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Reconnaissance Study of Source Rock Potential of the Vaca Muerta Formation of the Zapala and Loncopue Areas, Argentina

by

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INTRODUCTION

Black calcareous shale of the Vaca Muerta Formation (Late Kimmeridgian to Early Cretaceous) has been considered one of the potential source rocks responsible for petroleum accumulations in the Neuquen Basin, Argentina (Kugler, 1985 and 1987). A three-day field trip to sample the Vaca Muerta Formation was organized by Roberto J. Merino under the direction of Norman N. Anderson (Amoco Argentina Oil Company) following the 13th World Petroleum Congress in Buenos Aires, Argentina. The objective of the trip was to collect representative samples of thermally immature Vaca Muerta Formation in sufficient quantities to conduct hydrous pyrolysis experiments to determine oil generation kinetics and oil expulsion efficiencies of this potential source rock.

RESULTS AND INTERPRETATIONS

Nine outcrops of the Vaca Muerta were examined on the western side of the Neuquen Basin in the Zapala and Loncopue areas of the Neuquen Province (Figure 1). Eighteen samples were collected from seven of the nine examined outcrops (Table 1). Data obtained by Kugler (1987) indicated the Vaca Muerta Formation is thermally immature in the Zapala area. No thermal maturity data on the Vaca Muerta Formation in the Loncopue Area was available, but good accessibility to the nearly complete exposure of this rock unit made it a good prospect for sample collection on a limited time schedule.

Zapala Area

The Vaca Muerta Formation in this area has been divided into three members by Leanza and Zeiss (1990). The Lower Vaca Muerta Member occurs at the base of the formation and consists of 164 m of bituminous shale and marlstone. This member is overlain by the Los Catutos Member, which consists of 70 m of lithographic limestone. The Upper Vaca Muerta Member occurs at the top of the formation and consists of 94 m of siltstone, shale, and marlstone.

Picun Leufu Outcrop: This outcrop is a good exposure of the Picun Leufu Limestone, Vaca Muerta Formation, and Lotena Formation, in a road cut and an adjacent stream cut. The exposure occurs approximately 33 km south of Zapala on Highway 40, immediately south of the bridge over the Picun Leufu Arroyo. Although Kugler (1987) reports samples from the Vaca Muerta Fm. with 2.8 to 6.4 wt. % organic carbon from this locality, the entire exposure consists of a light reddish, earthy saprolite with fracture fillings of gypsum and jarosite. Digging back into this exposure verified that it has been altered by pedogenic weathering and no samples of the saprolite were collected. This observation is an obvious discrepancy with the samples collected by Kugler (1987).

Pichi Moncol Hill: This outcrop is a poor exposure of the Upper Vaca Muerta Member that comprises the Pichi Moncol Hill, which is capped by the basal Picun Leufu Formation. This prominent topographic feature occurs approximately one kilometer south of the town of Los Catutos. The upper member in this area consists of 94 m of marlstone (Leanza and Zeiss (1990). Similar to the Picon Leufu outcrop, pedogenic weathering has left only a saprolite exposed on the hillside and no samples were collected.

Cementera Loma Negra Quarry: An excellent exposure of the uppermost limestone unit (i.e., W-limestone) in the Los Catutos Member occurs in this active quarry, 1.5 km east of Pichi Moncol Hill and accessible from Highway 22. The entire Los Catutos Member is about 70 m thick and consists of the 10-m thick "**W**" limestone, 12-m thick "**Z**" limestone, 11-m thick "**Y**" limestone, 16-m thick "**X**" limestone and 14-m thick "**X+α**" limestone, which are separated by 1 to 3 m of marlstone (Leanza and Zeiss, 1990). The "**W**" limestone examined at this locality consists of a basal dark-gray, laminated, massive limestone overlain by a dark-gray, structureless, massive limestone (Figure 2).

Rock-Eval data on samples collected from the basal laminated limestone and the upper structureless limestone are given in Table 2 (911024-5 and -6. Neither of these two lithologies appear to be potential source rocks, because their low organic carbon contents (<2.5 wt. %) are not likely to form a continuous bitumen network during early stages of maturation (Lewan, 1987). Although the generated hydrocarbons (S_2) and hydrogen index (HI) do show that these rocks can produce some hydrocarbons under the unnatural laboratory conditions employed by Rock-Eval pyrolysis, it is unlikely that these vaporized hydrocarbons would be expelled from a rock under natural maturation (Lewan, in press). The low T_{max} and production index values for these two samples suggest they are thermally immature. This tentative maturity assessment is in agreement with vitrinite reflectance values of less than 0.6% R_o suggested by Kugler (1987) for the Vaca Muerta Fm. in this general area.

Los Catutos Quarry: An excellent exposure of the basal section of the Los Catutos Member and the uppersection of the underlying Lower Vaca Muerta Member occurs in this abandoned quarry. The quarry is accessible by a dirt road that intersects Highway 22 approximately 15 km northwest of Zapala. The upper few meters of limestone in the quarry represent a saprolite horizon resulting from pedogenic weathering. This saprolite grades downward into the dark-gray limestone along regional fractures with light-yellowish gray saprolite rinds extending into the rock perpendicular from the fracture planes. The thickness of

these saprolite rinds diminishes with depth until only the dark-gray massive limestone occurs.

Laminated and structureless dark-gray, massive limestones are the two major lithologies exposed in the basal section of the Los Catutos Member. The upper 9 m of the 16-m thick, "**X**" limestone consists of the laminated lithology, and the underlying 14-m thick "**X+α**" limestone consists mostly of the structureless lithology. Four samples of laminated dark-gray massive limestone were collected from the "**X**" limestone (Figure 3). As shown in Table 2 (samples 911024-1 through -4, this rock unit is not likely to be an effective source rock because its organic carbon content is below 2.5 wt. %. Similar to the "**W**" limestone at the Cementera Loma Negra Quarry, the low T_{max} and production index values suggest they are thermally immature.

At the most eastward part of the quarry, the uppermost 5 m of the Lower Vaca Muerta Member are exposed. The marlstone and shale exposed in a prominant gully have been subjected to pedogenic weathering and only saprolite is exposed. No samples of this badly weathered rock were collected.

Loncopue Area

The Vaca Muerta Formation and the underlying Tordillo Formation are well exposed in the Cajon de Almaza Valley southeast of Loncopue. State Highway 32 follows this valley eastward from the Agrio River (Figure 1). More than 700 m of the Vaca Muerta Formation has been measured in this valley (R. J. Merino, 1991, person. comm.). Late Cenozoic igneous intrusions commonly penetrate the Vaca Muerta Formation in this area. Lenses and lenticular beds of limestone occur within the predominantly dark-gray calcareous shales, but in this area the Los Catutos Member is not observed. Five outcrops along this continuous exposure were examined and sampled where igneous intrusions were not apparent.

The *first outcrop* examined is approximately 60 m above the basal contact of the Vaca Muerta Formation in a gully on the north side of the valley. This basal part of the section is poorly exposed and consists of friable to moderately indurated black shale penetrated by veins and veinlets of secondary gypsum. Discoloration of some portions of the shale to a reddish-brown suggest some pedogenic weathering of the section has occurred. These zones of discoloration were avoided during sampling and three samples (911025-1 to -3) were collected from a hole dug 1 m into the side of the outcrop. The organic carbon contents of these shales exceeded the 2.5 wt. % limit for potential source rocks (Table 2), but the high level of thermal maturity, as indicated by the low yield of generated hydrocarbons and low hydrogen indices prevents determining whether the original organic matter was oil prone.

The *second outcrop* examined is approximately 80 m above the basal contact of the Vaca Muerta Formation on the west facing slope of the next major gully to the east. Unlike the underlying section, this exposure has less vegetation and gypsum veins are limited to parting separations along bedding planes. One representative

sample (911025-4) was collected from a hole dug one meter into the slope. The low organic carbon content of this sample (1.5 wt. %, Table 2) indicates it is not a potential source rock. Similar to the previous samples from the first outcrop, the high level of thermal maturity, as indicated by the low yield of generated hydrocarbons and the low hydrogen index, prevents determining whether the original organic matter was oil prone.

The *third outcrop* is a small road-cut into the Vaca Muerta Formation where an ephemeral tributary enters the valley from the south. Black calcareous shale predominates the section with a few interbedded lenticular limestones. The shale is well indurated and blocky, with no jarosite and only minor occurrences of gypsum. This outcrop is approximately 100 m above the basal contact of the Vaca Muerta Formation. One representative sample of shale (911025-5) was collected from this outcrop. As shown in Table 2, the organic carbon content of this sample is less than 2.5 wt. %, but its high level of thermal maturity, as indicated by the low hydrogen index, suggests its original organic carbon content may have originally exceeded this limiting value. Hydrous pyrolysis experiments on thermally immature source rocks (Lewan, 1985) show that typically about one-third of the original organic carbon of Type-II kerogens is lost as oil and gas at vitrinite reflectance values greater than 1.5% R_O. Although recalculating the original organic carbon content by this carbon loss would make the rock a potential source rock (i.e., 2.2/0.667 = 3.3 wt. %), the high thermal maturity, as indicated by the low hydrogen index, prevents determining whether the original organic matter was oil prone.

The *fourth outcrop* is an excellent exposure of the Vaca Muerta Fm. where the main stream has cut into the north side of the valley. Approximately 50 m of black calcareous shale with periodic interbeds of lenticular limestone was measured and sampled (Figure 4). This part of the section is approximately 350 to 400 m above the basal contact of the Vaca Muerta Formation. The shale is well indurated and blocky with no jarosite coatings and only minor occurrences of gypsum. The six samples (911025-7 to -12) collected from this outcrop all have organic carbon values less than 2.5 wt. % and low hydrogen-indices indicative of high thermal maturities past the stage of oil generation. Only two of the samples (911025-10 and-11) may have had original organic carbon contents above 2.5 wt. %, but once again, the high thermal maturity prevents determining whether the original organic matter was oil prone.

The *fifth outcrop* occurs on the south side of the valley and is the most eastward exposure examined. This part of the section is approximately 450 to 550 m above the base of the Vaca Muerta Formation. Similar to the *third* and *fourth outcrops*, the section consists of black calcareous shale with interbeds of lenticular limestones. One representative sample (i.e. 911025-6) of the well indurated and blocky shale was collected from this outcrop. Similar to the *third outcrop*, the original organic carbon content of this shale may have exceeded the 2.5 wt. % limit for a potential source rock (2.22/0.667 = 3.3 wt. %), but the high thermal maturity prevents determining whether the original organic matter was oil prone.

CONCLUSIONS

The rock samples collected and analyzed in this reconnaissance study do not unequivocally establish the black calcareous shale of the Vaca Muerta Formation as a major petroleum source rock in the Neuquen Basin. This uncertainty arises from pedogenic weathering in the Zapala area and high thermal maturity in the Loncopue area. The lower 80 m of the Vaca Muerta Formation does have organic carbon contents high enough to suggest it may be a potential source rock, but it has not been established that this organic matter is oil prone. Kugler (1985, 1987) has also observed organic carbon contents in excess of 2.5 wt. % in the basal 50 m of the Vaca Muerta Formation in the Lindero Atravesado Field. However, no evaluation of organic matter type has been made other than visually noting that the kerogen is amorphous in appearance. Further study of outcrops and subsurface cores of the basal section of the Vaca Muerta Formation are needed to unequivocally establish this rock unit as a petroleum source rock. In addition, correlations between produced oils and possible source rocks in the Neuquen Basin are needed for further confirmation.

Unreliable T_{max} and production index values for the samples from the Loncopue area make it difficult to assess thermal maturity with only Rock-Eval data. However, the extremely low S_2 yields responsible for the unreliability of these two parameters suggest that thermal stress experienced by these rocks was in excess of that required to attain vitrinite reflectance values greater than 1.5% R_O. Kugler (1987) does not report vitrinite reflectance values from this area, but east and north of the Rio Neuquen he reports values between 0.6 and 1.35% R_O for the Vaca Muerta. As discussed by Kugler (1987), the thermal history of the Neuquen Basin is complicated by uplift and higher thermal gradients in the western part of the basin. Future attempts to obtain sufficient quantities of thermally immature samples of the Vaca Muerta Formation for hydrous pyrolysis experiments obviously should avoid this area.

Sufficient quantities of thermally immature source rocks from the Vaca Muerta Formation for hydrous pyrolysis experimentation were not obtained in this reconnaissance study. However, the samples of limestone from the Los Catutos Member may be useful in testing the hypothesis that carbonate source rocks only require organic carbon contents in excess of 0.3 to 0.5. wt. % to generate and expel petroleum (Hunt, 1967; Palacas, 1978; and Gardner and Bray, 1984). The samples from the "**W**" and "**X**" limestones have organic carbon contents (0.6 to 1.2 wt. %) between this lower limit and 2.5 wt. %. The higher temperatures (300° to 365°C) used in hydrous pyrolysis to simulate petroleum formation in a period of days rather than hundreds of millenniums at lower subsurface temperatures (80° to 150°C), are considered to exaggerate the amount of generated oil that is expelled from a source rock (Lewan, 1992 and 1993). A corollary to this assessment is that thermally immature rocks incapable of generating an expelled oil in hydrous pyrolysis experiments will definitely not be capable of generating an expelled oil in subsiding sedimentary basins. Several of the limestone samples of the Los Catutos Member

may be subjected to hydrous pyrolysis at experimental temperatures of 350° to 360°C for 72 hours to determine their effectiveness in generating an expelled oil.

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Table 1. Areas, outcrops, rock units, and samples studied in the Neuquen Basin, Argentina

Area	Outcrop Name	Rock Unit Exposed	Sample Numbers
ZAPALA	Picun Leufu	Undiff. Vaca Muerta Fm.	no samples
	Pichi Moncol Hill	Upper Vaca Muerta Mb.	no samples
	Cementera Loma Negra Quarry	Los Catutos Mb. "**W**" Limestone	911024-5 911024-6
	Los Catutos Quarry	Los Catutos Mb. "**X**" Limestone	911024-1 911024-2 911024-3 911024-4
	Los Catutos Quarry	Lower Vaca Muerta Mb.	no samples
LONCOPUE (Cajon de Almaza)	First Outcrop	Vaca Muerta Fm. ~ 60 m above base*	911025-1 911025-2 911025-3
	Second Outcrop	Vaca Muerta Fm. ~ 80 m above base*	911025-4
	Third Outcrop	Vaca Muerta Fm. ~ 100 m above base*	911025-5
	Fourth Outcrop	Vaca Muerta Fm. ~ 350-400 m above base*	911025-7 911025-8 911025-9 911025-10 911025-11 911025-12
	Fifth Outcrop	Vaca Muerta Fm. ~ 450-550 m above base*	911025-6

*Above base refers to contact between the Vaca Muerta Fm. and underlying Tordillo Fm.

Table 2. Results from Rock-Eval pyrolysis on samples of the Vaca Muerta Formation, Neuquen Basin, Argentina. Analyst T. A. Daws, U.S.G.S., Laboratory Job Number 92-016.

Outcrop Name	Sample Numbers	Organic Carbon (wt. %)	Evolved Hydrocarbons S_1 (mg/g)	S_2 (mg/g)	Production Index $S_1/[S_2+S_2]$	Hydrogen Index $([S_2/Org]x100)$	T_{max} (°C)
Cementera Loma Negra	910024-5	0.56	0.00	1.44	0.00	257	432
	911024-6	1.08	0.09	4.18	0.02	387	427
Los Catutos	911024-1	1.01	0.04	2.91	0.01	288	433
	911024-2	1.18	0.19	4.00	0.05	338	428
	911024-3	0.88	0.09	3.44	0.03	390	428
	911024-4	0.79	0.05	2.21	0.02	279	432
Cajon de Almaza							
1st Otc.	922025-1	2.98	0.00	0.04	0.00	1	n.d.
	911025-2	4.15	0.00	0.09	0.00	2	n.d.
	911025-3	4.62	0.03	0.13	0.19	2	n.d.
2st Otc.	911025-4	1.47	0.00	0.09	0.00	6	n.d.
3rd Otc.	911025-5	2.20	0.03	0.26	0.11	11	n.d.
4th Otc.	911025-7	1.42	0.04	0.18	0.18	12	n.d.
	911025-8	1.33	0.06	0.21	0.23	15	n.d.
	911025-9	1.10	0.06	0.14	0.30	12	n.d.
	911025-10	2.05	0.19	0.54	0.26	26	n.d.
	911025-11	1.69	0.15	0.31	0.33	18	n.d.
	911025-12	1.13	0.07	0.15	0.32	13	n.d.
5th Otc.	911025-6	2.22	0.02	0.11	0.17	4	n.d.

n.d. = Temperature at maximum S_2 yield was not determined because of extremely low S_2 yield.

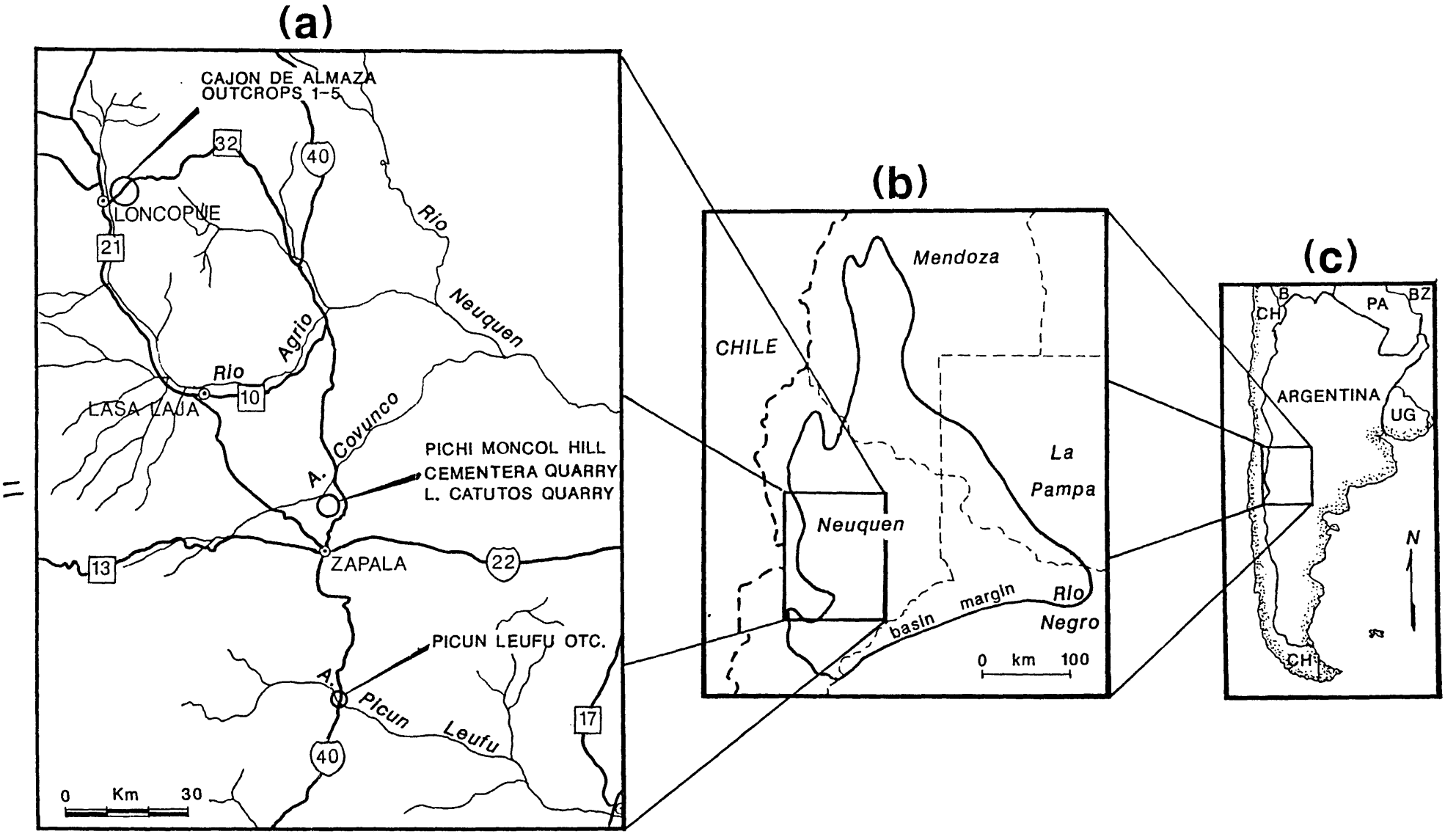

Figure 1. (a) Map of Zapala and Lonopue areas showing location of outcrops of Vaca Muerta Fm. relative to major highways and drainage. (b) Map of Neuquen Basin showing basin margin and province boundaries. (c) Map of Argentina showing its boundaries with Chile (CH), Bolivia (B), Paraguay (PA), Uruguay (UG), and Brazil (BZ).

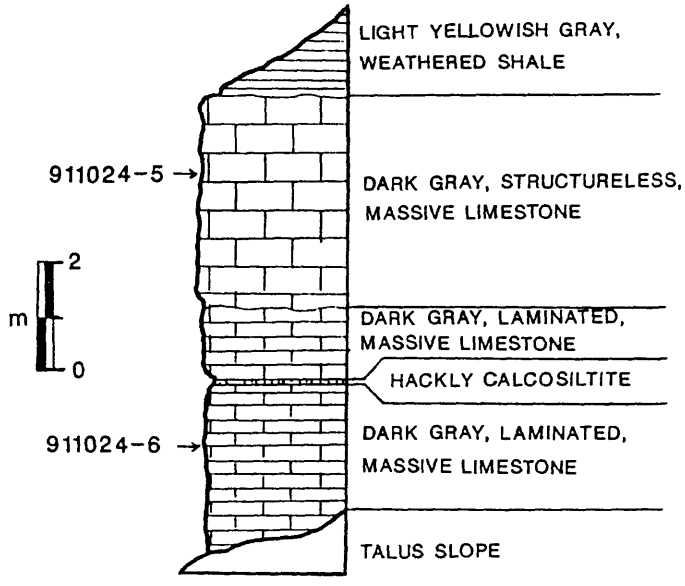

Figure 2. Measured section showing sample locations in the upper part of the "W" limestone of the Los Catutos Member in the Cementera Loma Negra Quarry. Section was measured with a steel measuring tape.

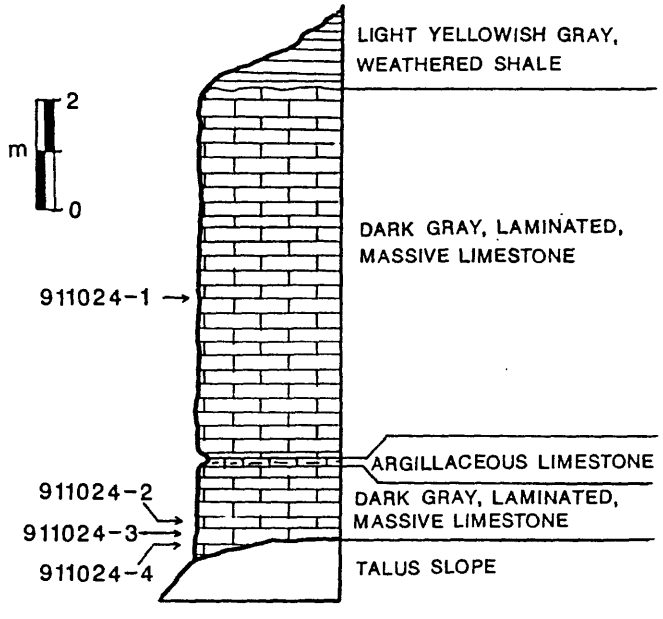

Figure 3. Measured section showing sample locations in the upper part of the "X" limestone of the Los Catutos Member in the Los Catutos Quarry. Section was measured with a steel measuring tape.

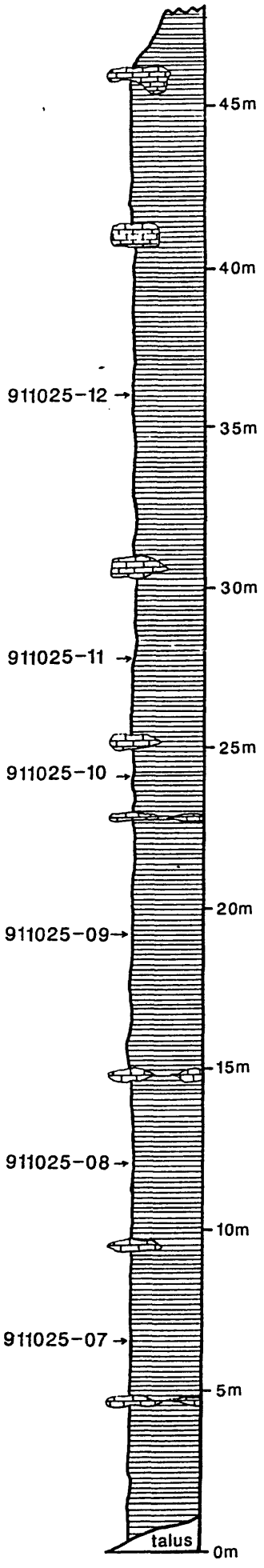

Figure 4. Measured section showing sample locations in the Vaca Muerta Formation exposed at the fourth outcrop in the Cajon de Almaza Valley. Section consists predominantly of well indurated, black, calcareous shale (fine-line pattern) with periodic interbeds of lenticular limestones (offset block pattern). The section was measured by eye-leveling with a Brunton compass and one-meter staff. Attitude of beds was measured on the top of several limestone beds, which gave an average strike of N36°E and a dip of 14° to the southwest. This part of the section has been estimated to be 350 to 400 meters stratigraphically above the base of the Vaca Muerta Formation. This estimate is based on available geological maps, regional dip, and measured distance along Highway 32.