in* Hill, F.L., Coordinator, Energy Exploration and Politics pre-print: California Division of Oil and Gas, 27 p.

Chapter B

Comparison of Molecular Markers in Oil and Rock Extracts

By KEITH A. KVENVOLDEN, JOHN B. RAPP,
FRANCES D. HOSTETTLER, and PARKE D. SNAVELY, JR.

U.S. GEOLOGICAL SURVEY BULLETIN 1892

PRELIMINARY EVALUATION OF THE PETROLEUM POTENTIAL OF THE TERTIARY ACCRETIONARY TERRANE, WEST SIDE OF THE OLYMPIC PENINSULA, WASHINGTON

CONTENTS

FIGURES

TABLES

Comparison of Molecular Markers in Oil and Rock Extracts

By Keith A. Kvenvolden, John B. Rapp, Frances D. Hostettler, *and*
Parke D. Snavely, JR.

Abstract

A petroleum geochemical assessment has been made of the middle and upper Eocene Ozette melange and broken formation and the upper Oligocene and middle Miocene Hoh melange and broken formation exposed in coastal outcrops along the west side of the Olympic Peninsula, Wash. Molecular markers in extracts of eight samples of melange have been compared with molecular markers in crude oil obtained from reservoirs in the middle Miocene Hoh melange from the Sunshine Mining Co. Medina No. 1 well and with oil from the Jefferson oil seep located 80 km north of the well. Our results suggest that the oil from the well and the seep are genetically related. Furthermore, molecular markers in extracts of middle Eocene Ozette melange smell muds, so-called because they emit a petroliferous odor, indicate that the extracts have many features in common with those from oil of the Medina No. 1 well and Jefferson oil seep; thus, the smell muds contain small amounts of migrated petroleum. Thus, hydrocarbon mixtures having similar molecular characteristics occur along coastal Washington from Grays Harbor north almost to Cape Flattery, a distance of about 140 km. The probable source of these hydrocarbon mixtures is the Eocene Ozette melange, although its source-rock characteristics are marginal. Thrust faults in this unit probably provide the conduits for the migration of hydrocarbons.

INTRODUCTION

One important advance in petroleum geochemistry has been the recognition and use of specific organic compounds, here called molecular markers, for the understanding of possible relations among crude oils and their potential source rocks. Increasingly complex hydrocarbon molecules, such as straight-chain alkanes, branched-chain alkanes, and cycloalkanes, are used for correlation purposes. These kinds of molecules can be considered chemical fossils in that their original carbon skeletons were initially established by their biological precursors. Molecular markers, particularly the cycloalkanes, triterpanes, and steranes, provide powerful tools for understanding the petroleum geochemistry of rocks and oils (Seifert and Moldowan, 1978; Mackenzie, 1984; Philp, 1985a).

In our study of the deep-source hydrocarbon potential of the Olympic Peninsula of Washington, we have focused on the regional properties of kerogen relative to deep-source hydrocarbons (see Snavely and Kvenvolden, chap. A of this report) and on the hydrocarbon chemistry of gas seeps (see Kvenvolden, Golan-Bac, and Snavely, chap. C of this report). This work, interpreted within the complex geologic framework of the area, has led to the tentative conclusion that the probable source of gas, and perhaps oil, is in the middle Eocene Ozette melange. Although this unit has only marginal source-rock characteristics, it is the most likely candidate. Our results, in which we have applied molecular marker geochemistry, support this interpretation regarding the source-rock potential of the Ozette melange.

ACKNOWLEDGMENTS

This project was partially funded by the Department of Energy under Interagency Agreement No. DE–AI21–87–MC20422.502. We are particularly grateful to W.J. Gwilliam, Department of Energy, for his support of this project and to K. Peters, Chevron Oil Field Research Company, for constructive comments and suggestions.

METHODS

Eight samples of melange were selected from coastal outcrops along the west side of the Olympic Peninsula, Wash. (fig. 1). The samples are described in table 1 and are referred to by sample number or locality. Our original strategy was to examine two widely spaced samples of middle Eocene Ozette melange smell muds, so-called because they emit a petroliferous odor; smell mud sample S85–119 was collected at Ruby Beach and S85–121 at Shi Shi Beach (fig. 1). These samples were compared with smell mud sample S84–31 from a locality at Giants Graveyard; the age of this sample is uncertain and may be either middle Miocene Hoh melange or middle Eocene Ozette melange. These smell muds were compared in turn with a sample (S84–21), which had no petroliferous odor, from the Hogsback locality of Hoh melange. An additional four

---

Manuscript approved for publication, April 20, 1989.

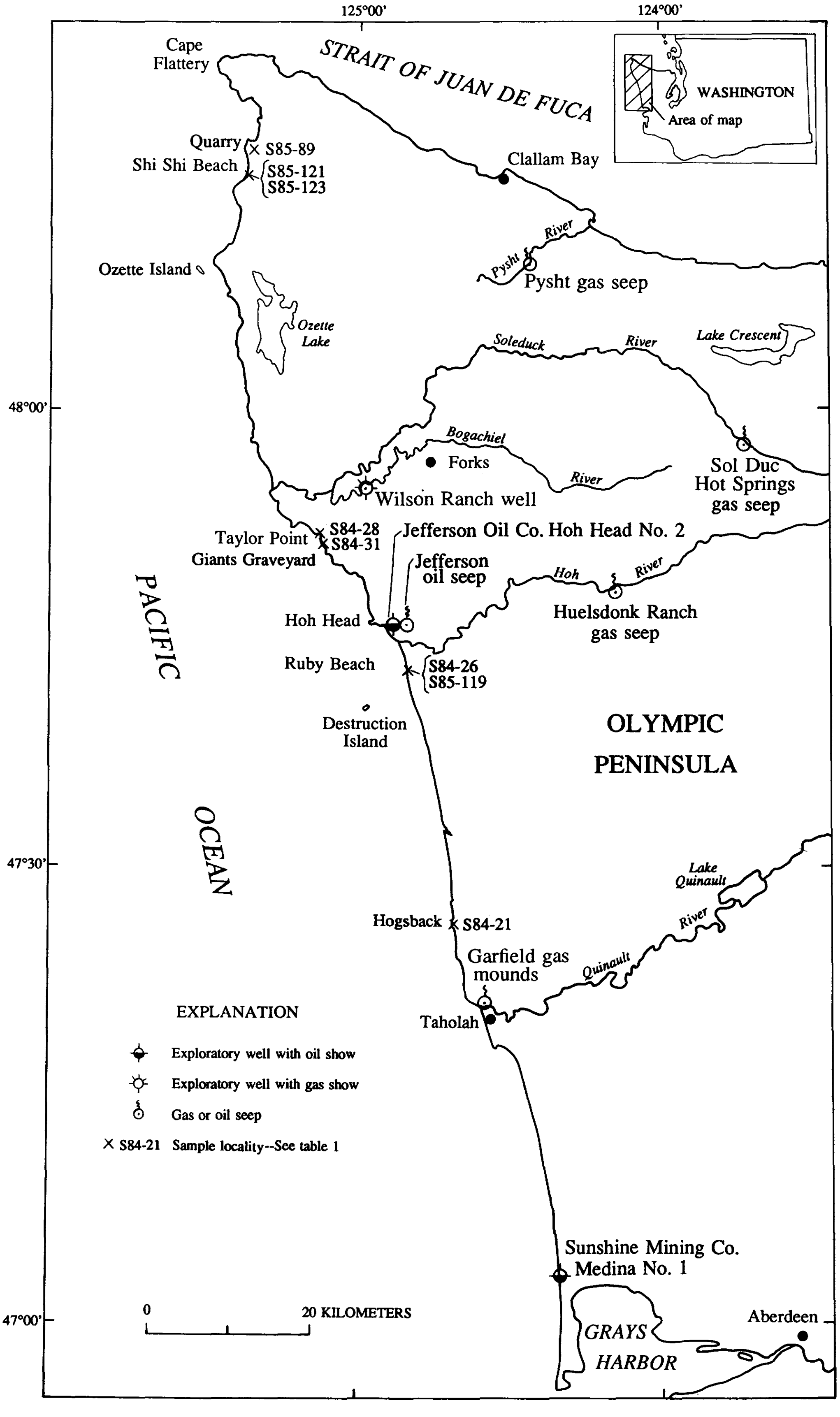

Figure 1. Outcrop and oil-sample localities on west coast of Olympic Peninsula, Washington.

samples were analyzed to answer questions raised by the results obtained from the first four samples. These additional samples include a second sample (S85–123) from Shi Shi Beach, a sample (S85–89) of Ozette melange that also had no petroliferous odor, a second sample (S84–28) of Hoh melange having no petroliferous odor, and a Hoh melange sandstone sample (S84–26) having a slight petroleum odor (fig. 1).

The results obtained from these eight rock samples were compared with results from the analysis of two oil samples (table 2). One oil sample came from the Sunshine Mining Co. Medina No. 1 well located north of Grays Harbor (fig. 1). This well produced a total of 12,000 barrels of 38° API (American Petroleum Institute) gravity, paraffin-base oil reservoired in middle Miocene Hoh melange and broken formation. The second oil sample came from the Jefferson oil seep and was collected from a standpipe near the Jefferson Oil Co. Hoh Head No. 2 well, which is located about 80 km north of the Medina No. 1 well. For geochemical analyses, samples of each oil were weighed (50 mg) and diluted to 5 mL with n-hexane.

The eight rock samples were crushed, and portions were removed for Rock-Eval pyrolysis,[1] kerogen isolation and examination,[1] and for extraction and detailed analytical geochemical measurements. For Rock-Eval pyrolysis about 100 mg of crushed sample was analyzed directly to yield the standard Rock-Eval parameters (Tissot and Welte, 1984) plus total organic carbon (TOC). For kerogen isolation, all samples were treated with HCl, HF, and hot HCl. Rock and organic residues were rinsed and density separated by zinc chloride flotation. Plastic resin strew slides were made from a portion of the organic residues for visual kerogen analysis, which included microscopic examination at 100X for kerogen content and thermal-alteration index (TAI). Another portion of the residue was dried at low temperature and suspended in slow-curing plastic resin on a petrographic slide. The hardened resin mount was ground and polished to 0.05 microns for determination of vitrinite reflectance (R_o). R_o measurements were made on as many as 100 maceral surfaces under oil using 546 micron incident light on a Zeiss Universal microscope. A mean R_o value for each sample was determined from a histogram representing all of the R_o values determined for vitrinite macerals in that sample.

A portion of each rock sample was pulverized in a mortar and pestle. The procedures for extracting and identifying hydrocarbons followed those of Kvenvolden and others (1985) and are briefly summarized here: 50 g of pulverized (<32 mesh) rock were triple extracted with dichloromethane by shaking on a wrist-action shaker. The extracts, recovered by centrifugation, were combined, filtered, and concentrated by rotary evaporation. Sulfur was removed by filtration through activated copper. A portion of the filtrate was removed for determination of the weight of the extractable organic material (EOM). The dichloromethane solvent was then exchanged with n-hexane.

The rock extracts and oil samples in n-hexane were fractionated by liquid-solid chromatography using a column packed with activated silica gel and deactivated alumina. The column was sequentially eluted with n-hexane, benzene, and methanol to yield fractions containing aliphatic hydrocarbons, aromatic hydrocarbons, and polar organic compounds, respectively. Portions of the fractions were removed for weight determinations. The aliphatic hydrocarbons were studied in detail by high resolution, capillary gas chromatography using a 30 m x 0.3 mm DB–1 bonded-phase, fused-silica column. Chromatograms of the aliphatic hydrocarbons are shown in figure 2. Portions of the n-hexane fraction were examined by gas chromotography-mass spectrometry as described in Kvenvolden and others (1985). Single ion monitoring (SIM) of m/z 191 and 217 produced mass chromatograms from which terpanes and triterpanes (fig. 3) and steranes and diasteranes (fig. 4), respectively, were identified and compared. In addition, we monitored m/z 177 because this ion is useful in identifying nuclear demethylated hopanes, which are indicative of severe biodegradation (Volkman and others, 1983). We did not find demethylated hopanes even in biodegraded samples, but the m/z 177 mass chromatograms of all samples have three major closely spaced peaks having molecular ions of m/z 384 (fig. 5). The mass spectrum of the compound giving rise to chromatographic peak c on figure 5 has a mass spectral base peak of m/z 177 and major fragment ions at m/z 192, 217, 341, 369, and 384. The mass spectrum is similar to that of 17α(H)-23,28-bisnorlupane (Philp, 1985b, p. 190).

RESULTS AND DISCUSSION

General Geochemistry

Geochemical results obtained on the eight samples of melange are summarized in table 3. These results are interpreted following guidelines established by Hunt (1979), Poole and Claypool (1984), and Peters (1986). Organic carbon is a fundamental parameter in source-rock evaluations; however, its lower limit for potential source rocks has not been clearly established. R_o and TAI are used to judge the maturity of the kerogen present in the possible source rock. The Rock-Eval pyrolysis assay measures (1) free hydrocarbons in the rock (S_1), (2) hydrocarbons that evolve during pyrolysis (S_2), and (3) carbon dioxide released during pyrolysis (S_3). These measurements are used to interpret the quality, type, and maturity of organic matter in possible source rocks.

The TOC content of the eight melange samples used in this study range from 0.26 to 0.89 percent (table 3). This range of values makes these samples poor to fair source

---

[1] These determinations were made by Clark Geological Services, 43255 Mission Blvd., Suite C, Fremont, California 94539.

Table 1. Descriptions of rock samples and kerogen

[See fig. 1 for locations of samples]

Sample No.	Location	Geologic unit	Age	Sample description	Kerogen description
S85-119	Ruby Beach. Collected at coastal outcrop opposite Abbey Island.	Ozette melange	Middle Eocene	Sample of melange smell mud. Dark-gray mudstone associated with siltstone clasts.	Reflected light: Predominantly indigenous vitrinite. Very common amorphous material. Traces of exinite, inertinite, and reworked vitrinite. Transmitted light: Predominantly coaly fragments. Very common aggregated amorphous kerogen. Traces of fine amorphous kerogen, pollen, and spores.
S85-121	Shi Shi Beach. Collected at coastal outcrop at south end of beach north of Petroleum Creek.	Ozette melange	Middle Eocene	Sample of melange smell mud. Dark-gray mudstone.	Reflected light: Predominantly amorphous material. Abundant indigenous vitrinite. Transmitted light: Abundant coaly fragments. Very common fine amorphous and aggregated amorphous kerogen. Traces of pollen, spores, and woody fragments.
S84-31	Giants Graveyard. Collected at coastal outcrop south of point at Giants Graveyard.	Ozette(?) melange (May be middle Miocene Hoh melange)	Middle Eocene(?)	Sample of melange smell mud. Dark-gray mudstone.	Reflected light: Abundant amorphous material and indigenous vitrinite. Traces of exinite, inertinite, and reworked vitrinite. Indigenous vitrinite degraded. Transmitted light: Predominantly coaly fragments. Abundant aggregated amorphous kerogen. Traces of fine amorphous kerogen, and pollen, and spores.
S84-21	Hogsback. Collected at coastal outcrop between Hogsback and Little Hogsback south of Tunnel Island.	Hoh melange	Middle Miocene	Sample of melange mudstone (no petroliferous odor). Gray mudstone.	Reflected light: Predominantly amorphous material. Abundant indigenous and reworked vitrinite. Indigenous vitrinite degraded. Transmitted light: Abundant aggregated amorphous kerogen and fine-grained amorphous kerogen. Very common coaly fragments.
S85-123	Shi Shi Beach. Collected in same general area as S85-121.	Ozette melange	Middle Eocene	Sample of melange smell mud. Dark-gray mudstone.	Reflected light: Abundant amorphous material and indigenous vitrinite. Common exinite. Trace inertinite. Transmitted light: Abundant fine and aggregated amorphous kerogen. Common coaly and woody fragments. Traces of pollen and spores.

S85-89	Quarry north of Shi Shi Beach.	Ozette melange	Middle Eocene	Sample melange siltstone. Equivalent to melange at Shi Shi Beach, but having no petroliferous odor.	Reflected light: Predominantly indigenous vitrinite. Common amorphous material and inertinite. Trace of exinite. Transmitted light: Abundant aggregated amorphous kerogen and coaly fragments. Traces of pollen and spores.
S84-28	South of Taylor Point. Collected at coastal outcrop between Taylor Point and Giants Graveyard.	Hoh melange	Middle Miocene	Sample of gray-black mudstone melange (no petroliferous odor).	Reflected light: Abundant amorphous material and vitrinite. Traces of exinite, inertinite, and pyrite. Transmitted light: Predominantly aggregated amorphous kerogen. Abundant coaly particles. Traces of pollen, spores, and pyrite.
S84-26	Ruby Beach.	Hoh(?) melange and broken formation	Late Oligocene(?)	Sample of medium- to fine-grained sandstone having slight petroliferous odor.	Reflected light: Predominantly indigenous vitrinite. Common amorphous material. Traces of exinite, inertinite, pyrite, and recycled vitrinite. Transmitted light: Predominantly coaly fragments. Common fine amorphous kerogen. Traces of pollen, spores, and woody fragments.

rocks in the classification of Peters (1986), but inadequate source rocks in the guidelines of Poole and Claypool (1984).

Vitrinite-reflectance measurements for seven samples range from 0.36 to 0.71 percent, which suggests that the kerogen is marginally mature to barely mature with respect to oil generation and immature to marginally mature with respect to gas generation (Tissot and Welte, 1984). TAI values for these same samples support this interpretation. The kerogen in sample S84–21, from the Hogsback locality, has values of R_o=1.50 percent and TAI=3.5 and is overmature with respect to oil generation and mature with respect to gas generation.

The basic Rock-Eval parameters taken together suggest that the smell muds and sandstone from Ruby Beach (S85–119 and S84–26) and the smell muds from Shi Shi Beach (S85–121 and S85–123) have a fair content of EOM, but poor potential generation characteristics and moderate to poor source potential. The kerogen is immature to marginally mature and of mixed type II and mainly type III, indicating that it is moderately oil prone but mainly gas prone. The smell mud from Giants Graveyard (S84–31) has a poor content of EOM, poor potential for hydrocarbon generation, and poor source potential. The kerogen is marginally mature to mature and mainly type III. Mudstone and siltstone melange samples that are not smell muds (that is, samples S84–21, S85–89, and S84–28) have minimal EOM, minimal generation potential, and minimal source potential. Kerogen in these samples is type III.

The S_1 values from the Rock-Eval pyrolysis for smell muds from Ruby Beach (S85–119) and Shi Shi Beach (S85–121 and S85–123) are anomalously large relative to the TOC. This anomaly is confirmed by the EOM, which for these samples exceeds 1 mg/g. These results suggest that migrated hydrocarbons are present in these samples and to a lesser extent in the smell mud sample from Giants Graveyard (S84–31) and the sandstone sample from Ruby Beach (S84–26). The presence of migrated oil may cause the T_{max} values (table 3) for these samples to be low and unreliable.

Molecular Marker Geochemistry

Comparison of distributions of molecular markers relies heavily on the interpretation of gas chromatograms and mass chromatograms (figs. 2–4). In these figures, the samples are ordered such that the distribution of compounds in the two oils are considered first, followed by the distribution of compounds in extracts of four rock samples that in outcrop have petroliferous odors and extracts of two samples that do not have an obvious petroliferous odor.

The distribution of n-alkanes and isoprenoid hydrocarbons is shown in figure 2. All samples have a dominance of odd-carbon-numbered n-alkanes in the range above n-C_{22}. Isoprenoid hydrocarbons are also present in all

Table 2. Descriptions of oil samples

Sample No.	Location	Geologic unit	Age	Comment
Sunshine Mining Co. Medina No. 1 well	Ocean City area, near Grays Harbor.	Hoh melange (reservoir rock)	Middle Miocene	Sample of 38° API gravity oil. Well was drilled in 1957 and produced a total of 12,000 barrels in the interval 1,204 to 1,206 m. Plugged and abandoned in August 1962.
Jefferson oil seep	From standpipe near Jefferson Oil Co., Hoh Head No. 2 well.	Hoh(?) melange (reservoir rock)	Middle Miocene(?)	Natural oil seep later drilled by oil companies.

samples with pristane always significantly more abundant than phytane.

The distributions of terpanes and triterpanes are shown in figure 3; tricyclic terpanes, tetracyclic(?) terpanes, and pentacyclic triterpanes are present in the samples. The compounds are identified on table 4. These mass chromatograms are remarkably simple, and similar, with exceptions to be noted later. A general feature of these distributions is that the 17α(H),21β(H)-hopane always dominates the 17α(H),21β(H)-30-norhopane.

Sterane and diasterane distributions (fig. 4) are more complicated than the terpane and triterpane distributions (fig. 3), and there is more opportunity for peak overlap and misidentifications. Our identifications (table 4) are based on retention times and comparison with mass chromatograms from other studies. The peak assignments, therefore, should be considered tentative. At least two diasterane pairs (peaks a, b and d, f) appear to be present in all samples. The C_{29} sterane pair (peaks i, j) is usually more abundant than the other identified steranes.

Besides comparison of distributional patterns of molecular marker compounds, as shown in figures 2–4, ratios of certain compounds are useful for making correlations. We have chosen seven ratios to illustrate our results (table 5). These ratios are:

CPI = carbon-preference index. A measure of the distribution of odd-carbon-number to even-carbon-number n-alkanes, calculated over the range n-C_{22} to n-C_{32} following the method of Cooper and Bray (1963).

Pr/Ph = pristane/phytane. The ratio of concentrations of the two important isoprenoid hydrocarbons found in rock extracts and oils.

Tm/Ts = 17α(H)-22,29,30-trisnorhopane/18α(H)-22,29,30-trisnorhopane, described initially by Seifert and Moldowan (1978). The Tm/Ts ratio can be used as a maturity parameter if hydrocarbons are from a similar source, or if hydrocarbons have similar maturities, the ratio can be used as a source parameter.

C_{30}/C_{29} hopane = 17α(H),21β(H)-hopane/17α(H),21β(H)-30-norhopane. Ratio of the major pentacyclic triterpanes is used, for example, by Palacas and others (1984) for oil source-rock correlation.

C_{31} hopane 22S/22R = 17α(H),21β(H)-30-homohopane 22S/22R. The ratio of the 22S to 22R epimer of the C_{31} homohopane is a maturity parameter. Only the 22R configuration occurs in natural products. With increasing maturity the preference for 22R is lost in favor of about a 60:40 mixture of 22S and 22R epimers (Ensminger and others, 1974).

C_{29} sterane 20S/20R = 24-ethyl-5α(H),14α(H),17α(H)-cholestane 20S/20R. The ratio of the 20S to 20R epimer of the C_{29} sterane is a maturity parameter. The biologically derived 20R epimer is converted to nearly equal mixtures of 20R and 20S (Mackenzie and others, 1980).

C_{27} diasterane 20S/20R = 13β(H),17α(H)-diacholestane (20S/20R). The ratio of the 20S to 20R epimer of the C_{27} irregular sterane serves as a possible source parameter in this study.

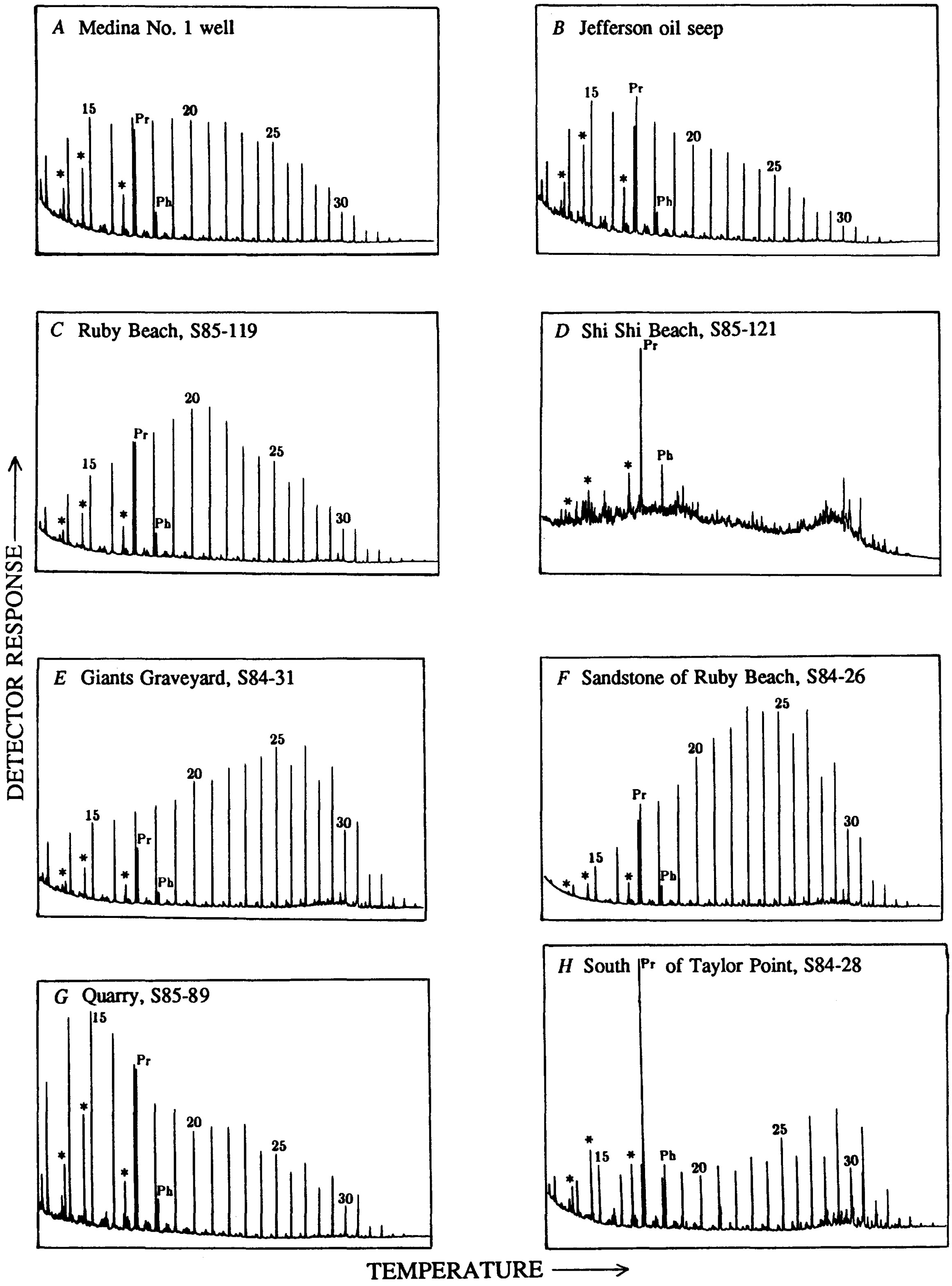

Figure 2. Gas chromatograms showing distribution of alkane and isoprenoid hydrocarbons in two oil samples (*A* and *B*) and six outcrop samples (*C–H*). Selected peaks are labeled by carbon number of n-alkanes. Pr, pristane; Ph, phytane; *, other isoprenoid hydrocarbons.

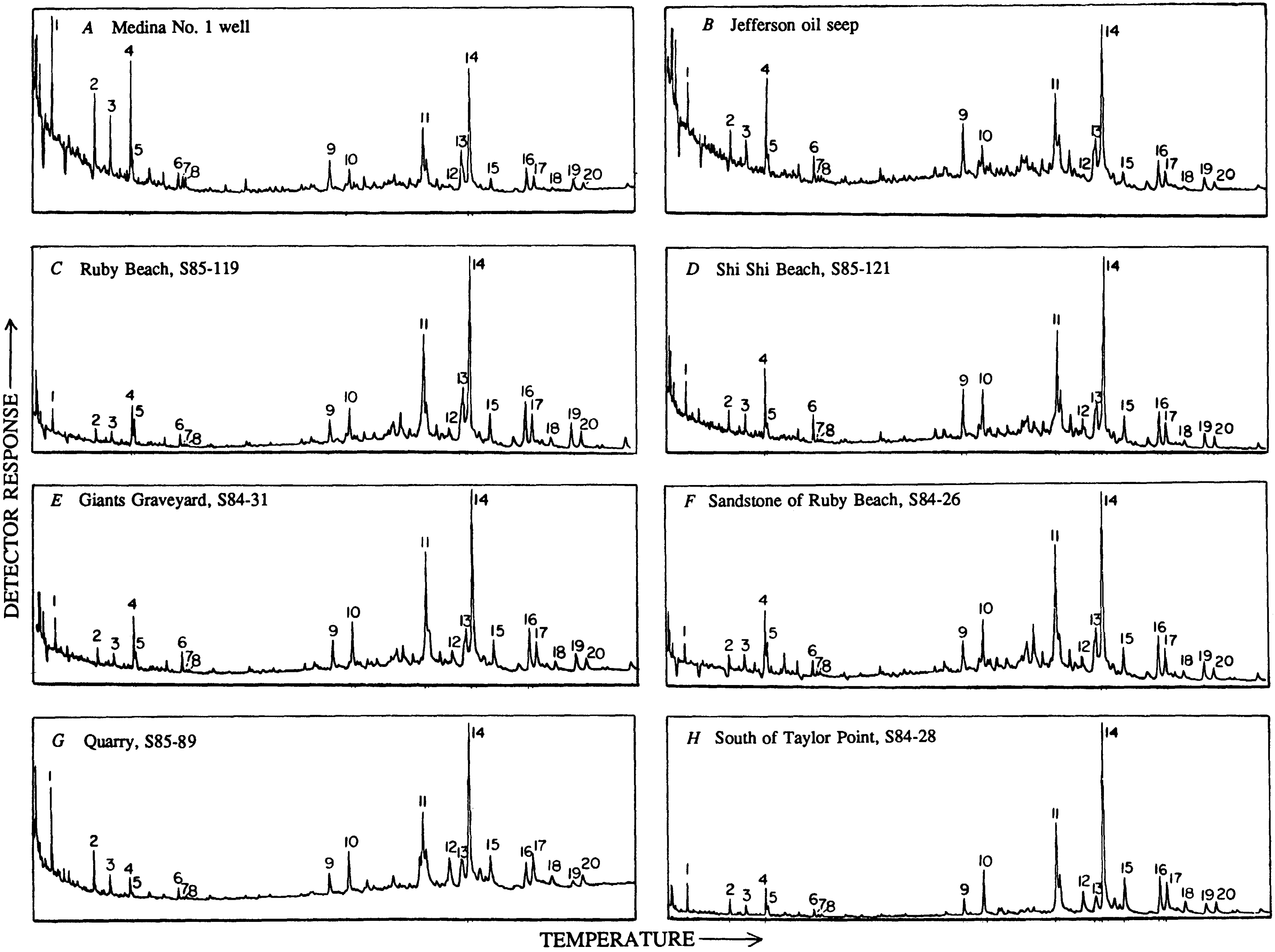

Figure 3. Mass chromatograms (m/z 191) showing distribution of terpanes and triterpanes in two oil samples (*A* and *B*) and six outcrop samples (*C–H*). Selected peaks are labeled by number and listed in table 4.

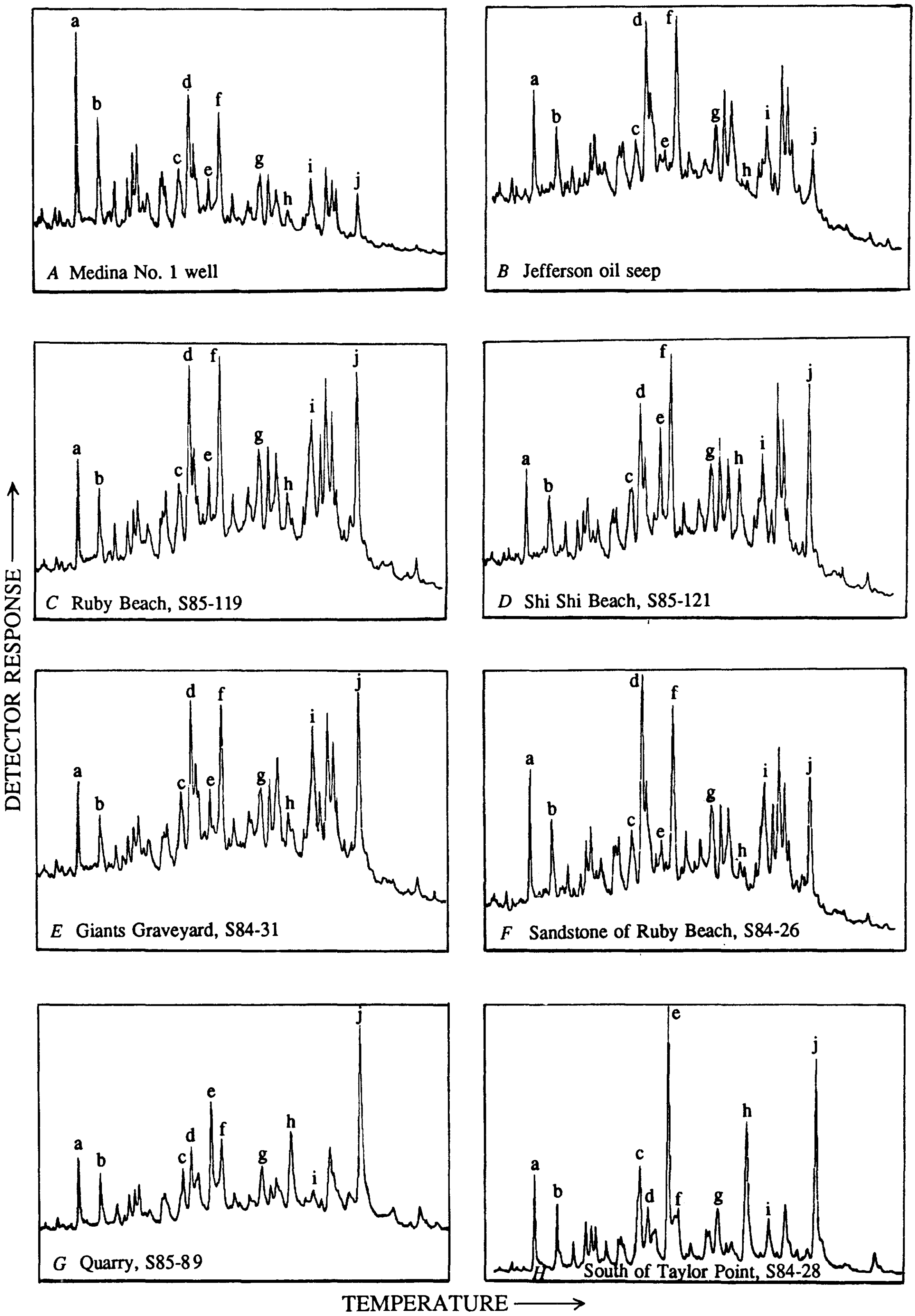

Figure 4. Mass chromatograms (m/z 217) showing distribution of steranes and diasteranes in two oil samples (*A* and *B*) and six outcrop samples (*C–D*). Selected peaks are labeled by letter and listed in table 4.

Comparison of Oils

Molecular marker geochemistry suggests that oil from the Medina No. 1 well near Grays Harbor is genetically related to oil from the Jefferson oil seep near Hoh Head (fig. 1). The distribution of aliphatic hydrocarbons from these two oil sources is compared in figure 2*A*, *B*. The distributions of n-alkanes are similar in most respects; both oils show a slight odd-carbon-number dominance of carbon numbers greater than about C_{25} (CPI=1.17 and 1.08). The Medina No. 1 oil has a slight even-carbon-number predominance in the region of C_{18} to C_{24} that is not present in the Jefferson oil seep. Pr/Ph ratios (table 5) of both oils are large (3.8 and 5.2), and the distributions of relative abundances of the isoprenoids i-C_{15} through i-C_{20} are similar.

The oils from Medina No. 1 and the Jefferson oil seep have similar distributions of terpanes and pentacyclic triterpanes (fig. 3*A*, *B*). Peak 4, which represents a dominant component of the terpane mixture, has a molecular ion m/z of 330 and is most likely a tetracyclic terpane. Peak 13 is a mixture of 18α(H)- and 18β(H)-oleanane, on the basis of a gas chromatographic and mass spectrometric comparison with authentic standards. The 18α(H)-oleanane is considered a marker for terrigenous source material (Philp, 1985a).

The distributions of the steranes and diasteranes in the oil samples is also similar (fig. 4*A*, *B*). The C_{27} and C_{29} diasterane pairs (peaks a, b, and d, f) are dominant compounds in both mixtures, and the C_{29} regular sterane pair (peaks i, j) appears to be more abundant than the C_{27} and C_{28} regular sterane pairs.

Both the Medina No. 1 oil and Jefferson oil seep contain the tentatively identified 17α(H)-bisnorlupane. This compound was first discussed in detail by Rullkötter and others (1982), who observed it in Tertiary sedimentary rocks from western Greenland and the Gulf of Suez. The compound has also been found in sediment and oil in the offshore Beaufort-Mackenzie Delta, Canada (Brooks, 1985). Like the 18α(H)-oleanane, this bisnorlupane is considered to be a marker for terrigenous plant input.

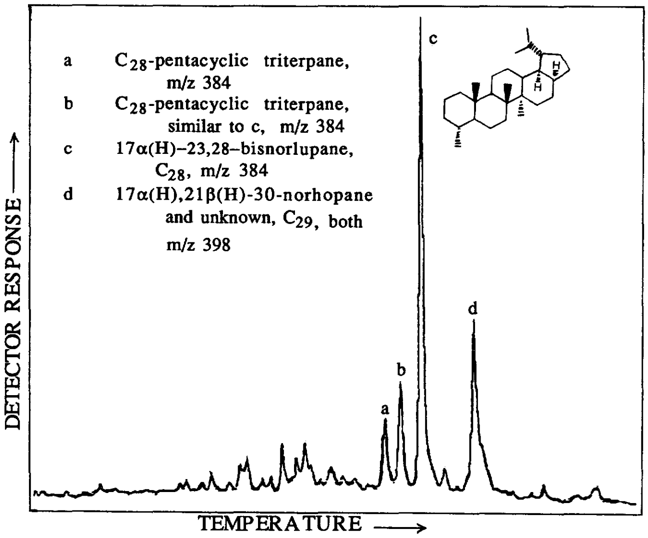

Figure 5. Mass chromatogram (m/z 177) showing distribution of triterpanes in sample S84–26 (sandstone of Ruby Beach).

The similar values of the various ratios shown on table 5 for these oils, the similar distribution patterns for the molecular markers (figs. 2*A*, *B*; 3*A*, *B*; 4*A*, *B*), and the common presence of compounds indicative of terrigenous plant sources suggest that these oils are related and may come from a common source.

Sediment Samples with Petroliferous Odor

Ozette melange samples that have a petroliferous odor were obtained from Ruby Beach (S85–119) and Shi Shi Beach (S85–121 and S85–123). The results obtained for S85–123 duplicated those found for S85–121; therefore, sample S85–123 will not be considered further. In addition to samples from Ruby Beach and Shi Shi Beach, a smell mud sample (S84–31) was also obtained at Giants Graveyard and a sample of sandstone (S84–26) with a slight petroleum odor was collected from a sandstone block in probable Hoh melange at Ruby Beach (fig. 1).

The distributions of n-alkanes and isoprenoid hydrocarbons in these samples are shown in figure 2*C*–*F*. The distribution of these compounds in the sample from Shi Shi Beach (S85–121) is completely different from the distributions in the other three samples. The hydrocarbons at Shi Shi Beach have been mildly biodegraded as indicated by the lack of identifiable n-alkanes and the unresolved complex mixture of hydrocarbons showing a distinct bimodal distribution. The only recognizable hydrocarbons are pristane and phytane. The other three samples contain mixtures of n-alkanes and isoprenoid hydrocarbons. CPI values for the n-alkanes range from 1.08 to 1.22. These values are similar to those of the oils, which measure 1.08 and 1.17 (table 5). As in the oils, the ratios of pristane to phytane (Pr/Ph) in these samples are large (2.8 to 5.6). The relative amounts of n-alkanes of lower molecular weights are smaller in the smell mud samples from Ruby Beach and from Giants Graveyard (S85–119 and S84–31), as well as in the sandstone sample from Ruby Beach (S84–26) than in the oils from the Medina No. 1 well and the Jefferson oil seep (fig. 2*A*–*F*). The apparent loss of lower molecular weight n-alkanes may have resulted from weathering at the outcrop of hydrocarbon mixtures, which originally may have been distributed similarly to those in the oils.

The distribution of terpanes and triterpanes (fig. 3*C*–*F*) and steranes and diasteranes (fig. 4*C*–*F*) in the four sediment samples are very similar. Even the distribution of these compounds in the apparently biodegraded Shi Shi Beach sample (S85–121) match closely the distributions in

Table 3. Geochemistry of melange samples, Olympic Peninsula, Washington

[HC, hydrocarbon; PI, production index, $S_1/(S_1+S_2)$; PC, pyrolyzed carbon, 0.083 $(S_1 + S_2)$; TOC, total organic carbon; T_{max}, temperature of maximum yield of S_2; HI, hydrogen index, S_2/TOC; OI, oxygen index, S_3/TOC; --, no data. See fig. 1 for locations of samples]

Sample No.	Location	TOC (pct)	EOM (mg/g)	Aliphatic HC (mg/g)	Aromatic HC (mg/g)	R_o (pct)	TAI	Rock-Eval pyrolysis parameters										
								S_1 (mg/g)	S_2 (mg/g)	S_3 (mg/g)	S_1+S_2 (mg/g)	PI	S_2/S_3	PC	PC/TOC (pct)	T_{max} °C	HI (mg/gC)	OI (mg/gC$_1$)
S85-119	Ruby Beach	0.60	1.79	0.41	0.48	0.71	2.7	0.79	1.36	0.04	2.15	0.37	34.0	0.18	29	434	227	7
S85-121	Shi Shi Beach	.49	2.66	.49	1.28	.49	2.6	.72	.81	.49	1.53	.47	1.7	.13	26	406	165	100
S84-31	Giants Graveyard	.76	.38	.08	.14	.62	2.5	.12	.83	.10	.95	.13	8.3	.08	10	441	109	13
S84-21	Hogsback	.89	.09	.05	.02	1.50	3.5	.05	.02	.13	.07	.71	.7	.01	.7	459	2	15
S85-123	Shi Shi Beach	.43	1.09	.25	.49	.36	2.6	.36	.65	.32	1.01	.36	2.03	.08	19	410	151	74
S85-89	Quarry	.26	.07	.01	.03	.44	2.4	.04	.14	.02	.18	.22	7.00	.01	6	441	54	8
S84-28	S. Taylor Point	.50	.11	.03	.04	.50	2.5	.02	.20	.15	.22	.09	1.3	.02	4	438	40	30
S84-26	Ruby Beach	.38	.59	.44	.10	.54	2.6	.29	.60	--	.89	.33	--	.07	19	428	158	--

Table 4. Identification of terpanes, triterpanes, steranes, and diasteranes

[See figs. 3 and 4]

Peak	Compound	Carbon Number
TERPANES and TRITERPANES (m/z 191)		
1	C_{21} tricyclic terpane	C_{21}
2	C_{23} tricyclic terpane	C_{23}
3	C_{24} tricyclic terpane	C_{24}
4	C_{24} tetracyclic terpane	C_{24}
5	C_{24} tetracyclic terpane	C_{24}
6	C_{24} tetracyclic terpane	C_{24}
7	C_{26} tricyclic terpane (S?)	C_{26}
8	C_{26} tricyclic terpane (R?)	C_{26}
9	18α(H)-22,29,30-trisnorneohopane (Ts)	C_{27}
10	17α(H)-22,29,30-trisnorhopane (Tm)	C_{27}
11	17α(H),21β(H)-30-norhopane	C_{29}
12	17β(H),21α(H)-30-normoretane	C_{29}
13	18α&18β(H)-oleanane	C_{30}
14	17α(H),21β(H)-hopane	C_{30}
15	17β(H),21α(H)-moretane	C_{30}
16	17α(H),21β(H)-30-homohopane(22S)	C_{31}
17	17α(H),21β(H)-30-homohopane(22R)	C_{31}
18	17β(H),21α(H)-30-homomoretane	C_{31}
19	17α(H),21β(H)-30,31-bishomohopane(22S)	C_{32}
20	17α(H),21β(H)-30,31-bishomohopane(22R)	C_{32}
STERANES and DIASTERANES (m/z 217)		
a	13β(H),17α(H)-diacholestane(20S)	C_{27}
b	13β(H),17α(H)-diacholestane(20R)	C_{27}
c	5α(H),14α(H),17α(H)-cholestane(20S)	C_{27}
d	24-ethyl-13β(H),17α(H)-diacholestane(20S)	C_{29}
e	5α(H),14α(H),17α(H)-cholestane(20R)	C_{27}
f	24-ethyl-13β(H),17α(H)-diacholestane(20R) plus ?	C_{29}
g	24-methyl-5α(H),14α(H),17α(H)-cholestane(20S) plus ?	C_{28}
h	24-methyl-5α(H),14α(H),17α(H)-cholestane(20R)	C_{28}
i	24-ethyl-5α(H),14α(H),17α(H)-cholestane(20S)	C_{29}
j	24-ethyl-5α(H),14α(H),17α(H)-cholestane(20R)	C_{29}

samples from Ruby Beach (S85–119 and S84–26) and Giants Graveyard (S84–31). The distributions of terpanes and triterpanes and steranes and diasteranes in these samples have many elements in common with the oils. Although the sediment samples and oils all contain terpanes and pentacyclic triterpanes, the relative abundance of terpanes is less in the sediments. The ratios of C_{30}/C_{29} hopanes and of C_{27} diasterane (20S/20R) in the sediments and oils are similar (table 5). On the other hand, ratios of Tm/Ts range from 1.0 to 1.6 in the sediments and are 0.6 and 0.7 in the oils (table 5). Ratios of C_{31} hopane (22S/22R) are at or near equilibrium. C_{29} sterane (20S/20R) in the sediments is slightly lower than in the oils (table 5). The latter ratio tends to reflect maturity of the hydrocarbons and suggest that the oils are slightly more mature than the sediment extracts. As in the oils, the C_{27} and C_{29} diasteranes (peaks a, b, d, f) are dominant compounds in the sterane and diasterane mixture in the sediments (fig. 4*C–F*) and the C_{29} (20S and 20R) sterane (peaks i, j) is the primary sterane compound present.

All four sediment samples having a petroliferous odor also contain the 18α+β(H)-oleanane and the tentatively identified 17α(H)-bisnorlupane. This observation, in conjunction with the distributions of the molecular markers, suggests that the extracts from these sediments and the oils are related. One possibility is that the smell muds contain a small fraction of migrated oil mixed with indigenous bitumen of the rock. An alternate interpretation is that the extracts from these smell muds are indigenous and have the same source as the oils but have not quite reached the same level of maturity as the oils (as reflected in the ratios Tm/Ts); C_{29} sterane (20S/20R) R_o values of most mudstone samples also reflect lower maturity. The sandstone (S84–26) is believed to contain migrated hydrocarbons with characteristics that match those in the smell muds.

Sediment Samples without Petroliferous Odor

To resolve the problem of migrated versus indigenous hydrocarbons in melange siltstones and mudstones, samples were selected that had no obvious petroliferous odor. Sample S85–89 was collected from a quarry exposure north of Shi Shi Beach (fig. 1). This siltstone is middle Eocene in age and considered part of the Ozette melange and broken formation, which is exposed to the south at Shi Shi Beach (Snavely and others, 1986); however, it is not a smell mud.

Geochemical information in table 3 shows that sample S85–89 is different in many aspects from the smell muds. Very obvious is the low amount of EOM, which is also reflected in the low value of S_1 compared to the smell muds. Sample S85–89 has only 0.07 mg/g EOM compared to values ranging from 0.38 to 2.66 mg/g for the smell muds. The low amount of EOM in this sample may represent the indigenous bitumen in the Ozette melange. The sample contains n-alkanes (fig. 2*G*) with a CPI=1.34 (table 5). Such a large CPI value suggests that the high molecular weight n-alkanes in this sample have a terrigenous source. This CPI value is larger than those found in smell muds, the sandstone sample, or the oils. Pristane/phytane ratios are comparable to those ratios discussed previously. The terpane distribution (fig. 3*G*) is similar to the distribution observed in the smell muds and oils, but the sterane distribution (fig. 4*G*) is much simpler and dominated by the C_{29} (20R) regular sterane. The maturity ratios (table 5), such as Tm/Ts, C_{31} hopane (22S/22R), and C_{29} sterane (20S/20R), along with the CPI ratio and the sterane distribution pattern show that hydrocarbons in this sample are less mature than those in the smell muds, the sandstone, and the oils. Sample S85–89 also contains 18α+β(H)-oleanane and 17α(H)-bisnorlupane, the source-related terrigenous plant markers seen in all the other samples. Thus, the evidence suggests that the hydrocarbons in this sample are related to the hydrocarbons in the smell muds, the sandstone, and the oils; but these hydrocarbons have not reached the same level of maturity and are indigenous (that is, not migrated).

Table 5. Ratios of various molecular markers in rock extracts and oils

[See text for discussion of ratios. --, no data]

Sample name or number	Location	CPI	Pr/Ph	Tm/Ts	C_{30}/C_{29} hopane	C_{31} hopane 22S/22R	C_{29} sterane 20S/20R	C_{27} diasterane 20S/20R
Medina No. 1 well	Grays Harbor	1.17	3.8	0.7	1.8	1.7	1.1	1.8
Jefferson oil seep	Hoh Head	1.08	5.2	.6	1.9	1.8	1.1	1.7
S85-119	Ruby Beach	1.22	5.6	1.4	1.8	1.5	.6	1.5
S85-121	Shi Shi Beach	--	2.8	1.0	1.8	1.5	.5	1.6
S84-31	Giants Graveyard	1.21	5.0	1.6	1.6	1.6	.7	1.8
S85-89	Quarry	1.34	4.6	1.9	2.1	.8	.1	1.4
S84-28	S. Taylor Point	1.61	4.1	2.5	2.2	1.3[1]	.2	1.5
S84-26	Ruby Beach	1.08	3.8	1.6	1.5	1.5	.8	1.7

[1] Value is considered to be too large because of peak interference (fig. 3H). Value should be <1.0 on the basis of measurement of C_{32} hopane 22S/22R epimers.

For comparison purposes with the Ozette melange, a sample of siltstone of Hoh melange without petroliferous odor was selected. The first sample of Hoh melange (S84–21) contained overmature organic matter having a R_o value of 1.50 percent and a TAI value of 3.5 (table 3). Our preliminary analyses of this sample showed that the terpanes and triterpanes and steranes and diasteranes were absent although the n-alkanes and isoprenoids were present. Because of the lack of measurable cyclic biomarkers, no more information on this sample is given here. Instead, we selected sample S84–28 of middle Miocene Hoh melange in which the R_o value of 0.5 percent and the TAI value of 2.5 are of comparable magnitude to those values measured in Ozette melange samples (table 3).

Hoh melange sample S84–28 contains n-alkanes and isoprenoid hydrocarbons (fig. 2*H*). The distribution is characterized by dominant pristane and a strong odd-carbon-number preference reflected in a CPI value of 1.61 (table 5), again signaling the presence of a terrigenous source. The terpane and triterpane pattern (fig. 3*H*) of this sample is similar to other samples of this study. One ambiguity involves the C_{31} hopane (22S/22R) ratio of 1.3 (table 5). This ratio may be too large in that the C_{32} homohopane (22S/22R) ratio (ratio of peak 19 to peak 20 in fig. 3*H*) is less than 1. A ratio of less than 1 is more consistent with other maturity data. For example, the C_{29} sterane (20S/20R) ratio of this sample is 0.2, a value comparable to that measured in the Ozette melange sample S85–89. The sterane and diasterane mass chromatogram (fig. 4*H*) is simple, but different from that of sample S85–89; a major difference is that the C_{27} (20R) regular sterane is the dominant component in the mixture. In other samples, the C_{29} sterane is the prominent sterane. This sample also contains 18α+β(H)-oleanane and 17α(H)-bisnorlupane. The distributional characteristics of molecular markers in the middle Miocene Hoh melange sample S84–28 are similar to those in middle Eocene Ozette melange sample S85–89, except for the dominant C_{27} regular sterane in the Hoh melange. Although these samples are of different geologic age, the original depositional environments must have been similar and contained similar kinds of organic materials including abundant terrigenous material. Kerogen descriptions of these samples (table 1) support the notion of the presence of terrigenous organic materials.

CONCLUSIONS

Our study shows that oils from the Medina No. 1 well and from the Jefferson oil seep are probably related; that is, most of the measured hydrocarbon characteristics are very similar. Also, hydrocarbons in an Ozette melange sample from a quarry (S85–89) are similar to the oils but show a lower level of maturity. We believe that the indigenous hydrocarbons in sample S85–89 would, upon sufficient maturation, produce a hydrocarbon mixture having molecular characteristics essentially the same as that in the smell muds and in the oils from the Medina No. 1 well and Jefferson oil seep. However, the amount of hydrocarbons that could be generated from this rock is very small; that is, the rock has very poor source-rock potential (table 3).

The molecular geochemistry of smell muds can best be accounted for as mixtures of indigenous hydrocarbons and small amounts of migrated oil of the Medina No.1 well and Jefferson oil seep type, but the level of maturity is slightly lower than the oil. Likewise, the oil in the Hoh (Ruby Beach) sandstone has a slightly lower level of maturity than does the oil of the Medina No. 1 well and Jefferson oil seep. The distributional patterns of n-alkanes show an odd-carbon-number dominance in the smell muds, the sandstone, and in the oils (fig. 2). Differences in distributional patterns of n-alkanes in the oils compared with those in smell muds and sandstone may be due in part to weathering at the outcrop. The distributional patterns of terpane, triterpanes, steranes, and diasteranes in the smell muds, the sandstone, and in the two oils are remarkably similar (figs. 3 and 4). Values of maturity parameters such as CPI, Tm/Ts, and C_{29} sterane (20S/20R) (table 5) in the smell muds and sandstone are intermediate between lower maturity values inferred to represent indigenous hydrocarbons (sample S85–89) and values present in the more mature oils (Medina No. 1 well and Jefferson oil seep).

The presence of the tentatively identified 17α(H)-23,28-bisnorlupane and 18α(H) and 18β(H)-oleanane in both rock and oil samples from Washington seems to tie the hydrocarbons to a common source. The bisnorlupane has been observed only rarely; for example, in Tertiary sediments from western Greenland and the Gulf of Suez (Rullkötter and others, 1982) and in sediment and oil in the offshore Beaufort-Mackenzie Delta, Canada (Brooks, 1985). The compound is thought to be derived from terrestrial higher plants. The presence of 18α(H)-oleanane also suggests terrigenous source material based on a number of studies reviewed by Philp (1985a). In addition, the odd-carbon-number dominance of the n-alkanes and the dominance of the C_{29} regular sterane support the premise of a terrigenous source. The kerogen descriptions in table 1 show that our .samples contain plant remains including pollen, spores, wood fragments, and coal. The presence of these materials is consistent with the finding of molecular marker compounds that signal terrigenous materials as a source from which the oils at the Medina No. 1 well, the Jefferson oil seep, the smell muds, and the sandstone were generated.

Major thrust faults mapped in the Ozette and Hoh melanges and broken formations along coastal Washington likely serve as conduits for migrating oil resulting in the petroliferous odor emitted by the smell muds and the sandstone. The amount of migrating oil may vary with time; we have observed widely varying intensities of petroleum odor at the same smell mud outcrop in different years. The reservoired oil at the Medina No. 1 well, the oil at the Jefferson oil seep, and the oil in the sandstone and at the microseeps in melange at Ruby Beach, Giants Graveyard, and Shi Shi Beach appear to be related; however, the microseep oils of the smell muds are not as mature as the oils at the Medina No. 1 well and Jefferson oil seep. The petroleum province along coastal Washington north of Grays Harbor apparently has an oil type that was generated from a common source rock containing terrigenous plant materials. The middle Eocene siltstone and mudstone of the Ozette melange and broken formation are considered the most likely source-rock candidates (Snavely and Kvenvolden, chap. A of this report). Oils of variable maturity have apparently migrated from this Eocene source as evidenced by the observation of mature oil reservoired in Hoh melange at the Medina No. 1 well and less mature oil in the Hoh sandstone sample from Ruby Beach.

REFERENCES CITED

Brooks, P.W., 1985, Unusual biological marker geochemistry of oils and possible source rocks, offshore Beaufort-Mackenzie Delta, Canada: Organic Geochemistry, v. 10, p. 401–406.

Cooper, J.E., and Bray, E.E., 1963, A postulated role of fatty acids in petroleum formation: Geochimica et Cosmochimica Acta, v. 27, p. 1113–1127.

Ensminger, A., van Dorsselaer, A., Spyckerelle, C., Albrecht, P., and Ourisson, G., 1974, Pentacyclic triterpanes of the hopane type as ubiquitous geochemical markers—origin and significance, *in* Tissot, B. and Bienner, F., eds., Advances in Organic Geochemistry 1973: Paris, Editions Technip, p. 245–260.

Hunt, J.M., 1979, Petroleum geochemistry and geology: San Francisco, W.H. Freeman, 617 p.

Kvenvolden, K.A., Rapp, J.B., and Bourell, J.H., 1985, Comparison of molecular markers in crude oils and rocks from the North Slope of Alaska, *in* Magoon, L.B., and Claypool, G.E., eds., Alaska North Slope Oil/Rock Correlation Study: American Association of Petroleum Geologists Studies in Geology, no. 20, p. 593–617.

Mackenzie, A.S., 1984, Application of biological markers in petroleum geochemistry, *in* Brooks, J., and Welte, D., eds., Advances in Petroleum Geochemistry: v. 1, London, Academic Press, p. 115–214.

Mackenzie, A.S., Patience, R.L., Maxwell, J.R., Vandenbroucke, M., and Durand, B., 1980, Molecular parameters of maturation in the Toarcian shales, Paris Basin, France–I. Changes in the configuration of acyclic isoprenoid alkanes, steranes, and triterpanes: Geochemica et Cosmochimica Acta, v. 44, p. 1709–1721.

Palacas, J.G., Anders, D.E., and King, J.D., 1984, South Florida Basin—A prime example of carbonate source rocks of petroleum, *in* Palacas, J.G., ed., Petroleum geochemistry and source rock potential of carbonate rocks: American Association of Petroleum Geologists Studies in Geology, no. 18, p. 71–96.

Peters, K.E., 1986, Guidelines for evaluating petroleum source rock using programmed pyrolysis: American Association of Petroleum Geologists Bulletin, v. 70, p. 318–329.

Philp, R.P., 1985a, Biological markers in fossil fuel production: Mass Spectrometry Reviews 1985, v. 4, p. 1–54.

———1985b, Fossil fuel biomarkers, applications and spectra: Methods in Geochemistry and Geophysics (v. 23): Amsterdam, Elsevier, 294 p.

Philp, R.P., and Gilbert, T.O., 1986, Biomarker distributions in Australian oils predominantly derived from terrigenous source material: Organic Geochemistry, v. 10, p. 73–84.

Poole, F.G., and Claypool, G.E., 1984, Petroleum source-rock potential and crude-oil correlation in the Great Basin, *in* Woodward, J., Meissner, F.F., and Clayton, J.L., eds., Hydrocarbon Source Rocks of the Greater Rocky Mountain Region: Rocky Mountain Association of Geologists, p. 179–229.

Rullkötter, J., Leythaeuser, D., and Wendisch, D., 1982, Novel 23, 28-bisnorlupanes in Tertiary sediments—wide-spread occurrence of nuclear demethylated triterpanes: Geochimica et Cosmochimica Acta, v. 46, p. 2502–2509.

Seifert, W.K., and Moldowan, J.M., 1978, Application of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils: Geochimica et Cosmochimica Acta, v. 42, p. 77–95.

Snavely, P.D., Jr., MacLeod, N.S., Niem, A.R., and Minasian, D.L., 1986, Geologic map of Cape Flattery area, northwestern Olympic Peninsula, Washington: U.S. Geological Survey Open-File Report 86–344B.

Tissot, B.P., and Welte, D.H., 1984, Petroleum formation and occurrence (2d ed.): Berlin, Springer-Verlag, 699 p.

Volkman, J.K., Alexander, R., Kagi, R.I., and Woodhouse, G.W., 1983, Demethylated hopanes in crude oils and their applications in petroleum geochemistry: Geochimica et Cosmochimica Acta, v. 47, p. 785–794.

Chapter C

Composition of Natural Gases in Seeps, Outcrops, and a Test Well

By KEITH A. KVENVOLDEN, MARGARET GOLAN-BAC, and PARKE D. SNAVELY, JR.

U.S. GEOLOGICAL SURVEY BULLETIN 1892

PRELIMINARY EVALUATION OF THE PETROLEUM POTENTIAL OF THE TERTIARY ACCRETIONARY TERRANE, WEST SIDE OF THE OLYMPIC PENINSULA, WASHINGTON

CONTENTS

FIGURES

TABLES

Composition of Natural Gases in Seeps, Outcrops, and a Test Well

By Keith A. Kvenvolden, Margaret Golan-Bac, *and* Parke D. Snavely, Jr.

Abstract

The stable carbon and hydrogen isotopic abundances of methane in gas samples collected along the west side of the Olympic Peninsula suggest that all gases are thermogenic and may be related to a similar source. Samples were obtained from a test well, three natural gas seeps, and three smell mud localities. At two seeps, methane constitutes more than 99.9 percent of the hydrocarbon mixture, yet the isotopic composition of the methane indicates thermogenic rather than a microbial source. Outcrop samples of smell muds contain gas that is compositionally distinct from the seep gas; outcrop gas is composed not only of methane but has significant amounts of the higher molecular weight hydrocarbon gases. The relation between seep gas and outcrop gas is uncertain.

INTRODUCTION

As part of our study to evaluate the hydrocarbon potential of the middle Eocene to middle Miocene accretionary terranes along the west coast of the Olympic Peninsula, Wash. (see chaps. A and B), we have also examined the hydrocarbon composition of natural gas samples from several different localities (fig. 1). Samples were collected from a test well, three natural seeps, and twelve outcrop samples of melange smell muds, so-called because they emit a distinct petroliferous odor. Our purpose was to characterize the hydrocarbon compositions of these gases, to determine the stable carbon and hydrogen isotopic compositions of the methane, to compare gas compositions with published data, and to determine the source of the gas.

ACKNOWLEDGMENTS

This work was partially funded by the U.S. Department of Energy under Interagency Agreement No. DE–AI21–87–MC20422.502. We are grateful to W.J. Gwilliam, Department of Energy, for his support, to Larry Workman, Quinault Indian Reservation, and Kevin Warren, Eagle Air Company for assistance in obtaining gas samples, and to Kenneth Peters, Chevron Oil Field Research Company, for constructive comments and suggestions.

SAMPLING LOCALITIES AND METHODS

Samples of natural gas were obtained from an exploration well drilled in 1924 by the Sol Duc Oil Co. on the Wilson Ranch near the Bogachiel River (fig. 1). The stand pipe of the well had a valve with rubber hose conveniently attached, and gas was allowed to escape through the hose into a bucket of water. Gas collection bottles (about 250 mL volume), filled with distilled water, were inverted in the bucket so that the gas could displace the water in the bottles. When each bottle was full of gas, the spring-loaded rubber and ceramic stopper was closed. A small amount of water was left in the collection bottle to enhance the seal against gas leakage. Bottles were stored in the inverted position until analyzed.

Natural gas seeps were sampled at three widely separated localities: the Garfield gas mounds, Huelsdonk Ranch gas seep, and Sol Duc Hot Springs gas seep (fig. 1). The Garfield gas mounds are located near the mouth of the Quinault River on the Quinault Indian Reservation. During our first visit to this site in 1984, we noticed gas seepages at two locations on one mound; the lower seepage was sampled because the gas flow seemed greatest there. The seeps can best be described as muddy ponds, less than a meter in diameter, where gas bubbled up at irregular intervals. To collect gas samples, the same kind of gas collection bottle was used as in sampling the test well. Each bottle was filled with water and inverted so that the mouth of the bottle was below the level of the pond. Then a funnel was submerged in the pond to help divert the gas into the collection bottle. When the gas had displaced the water in the collection bottle, the seal was closed. The bottles were stored in the inverted position. In 1985, the upper seep on the same mound was sampled using the same procedure.

The Huelsdonk Ranch seep south of the Hoh River has formed a small mound in the meadow south of the ranch house (fig. 1). This seep site served as an alternate to the Devils Mush Pot—a seep locality noted in early studies (Lupton, 1915)—which has since been washed away by a change in course of the Hoh River. Gas samples were collected at the Huelsdonk Ranch seep by the same water displacement method as described earlier.

Manuscript approved for publication, April 20, 1989.

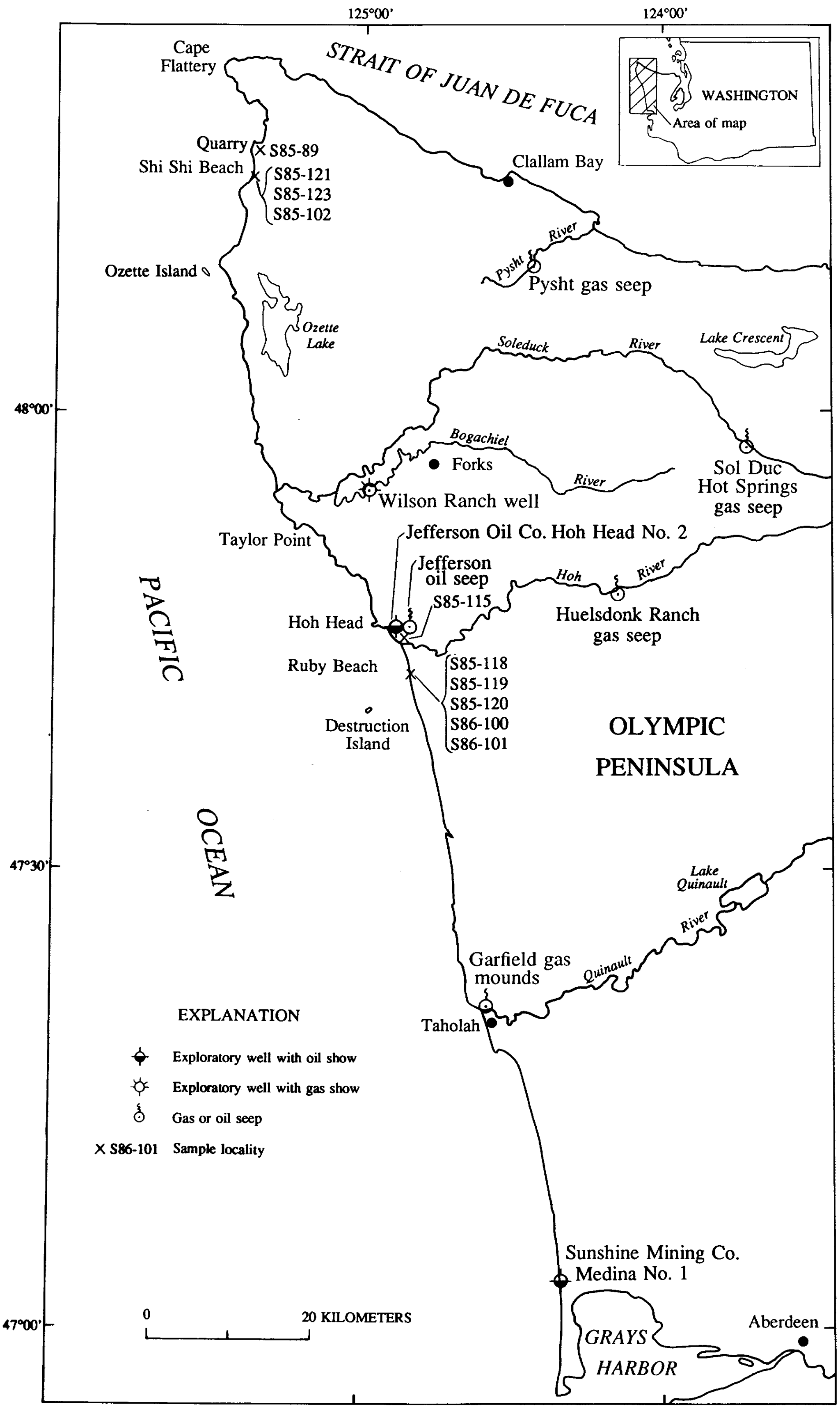

Figure 1. Natural gas sample localities, west coast of Olympic Peninsula, Washington.

Gas samples from the Sol Duc Hot Springs seep (fig. 1) were obtained by the same water displacement procedure. In this case, however, gas was collected from water within a 12-foot-deep cistern where gas bubbled from the rock floor.

An attempt was made to sample the Pysht gas seep, located near the Pysht River in the north part of the study area (fig. 1). Although this was an active seep for more than 40 years, in 1985 the seep could not be located because of debris cover from recent logging. An analysis by Mobil Oil Co. of the composition of gas at this site was published by Snavely (1987).

Middle Eocene Ozette melange crops out in seacliffs along coastal Washington. In many places, freshly broken surfaces of these rocks are characterized by a petroliferous odor and, hence, are referred to as smell muds. During the course of two years (1985–1986), we collected nine samples of these smell muds and one melange sample with no petroliferous odor (fig. 1). These samples were placed in sealed containers in order to examine the composition and distribution of gases. The procedure for the extraction of hydrocarbon gases from these outcrop samples was similar to methods used for oceanic sediments collected during marine geochemical surveys (for example, Kvenvolden and Redden, 1980). Briefly, a known weight of sediment was placed in a pint- or quart-sized can that had been previously prepared with septa mounted near the top. Water was added to the can to establish a 50- or 100-cm^3 headspace. The can was sealed with a double-friction seal lid and refrigerated until analyses for hydrocarbons could be done (usually within one week). In addition, one can was sealed with distilled water to serve as a blank.

Laboratory Analyses

Gas samples from the test well and the seeps were analyzed gas chromatographically at U.S. Geological Survey (USGS) laboratories in Menlo Park, Calif., and Denver, Colo. At each of these laboratories, portions of the gases were removed from the collection bottles that were opened after being inverted and partially immersed in water baths. At Menlo Park, the hydrocarbon composition was determined by means of a gas chromatograph designed specifically for natural gas (Kvenvolden and Redden, 1980). Confirmation of the quantities of major constituents was obtained in the Denver laboratory following procedures of Claypool and others (1980). Results reported in table 1 are normalized to 100 volume percent.

For isotope mass spectrometry, done at the Denver laboratory, the methane peak from gas chromatography was quantitatively collected and converted to CO_2 in a vacuum-combustion system. The stable carbon isotope ratio was measured by mass spectrometry, and the results are reported in the δ notation (parts per thousand) relative to the Peedee belemnite (PDB) standard: $\delta^{13}C$ per mil=$(R_{sample}/R_{standard} - 1) \times 10^3$, where R=$^{13}C/^{12}C$. The stable hydrogen isotope ratio was measured at Global Geochemistry Corporation and the results are also reported in the δ notation (δD), as above, where R= the deuterium to hydrogen ratio, and the standard is Standard Mean Ocean Water (SMOW).

The outcrop samples were analyzed at the USGS in Menlo Park. The sealed cans were warmed to room temperature and shaken vigorously. Samples of the headspace gas were removed through the septa by means of a syringe and analyzed by gas chromatography as described previously for the well and seep samples. Hydrocarbons that have five carbon atoms or more (C_{5+}) were detected as a backflush peak, and an approximate concentration was calculated on the basis of the response of n-pentane in our standards. Contributions from the water blank were subtracted to obtain the final results, which are reported for the outcrop samples in microliters of hydrocarbon gas per kilogram of sediment (table 2).

RESULTS AND DISCUSSION

Test Well and Seeps

The composite results for the test well and the seeps (table 1) are compared with published information from the Pysht seep (Snavely, 1987) and for the Taholah seep (Rau and Grocock, 1974). Locations of the seeps, except the Taholah seep, are shown on figure 1; unfortunately, we have been unable to locate the Taholah seep, which was present on the coast near Taholah and the Garfield gas mounds, and we presume that a coastal landslide has buried the site.

The hydrocarbon compositions of the gas from the Wilson Ranch well and the Pysht and Taholah seeps are similar in that all three contain measurable quantities of ethane and higher molecular weight hydrocarbons, in addition to methane. In contrast, the gas at the Garfield gas mounds, Huelsdonk Ranch seep, and Sol Duc Hot Springs seep is composed mainly of methane and contains very little, if any, of the higher molecular weight hydrocarbons. When we first observed that gas at the Garfield gas mounds lacked the higher molecular weight hydrocarbons, we again sampled the seep and analyzed the gas. We obtained the same compositional results (table 1). Because of the published results from the Taholah seep, located only 2.2 km northwest of the Garfield gas mounds (Rau and Grocock, 1974), we had expected that gas at the Garfield gas mounds would also show measurable amounts of ethane and higher molecular weight compounds. We cannot fully explain these differences. The lack of higher molecular weight hydrocarbon gases at the Garfield gas mounds, Huelsdonk Ranch seep, and Sol Duc Hot Springs seep may be the result of a stripping of these compounds during migration.

Table 1. Analyses of hydrocarbon gases from a test well and natural gas seeps, Olympic Peninsula, Washington
[Values in volume percent. n.d., not detected; n.r., not reported]

	Wilson Ranch Well	Garfield gas mounds		Huelsdonk Ranch gas seep	Sol Duc Hot Springs gas seep	Pysht[1] gas seep	Taholah[2] gas seep
Methane	95.8	99.9+	99.9+	99.9+	99.9+	94.33	97.55
Ethane	2.7	.0057	.0053	.0005	.051	3.50	1.48
Propane	.90	n.d.	n.d.	n.d.	n.d.	1.54	.37
Butanes	.30	n.d.	n.d.	n.d.	n.d.	.43	.22
Pentanes+	.27	.0012	.0020	n.d.	n.d.	.19	.21
Methane $\delta^{13}C$ per mil	-34.7	-34.5	-34.8	-51.6	-36.5	-31.5	n.r.
Hydrogen δD per mil	-135	-177	-196	-212	-174	n.r.	n.r.

[1] Snavely (1987)

[2] Rau and Grocock (1974)

Table 2. Hydrocarbon gases in outcrop samples, Olympic Peninsula, Washington
[Values in microliters per kilogram of sediments. n.d., not detected]

	Ruby Beach					Shi Shi Beach			Others	
Sample no.	S85-118	S85-119	S85-120	S86-100	S86-101	S85-121	S85-123	S86-102	S85-115	S85-89
Methane	300	180	6.9	310	24	0.74	2.0	7.9	16	2.6
Ethane	1,100	160	.19	490	49	.039	.068	.23	22	.36
Ethene	.013	n.d.	.082	n.d.	.047	.032	.032	.10	n.d.	.013
Propane	1,400	590	.37	1,100	280	.031	.064	.16	19	.46
Propene	n.d.	n.d.	.016	n.d.	n.d.	.016	.014	.096	n.d.	.004
i-Butane	170	380	.47	260	120	n.d.	n.d.	.73	16	n.d.
n-Butane	310	1,100	3.4	640	880	.008	.032	.18	8.4	.30
C_{5+}	130	3,900	180	970	14,000	5.7	16	220	100	1.6

This kind of process has been discussed briefly by Jenden and Kaplan (1986) to explain some unusual compositional variations of natural gases.

Carbon isotopic compositions of methane for the test well and seep samples fall within a narrow range from –31.5 to –36.5 per mil with the exception of the Huelsdonk Ranch sample that has a more negative value of –51.6 per mil (table 1). Duplicate analyses of methane from the test well and the seep at Garfield gas mounds are within 0.3 per mil. Except for the sample from the Huelsdonk Ranch seep, the methane isotopic composition of the other samples fall within the field of values (fig. 2) usually associated with thermogenic gases (Schoell, 1980, 1983; Jenden and Kaplan, 1986). Methane in the Huelsdonk Ranch seep is isotopically lighter and may represent a unique mixture with a strong microbial gas component.

Hydrogen isotopic compositions of methane from the Wilson Ranch well and from the seeps are more variable than are the carbon isotopic compositions. The hydrogen isotopic composition of methane in the seep gases is always more negative than that in the test well (fig. 2). With the exception of the Huelsdonk Ranch seep, the δD values of the other samples are within the range attributed to thermogenic gas (Schoell 1980, 1983; Jenden and Kaplan, 1986), a result in line with the carbon isotopic compositions. The more negative δD methane (–212 per mil) at the Huelsdonk Ranch seep suggests a gas with at least a partial microbial source; the δ^{13}C value (–51.6 per mil) supports this interpretation. On figure 2 this sample falls just outside the field for thermogenic gas. The gas may be a mix of thermogenic and microbial gas. The measurement of δD of methane at the Garfield gas mounds was not duplicated in that two very different values (δD = –196 and –177 per mil) were obtained. It is uncertain why these results are so different when the respective carbon isotopic compositions are so similar (δ^{13}C = –34.8 and –34.5 per mil, table 1).

The molecular and isotopic compositions of gases from natural seeps in this area do not present a totally consistent scenario. The molecular compositions of some but not all seep gases may have been modified by the stripping of hydrocarbons larger than methane. With the exception of the Huelsdonk Ranch seep, the isotopic compositions are all consistent with a thermogenic source for the gases. It is uncertain whether or not the gases were generated from the same source rocks, but the carbon isotopic compositions suggest they may have been.

The geologic settings at the well and seep sites provide some constraints to the identification of the source or sources of the gas. Melanges and broken formations of two ages are present in the area: the middle and upper Eocene Ozette melange and broken formation and the upper Oligocene and middle Miocene Hoh melange and broken formation. Either of these units could serve as a source for the gas on the basis of considerations in Snavely and Kvenvolden (chap. A of this report). Most smell muds that we found, however, are part of the Ozette melange. Because the Ozette melange and broken formation is present in the sections at the well and seep sites, it is a primary candidate for the source of the gas.

At the Wilson Ranch well, gas is trapped along an unconformity between the middle Eocene Ozette melange and the overlying upper Miocene or Pliocene Quillayute Formation. Because the middle Miocene Hoh melange is absent in the Forks area, the Ozette melange is a likely source for the gas at the Wilson Ranch well and in other wells that had significant gas shows in the Forks area (Rau and McFarland, 1982).

The gas at the Garfield gas mounds bubbles up through a muddy slurry that contains middle Miocene foraminifers derived from the Hoh melange. Because strata equivalent to the Ozette melange probably underlie the Hoh melange, it is uncertain which of these melanges is the source of the gas. Because the carbon isotopic composition of methane from the well and from this seep are almost identical, we believe that the Ozette melange is more likely the source of the gas.

Gas at the Huelsdonk Ranch seep is presumed to have migrated through a thick section of glacial till in the Hoh River valley. The unique carbon and hydrogen isotopic signature of methane at this site may reflect a gas derived in part from these glacial deposits. In general, methane in glacial deposits is microbial in origin and has a more negative carbon and hydrogen isotopic composition than does methane from a thermogenic source (Schoell, 1980). Because Ozette melange is present at depth at the Huelsdonk Ranch site, it could have contributed some thermogenic gas to the final gas mixture.

Gas and thermal water at the Sol Duc Hot Springs seep probably migrates up a shear zone in middle(?) Eocene sandstone and siltstone (Tabor and Cady, 1978) that are correlative with the Ozette melange. Therefore, the source of the gas is likely the middle Eocene Ozette melange or the older lower(?) and middle Eocene strata in the western core rocks of the Olympic Mountains.

The Pysht seep releases gas through steeply dipping Eocene strata in the upper plate of the Crescent thrust fault. Although the source of this gas is speculative, it is interpreted to have been generated from Eocene strata in the lower plate of the thrust (Snavely, 1987). On the basis of the rough equivalence of carbon isotopic compositions of methane in the Pysht gas (–31.5 per mil) and in the seep gases that apparently originated from the Ozette melange (–34.5 to –36.5 per mil) (table 1), the source rocks for the Pysht gas are probably underplated Eocene strata correlative with the Ozette melange.

The Taholah gas seep was apparently located near the fault contact between middle Miocene Hoh melange and Pliocene sedimentary rocks. As at the nearby Garfield gas mounds, there is insufficient evidence to assign a source for this gas. However, because the Ozette melange is a likely source for the gas at the Wilson Ranch well and at some of the other seeps, we believe that the Ozette melange is also a primary gas source for the Taholah seep.

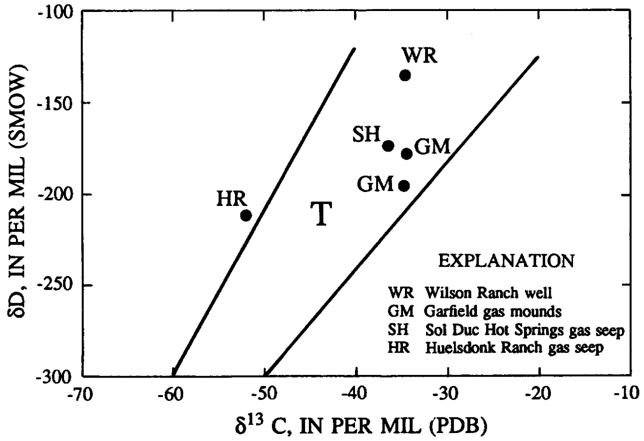

Figure 2. Stable-isotope values for methane from natural gas seeps and test well. Region marked "T" between two solid lines is modified from Schoell (1983) and from Jenden and Kaplan (1986) and represents range of isotopic compositions observed in thermogenic gases. PDB, Peedee belemnite standard; SMOW, Standard Mean Ocean Water.

Outcrops

The distribution of hydrocarbons extracted from the outcrops of middle Eocene Ozette melange and broken formation is summarized in table 2. Sample numbers include the year of collection, and sample sites are located on figure 1. Five melange samples were collected at Ruby Beach, where all of the samples had a petroliferous odor; sample S85–119 had the strongest smell. Saturated hydrocarbon gases from methane to C_{5+} are present in all samples and the unsaturated hydrocarbon gases, ethane and propane, are present in most samples. Nitrogen and carbon dioxide were not determined. Except for samples S85–118 and S86–100, where propane is the largest component, C_{5+} is most abundant in the other samples. Sample S85–120 has the lowest total amount of hydrocarbons; however, sample S86–101, from the same locality, has a significantly larger amount of hydrocarbons. This difference in concentration could represent differences in the intensity of the microseepage of hydrocarbons at this site in different years.

Three samples of melange smell muds from Shi Shi Beach (fig. 1) also contain the hydrocarbon gases from methane to C_{5+}. Sample S86–102 came from approximately the same site as S85–121, but more hydrocarbons were observed in the sample collected in 1986. The amounts of hydrocarbons and their relative compositions in samples S85–121 and S85–123 are virtually the same. C_{5+} compounds dominate the gas mixture, and overall concentrations of hydrocarbons are significantly lower than those present in the melange at Ruby Beach.

Gas analyses for two other samples (S85–115 and S85–89) are shown in table 2. Sample S85–115, which had a slight petroliferous odor, was collected near the mouth of the Hoh River (fig. 1). The dominant component in this sample is C_{5+}, and the other saturated hydrocarbons have concentrations between those observed in most samples from Ruby Beach and those detected in samples from Shi Shi Beach.

Siltstone sample S85–89 was collected from a quarry near Shi Shi Beach (fig. 1). This siltstone is middle Eocene in age and considered part of the Ozette melange and broken formation, which is exposed to the south at Shi Shi Beach (Snavely and others, 1986). Although the quarry sample had no apparent petroliferous odor, it contains concentrations of some hydrocarbon gases that, although low, exceed the concentrations of hydrocarbon gases at Shi Shi Beach in samples S85–121 and S85–123.

The rationale for analyzing the gases in these smell muds was to determine whether or not there was a relation between outcrop gases, which we believe to result from microseepage of hydrocarbons, and gases found in natural seeps and in the Wilson Ranch well. Compositionally, the hydrocarbon gases in the outcrops (table 2) and in the gas seeps (table 1) are quite different. The gas seeps contain very small amounts of hydrocarbons larger than methane, whereas the outcrops are dominated by compounds larger than methane. These differences may be due to differences in sources, processes, or both. Perhaps the melange is preferentially retaining the hydrocarbon gases larger than methane. Such a retention phenomena could possibly explain the differences between gas compositions and isotopic values for gases at the Garfield gas mounds, Huelsdonk Ranch seep, and Sol Duc Hot Springs seep. The molecular and isotopic compositions of the seep gases may be accounted for as follows: The sedimentary rocks through which a thermogenic gas mixture passes may retain the larger molecules, resulting in methane with a thermogenic isotopic signature, but with the gas mixture having a microbial-like molecular composition. An alternate explanation is that the methane associated with the heavier hydrocarbon gases was derived thermogenically from oil, whereas the methane without these heavier components was derived thermogenically from dispersed, solid organic matter.

We attempted to correlate the outcrop gas in sample S86–100 of Ruby Beach melange with gas from the Wilson Ranch well by obtaining, through the courtesy of Moses Chung (Mobil Oil Corp., written commun., 1987), measurements of the carbon isotopic composition of the hydrocarbon components in each sample. The results are shown in table 3. The carbon isotopic compositions of the hydrocarbon gases from the Wilson Ranch well follow an expected separation as described by James (1983). The $\delta^{13}C$ value of methane of –34.8 per mil (table 3) essentially matches the value (–34.7 per mil) obtained in the USGS Denver laboratory (table 1). The $\delta^{13}C$ values of ethane, propane, and the butane are less negative, ranging from –27.2 to –24.4 per mil. In contrast, the $\delta^{13}C$ values of ethane, propane, and the butane in the outcrop gas are more negative (–35.9 to –28.1 per mil) than the $\delta^{13}C$ value of methane in the test well (–27.3 per mil). The relations among these isotopic values of the components in the outcrop gas do not follow the fractionation scheme of James (1983). The $\delta^{13}C$ value of methane in the melange appears to be too heavy, a likely result of oxidation of the outcrop methane. A comparison of the carbon isotopic data suggests that the gases in the well and at the outcrop are not directly related.

CONCLUSIONS

This study has not demonstrated a clear relation among hydrocarbon gases found at a test well, in natural seeps, or in outcrop samples that have a petroliferous odor. Stable carbon and hydrogen isotopic compositions of methane at three seeps (Garfield gas mounds, Sol Duc Hot Springs seep, and Pysht seep) and at a test well (Wilson Ranch) suggest that the gas is thermogenic. However, the lack of hydrocarbons larger than methane at two seeps was unexpected for a gas from a supposed thermogenic source. The

Table 3. Carbon isotopic composition of hydrocarbon components in gas from a test well and from an outcrop of smell mud, Olympic Peninsula, Washington

[Data from Moses Chung (written commun., 1987). Values in per mil]

	methane	ethane	propane	i-butane	n-butane
Wilson Ranch well	-34.8	-27.2	-25.1	-25.9	-24.4
Sample S86-100, Ruby Beach	-27.3	-35.9	-30.2	-28.1	

missing hydrocarbons in the seep gases perhaps were stripped from the gas mixtures during migration to the surface. Alternatively, the methane with higher molecular weight hydrocarbons may have been derived from oil, whereas the methane without higher molecular weight components may have come from the dispersed, solid organic matter. The gas mixtures in outcrops of smell muds are dominated by higher molecular weight gases. The concentrations of these gases are greatest in smell muds from Ruby Beach. The relation between gas in the melange and natural seep gas is uncertain; however, the gas in outcrops of melange may result from microseeps, the rate of flow of which can vary from year to year.

REFERENCES CITED

Claypool, G.E., Threlkeld, C.N., and Magoon, L.B., 1980, Biogenic and thermogenic origins of natural gas in Cook Inlet Basin, Alaska: American Association of Petroleum Geologists Bulletin, v. 64, p. 1131–1139.

James, A.T., 1983, Correlation of natural gas by use of carbon isotopic distribution between hydrocarbon components: American Association of Petroleum Geologists Bulletin, v. 67, p. 1176–1191.

Jenden, P.D., and Kaplan, I.R., 1986, Comparison of microbial gases from the Middle America Trench and Scripps Submarine Canyon—implications for the origin of natural gas: Applied Geochemistry, v. 1, p. 631–646.

Kvenvolden, K.A., and Redden, G.W., 1980, Hydrocarbon gas in sediment from the shelf, slope, and basin of the Bering Sea: Geochimica et Cosmochimica Acta, v. 44, p. 1145–1150.

Lupton, C.T., 1915, Oil and gas in the western part of the Olympic Peninsula, Washington: U.S. Geological Survey Bulletin 581, p. 23–81.

Rau, W.W., and Grocock, G.R., 1974, Piercement structure outcrops along the Washington coast: Washington Division of Geology and Earth Resources Information Circular 51, 7 p.

Rau, W.W., and McFarland, C.R., 1982, Coastal wells of Washington: Washington Division of Geology and Earth Resources Report of Investigations 26, 4 sheets.

Schoell M., 1980, The hydrogen and carbon isotopic composition of methane from natural gases of various origins: Geochimica et Cosmochimica Acta, v. 44, p. 649–661.

———1983, Genetic characterization of natural gases: American Association of Petroleum Geologists Bulletin, v. 67, p. 2225–2238.

Snavely, P.D., Jr., 1987, Tertiary geological framework, neotectonics, and petroleum potential of the Oregon-Washington continental margin, *in* Scholl, D.W., Grantz, A., and Vedder, J.G., eds., Geology and resource potential of the continental margin of western North America and adjacent ocean basins—Beaufort Sea to Baja California: Houston, Texas, Circum-Pacific Council for Energy and Mineral Resources, Earth Science Series, Volume 6, p. 305–335.

Snavely, P.D., Jr., MacLeod, N.S., Niem, A.R., and Minasian, D.L., 1986, Geologic map of Cape Flattery area, northwestern Olympic Peninsula, Washington: U.S. Geological Survey Open-File Report 86–344B.

Tabor, R.W., and Cady, W.M., 1978, Geologic map of the Olympic Peninsula, Washington: U.S. Geological Survey Miscellaneous Investigations Map I–994, scale 1:125,000.