DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

Vitrinite Reflectance and Illite Crystallinity, Franciscan Central Belt and Yolla Bolly Terrane, Northern California

by

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INTRODUCTION

The Franciscan Complex of northern California contains several discrete tectonostratigraphic units (Fig. 1); each unit is characterized by general lithologic content, depositional age, structural style, metamorphic grade, and sandstone petrology (Blake et al., 1985). This report assesses the thermal maturity of Franciscan rocks collected from the Central belt and the Yolla Bolly terrane.

Levels of inorganic metamorphism within the Franciscan Complex of northern California are fairly well documented (Bailey et al., 1964; Blake et al., 1967; Cloos, 1983; Blake et al., 1987). Inorganic phases are sensitive to many variables, however, and key mineral assemblages typically span broad fields of P-T stability (Liou et al., 1985). Even though inorganic data place important limits on both maximum and minimum P-T conditions, most data do not yield precise estimates of paleotemperature, particularly for low grades of metamorphism. Consequently, we have analyzed vitrinite reflectance and illite crystallinity to quantify more precisely the thermal maturity of Franciscan strata.

Results presented herein are a continuation of a larger-scale project involving all major Franciscan terranes of northern California. Two complimentary Open-File Reports (Underwood and O'Leary, 1985; Underwood and Strong, 1986) describe levels of thermal maturity within adjacent field areas containing younger rocks (Fig. 2). These earlier reports also provide more detailed descriptions of both laboratory techniques and statistical treatment of data. Geologic interpretations of the paleothermal data are discussed in greater detail elsewhere (Underwood et al., 1987, 1988; Underwood, 1988).

GEOLOGIC BACKGROUND

The Yolla Bolly terrane (Fig. 1) is divided into four thrust-bounded units ranging from relatively coherent sequences of metagraywacke and chert to polymict melange (Blake et al., 1982, 1985, 1987). Igneous rocks include alkalic-titaniferous intrusive bodies and both intrusive and extrusive keratophyre and quartz keratophyre. Radiolarian microfossils and scarce megafossils indicate a Late Jurassic (Tithonian) to Early Cretaceous (Valanginian) protolith age for most of the terrane; however, middle Cretaceous (Cenomanian) fossils also occur locally. Two phases of penetrative deformation have been recognized, with the first phase accompanied by blueschist-facies metamorphism. The timing of metamorphism has been estimated at approximately 92 Ma (Blake et al., 1987). The key metamorphic minerals of the Yolla Bolly terrane are lawsonite and aragonite, which typically occur with either pumpellyite, sodic amphibole, or jadeitic pyroxene. Maps of metamorphic textural zones and mineral assemblages define an eastward increase in metamorphic grade (Blake et al., 1987). The estimated P-T conditions based upon inorganic phase equilibria range from 180°C and 6 kb in the west, to 285°C and 9 kb in the east.

The Central Franciscan belt (Fig. 1) is a tectonic melange containing mesoscopic blocks and megascopic slabs of graywacke, greenstone,

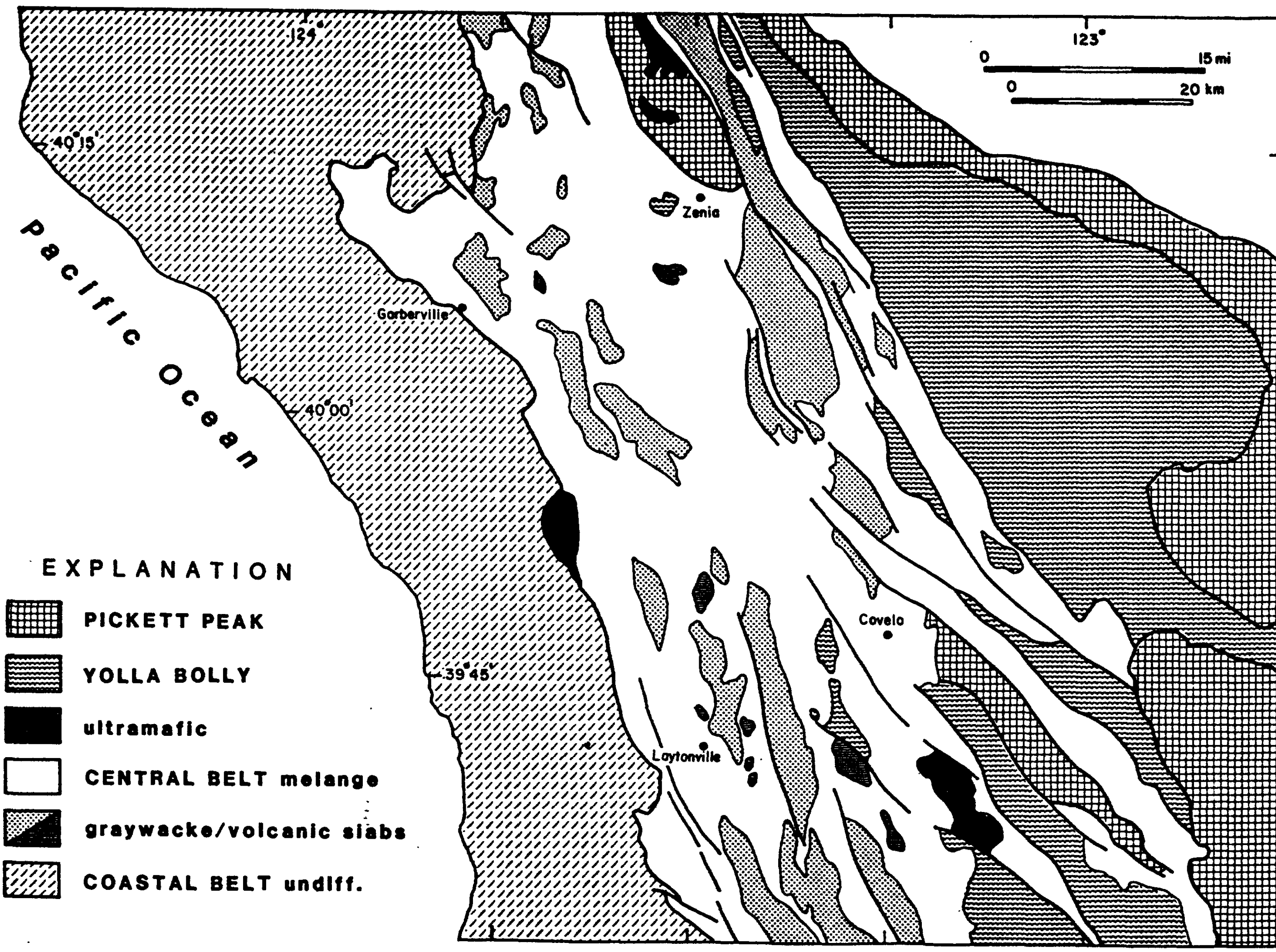


FIGURE 1. Simplified map of tectonostratigraphic terranes, Franciscan Complex, northern California. Modified from Blake et al. (1987).

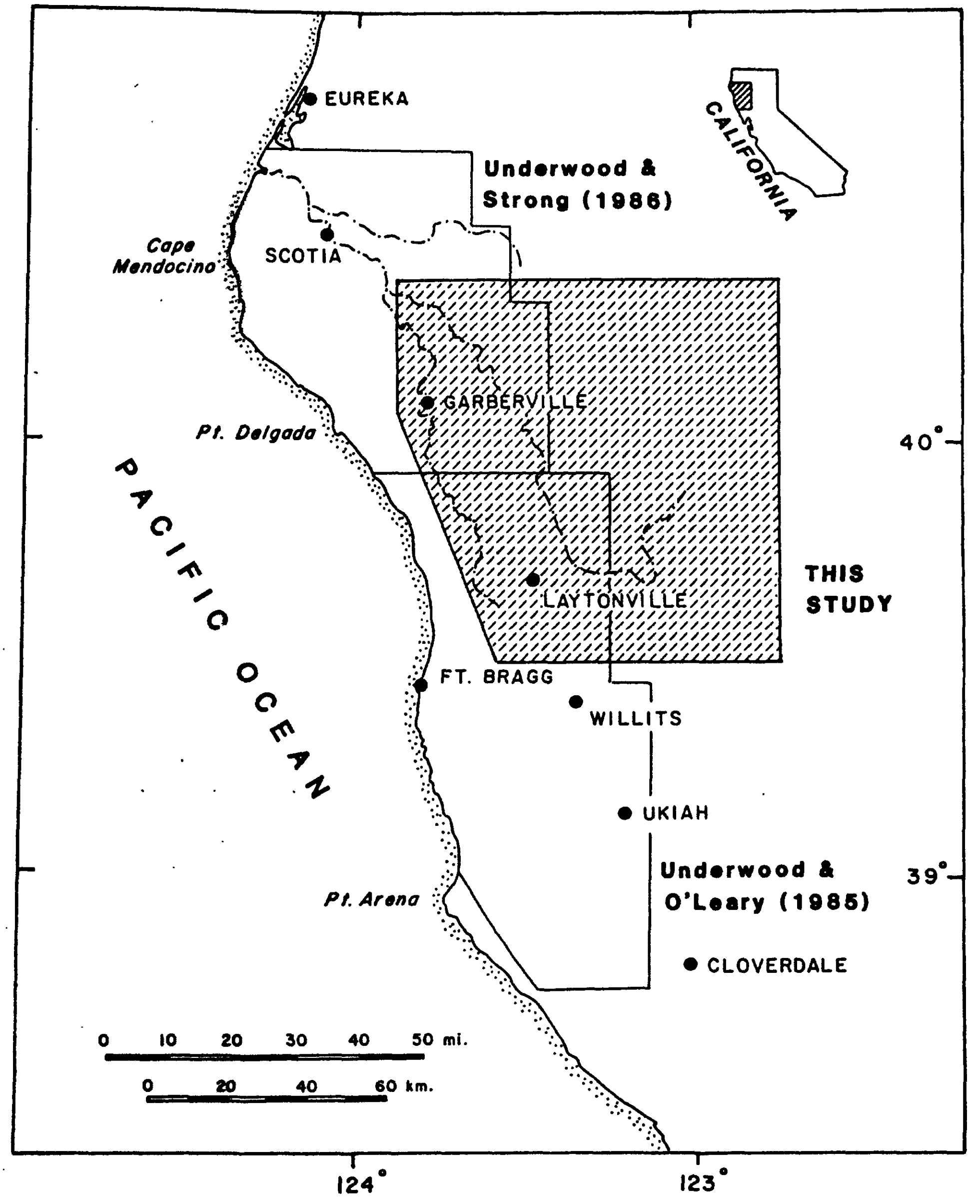


FIGURE 2. Map showing geographic limits of the study area. Results from overlapping regions are described in Underwood and O'Leary (1985) and Underwood and Strong (1986).

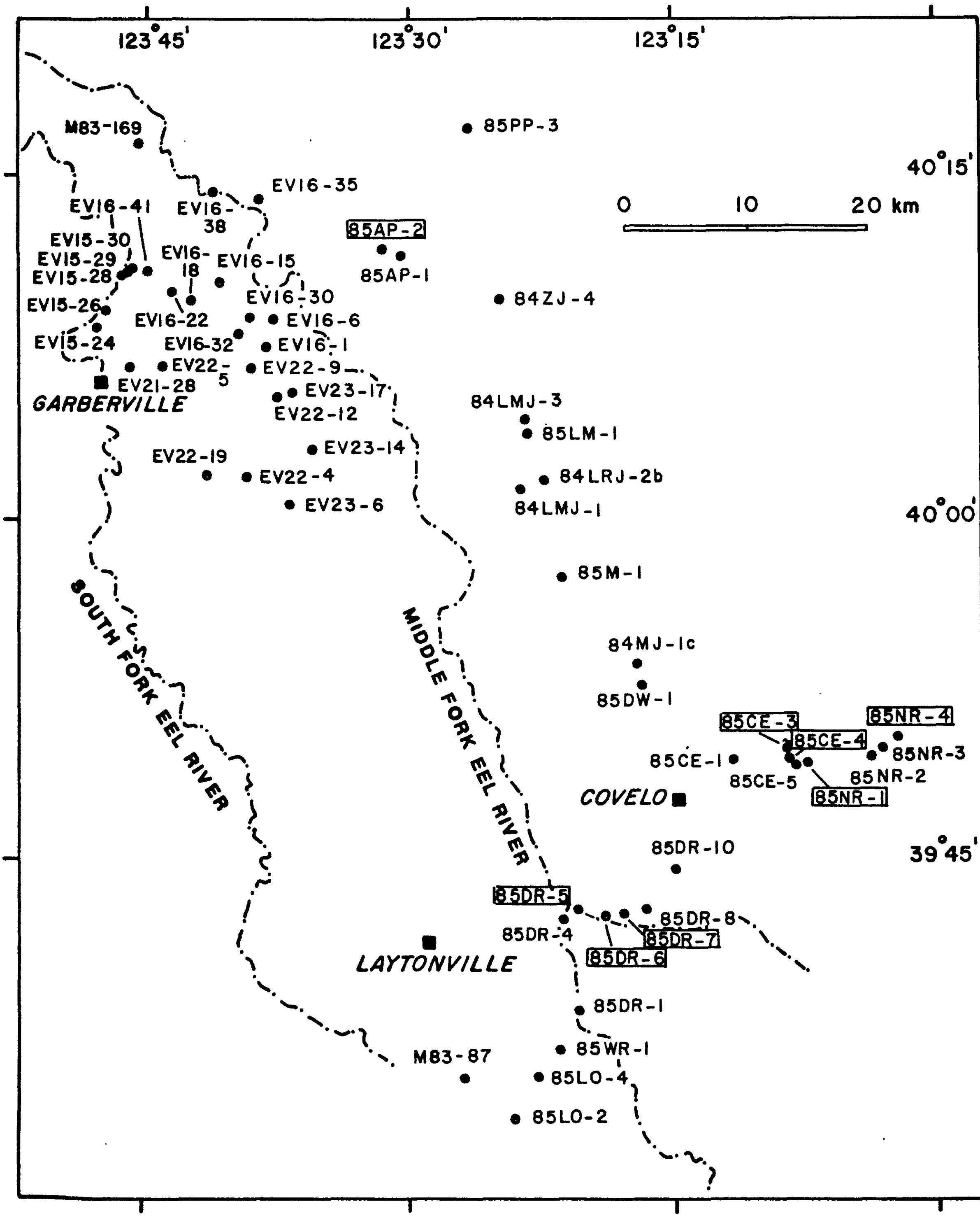


FIGURE 3. Map showing localities of sample sites. Sample numbers in boxes indicate sites within the Yolla Bolly terrane. All other sites are within the Franciscan Central Belt. See Appendix C for coordinates in terms of township, range, and section.

rather than millimeters. Additional descriptions of X-ray laboratory techniques appear in Appendix A.

Several procedures are available to derive estimates of peak paleotemperature from measured values of vitrinite reflectance. Some of these methods consider the effects of both temperature and heating time (Hood et al., 1975; Waples, 1980). Other workers, however, contend that Ro equilibration occurs within 10^4 to 10^6 years and that additional heating time has little or no influence on organic metamorphism (Barker, 1983; Price, 1983; Barker and Pawlewicz, 1986). The temperature estimates reported herein are based upon the Price (1983) correlation. We stress, however, that the consequences of variable heating duration remain controversial (e.g., Bostick, 1984; Kohsmann, 1985); our data, therefore, should be viewed as maximum values of paleotemperature. Based upon the scatter of Price's (1983) data, the statistical error associated with these temperature estimates is approximately $\pm 20^{\circ}C$.

RESULTS

Values of mean reflectance (Rm) for the Central belt and the Yolla Bolly terrane are shown in Figures 4 and 5, and listed in Appendix C. Values for the Yolla Bolly terrane range from 1.00% to 2.13%, and a distinct bimodal grouping is apparent. Based upon the Price (1983) correlation, these levels of thermal maturity suggest burial temperatures of between $183^{\circ}C$ and $285^{\circ}C$ (Fig. 6).

Rm values for the Central belt range from 0.68% to 1.69%; the corresponding temperature estimates are $137^{\circ}C$ to $254^{\circ}C$ (Fig. 6). The average values for the Central belt are Rm = 1.04% and T = $192^{\circ}C$. These temperature estimates are well within the stability fields of mineral assemblages containing pumpellyite + chlorite; this level of inorganic metamorphism is typical of both greenstone blocks and graywackes within the Central belt (see Liou et al., 1985, for phase equilibria data).

The spatial variations in vitrinite reflectance define an overall eastward increase in thermal maturity (Fig. 7) although there are several breaks in the pattern. In a crude sense, these variations in thermal maturity must be a function of differing amounts of uplift and uproofing of the Franciscan Complex from west to east. Local perturbations from the regional pattern can be attributed to the polyphase history of regional deformation, including late Cenozoic right-lateral strike-slip faulting (Herd, 1980; McLaughlin and Nilsen, 1982). The region south of Covelo displays a more disjointed thermal structure, and this could be due to juxtaposition of contrasting blocks by strike-slip faults or due to earlier mixing of larger coherent slabs within the melange.

We stress here that the number of analyses of Yolla Bolly strata is limited to eight, and all but one of the sample sites lie outside of the main, in situ portion of the terrane. Consequently, the results obtained from outliers of Yolla Bolly rocks may not be representative of the terrane as a whole.

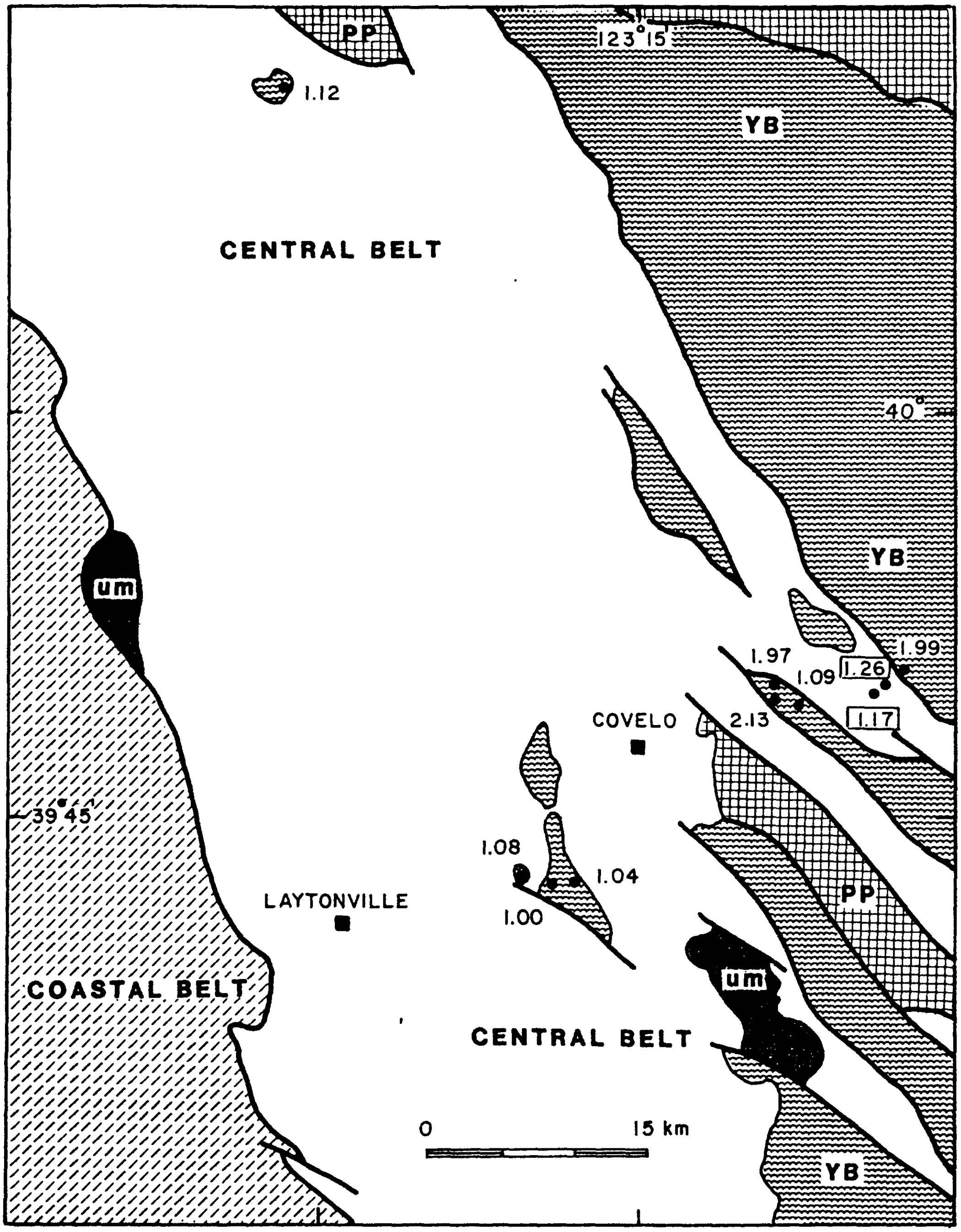


FIGURE 4. Map showing sample localities and values of mean vitrinite reflectance for the Yolla Bolly terrane. Two values from the Central Franciscan belt are enclosed in boxes. Other rock units include large slabs of ultramafic rock (um), the Picket Peak terrane (PP), the undifferentiated Coastal belt (Yager and Coastal terranes), and the Central belt (no pattern). Geologic base is from Blake et al. (1987).

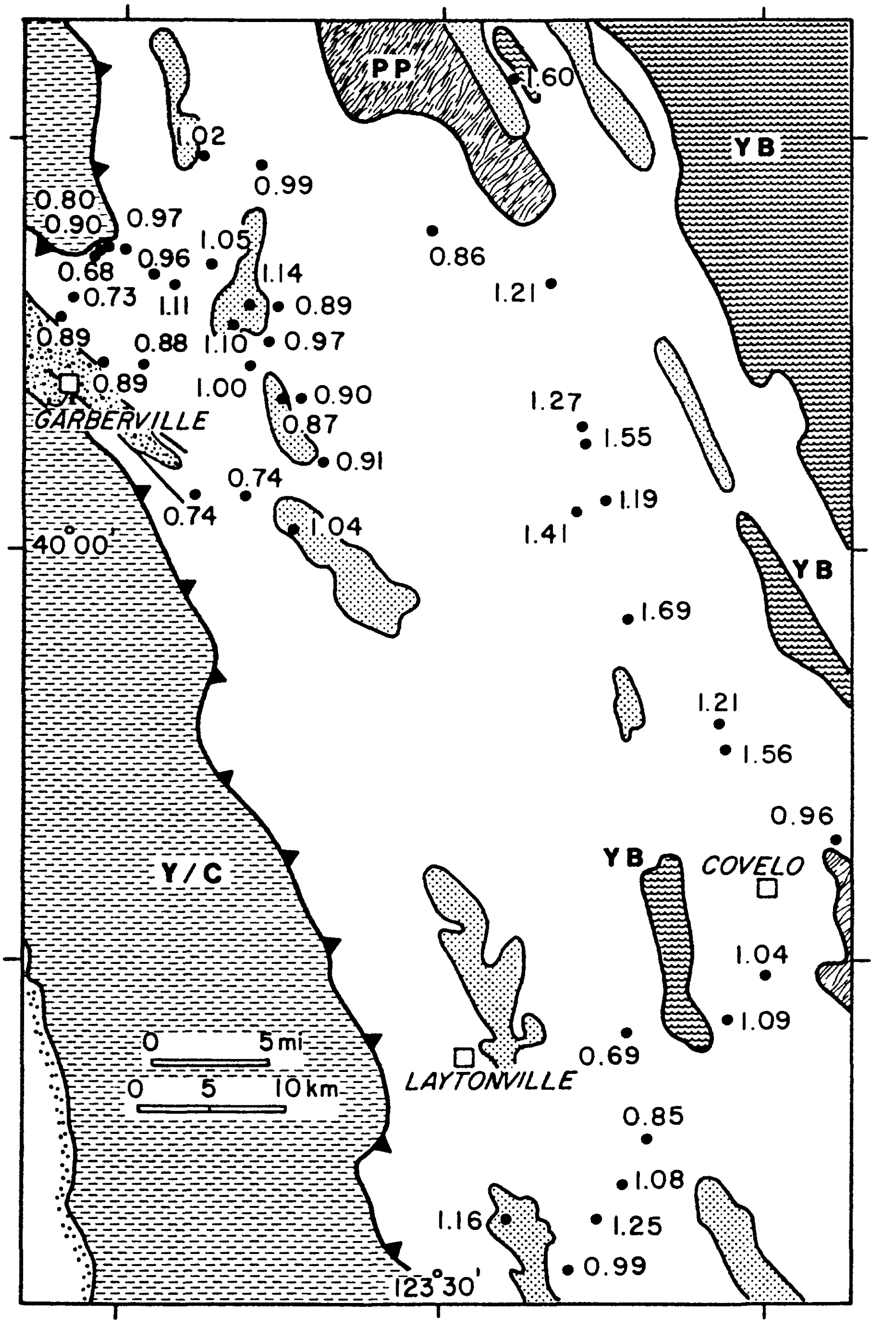


FIGURE 5. Map showing sample localities and values of mean vitrinite reflectance for the Central Franciscan belt, northern California. Blocks of relatively coherent strata are depicted with stippled pattern. Other terranes include the Yolla Bolly (YB), Picket Peak (PP), and undifferentiated Coastal/Yager (Y/C). Geologic base modified from Blake et al. (1985).

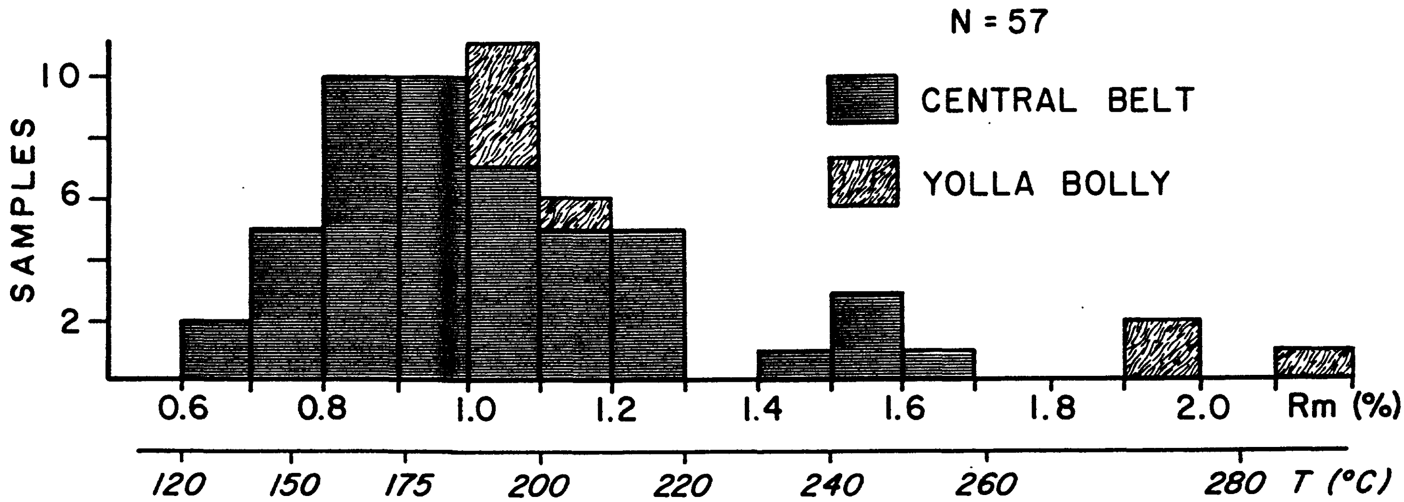


FIGURE 6. Histogram showing values of mean vitrinite reflectance for all samples within the study area. Conversion from Rm to peak paleotemperature follows the correlation established by Price (1983). Linear regression equation for this correlation is:

$$\text{Temp } (^{\circ}C) = 302.97 \log_{10} Rm + 187.33$$

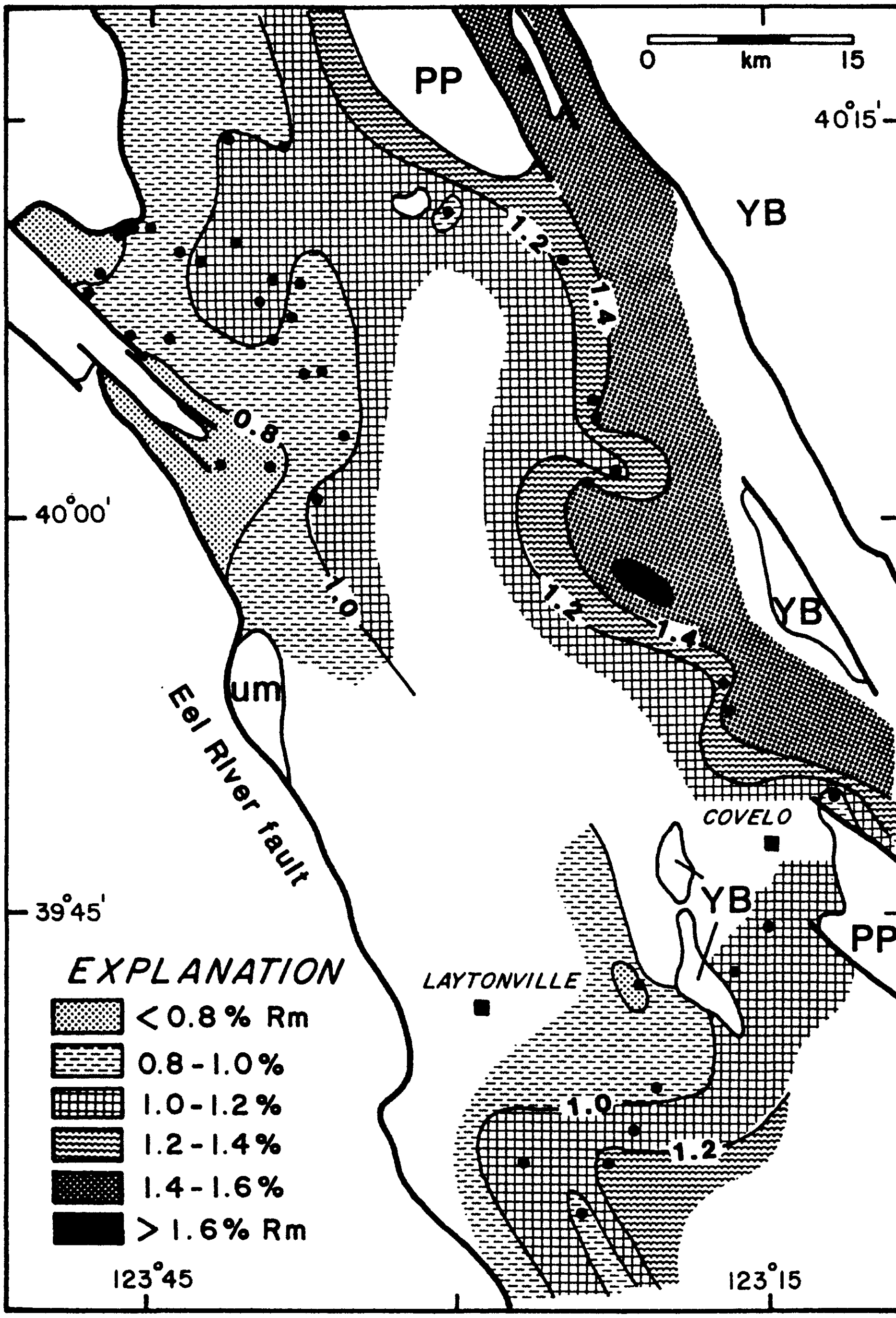


FIGURE 7. Isoreflectance map (mean vitrinite reflectance) for the Franciscan Central Belt, northern California. Terrane boundaries modified from Blake et al. (1987). PP = Picket Peak terrane; YB = Yolla Bolly terrane; um = ultramafic rocks. Eel River fault separates Central Belt from Tertiary strata of the Yager terrane. Solid dots indicate sample localities.

The correlation between vitrinite reflectance and illite crystallinity is shown in Figure 8. Compared to correlations already established for younger Franciscan strata of the Coastal belt (Underwood, 1987), the degree of scatter displayed by data from the Central belt is appreciable (i.e., much lower correlation coefficient). This relatively weak correlation could be a response to higher lithostatic pressures and/or larger deviatoric stresses. Geologic structures (faults, shear zones, etc.) can influence the degree of reflectance anisotropy in coals (Stone and Cook, 1979), and the standard deviation of Ro values about the mean is known to increase with increasing thermal rank (Stach et al., 1975). Consequently, the values of mean random reflectance from both the Central belt and Yolla Bolly terrane may have been perturbed by penetrative deformation, thereby decreasing the correlation with illite data. Weathering of strongly sheared argillites could have a negative effect on vitrinite as well. On the other hand, the direct influence of both pervasive shearing and high lithostatic pressure on illite crystallinity remains poorly known. In the absence of empirical or experimental data bearing directly on this issue, we are unable to attribute the relatively poor Rm-CI correlation to any single factor.

CONCLUSIONS

Estimates of Franciscan paleotemperature, based upon measurements of vitrinite reflectance, are compatible with phase-equilibria data from inorganic mineral assemblages. Maximum temperatures for eight samples collected from the Yolla Bolly terrane were no higher than 285°C, and values for matrix argillites of the Central belt melange range between 137°C and 254°C (average = 192°C). There is a crude eastward increase in levels of organic metamorphism; inconsistancies in this pattern are due to juxtaposition of contrasting slabs during polyphase deformation of the melange. The correlation between vitrinite reflectance and illite crystallinity is statistically significant for both Central belt and Yolla Bolly data, but the correlation coefficients are lower than coefficients for comparable data from the Franciscan Coastal belt.

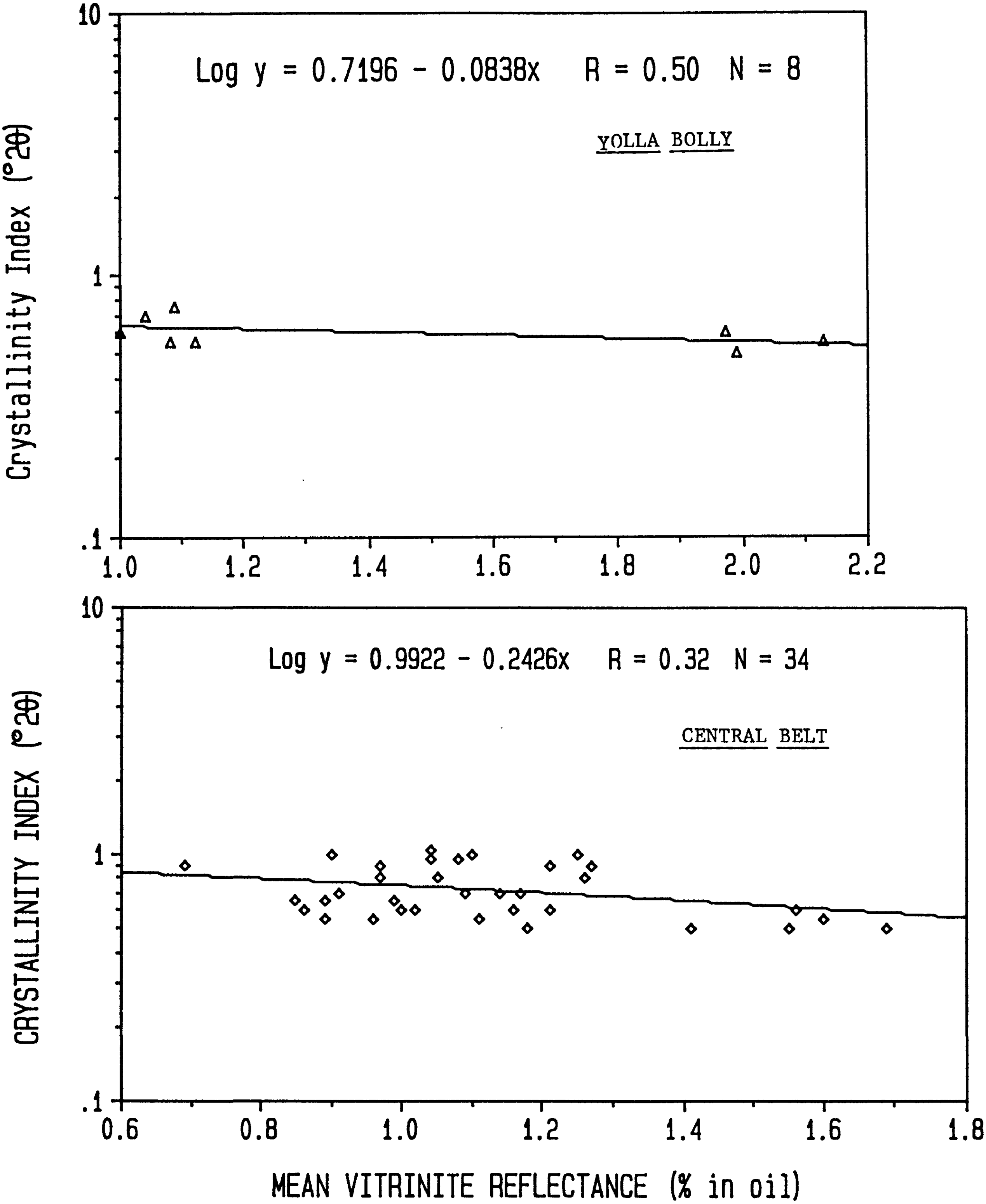


FIGURE 8. Correlations (from linear regression analysis) between mean vitrinite reflectance and illite crystallinity index, Central Franciscan belt and Yolla Bolly terrane. R = correlation coefficient; N = number of samples in data population.

APPENDIX A. TECHNIQUES OF SAMPLE SELECTION, PREPARATION, MEASUREMENT, AND STATISTICAL EVALUATION

Sample Selection

One problem with the technique of vitrinite reflectance is the potential alteration of vitrinite particles by weathering and oxidation at or near the surface. Surface weathering can produce multimodal patterns on histograms depicting random reflectance (Marchioni, 1983), and the weathering effect can extend as deep as 10 meters below the surface. In order to minimize this effect, pains were taken to select the freshest possible samples from roadcut and streambank exposures. It also should be noted that actual measurements made from oxidation halos yielded lower reflectance values than similar measurements made on unaltered cores.

Kerogen Concentration

Measurements of organic-carbon content demonstrate that most Franciscan shales from northern California are depleted in organic matter, with values typically ranging between 0.35 and 0.65 wt-% carbon (Underwood, 1985, 1987). Consequently, organic matter had to be extracted and concentrated before measurements of vitrinite reflectance could be completed. The pertinent laboratory methods are outlined in Underwood and Strong (1986).

Data Collection

Observations in reflected light were made using a 50x oil-immersion lens and a 16x ocular mounted on a Leitz Ortholux research microscope set up in the reflected light mode. A Keithly 244 high-voltage power supply and a Hewlett-Packard direct-current power supply provided stable power to the photometer and the light source, respectively. Reflected light was directed to a Leitz MPV-1 photometer through a 70-micron diameter diaphragm (constricted to a 4-micron opening during calibration), and each Ro value was read on a Keithly 177 Microvolt digital voltmeter. Calibration of the photometer for a linear response was performed using polished reflectance standards (0.299, 0.506, 0.940, 1.025, and 1.672%).

The criteria for selection of appropriate organic particles to measure are described in Dow and O'Connor (1982) and Underwood and Strong (1986). Briefly, vitrinite particles were chosen on the basis of morphology, color, and texture of the polished surface. Given the levels of maturation documented in our study, vitrinite can be identified on the basis of relative reflectivity or a "lowest gray" scale. Such methods require abundant kerogen, however, so that direct comparisons between macerals can be made within a single field of view. To avoid bias toward a "correct" reflectance value in lean samples, we depended strongly on morphologic criteria to select vitrinite particles (see Stach et al., 1975). About 50 data points were gathered from each sample to assure statistically valid results.

Data Reduction and Interpretation

It is a common practice to plot reflectance data in histogram form to help identify recycled vitrinite (Dow and O'Connor, 1982). Given a Gaussian distribution of Ro values, calculations of mean and standard deviation are completed using all available data points. Populations of vitrinite can be distinctly bimodal or multimodal, however. By convention, the mode showing the lowest reflectance is viewed as the indigenous population; higher values are labeled "reworked" and eliminated from calculations of mean reflectance. If a few isolated values are much higher than the majority, "recycled" grains are routinely eliminated. However, some Franciscan samples produce complicated multimodal patterns, and this inhibits objective identification of the "recycled" population (Appendix C). Multimodal distributions can be caused by surface weathering (Marchioni, 1983) or increasing anisotropy with grade, and turbiditic shales commonly are bimodal or multimodal (Castano and Sparks, 1974). Moreover, we believe the inference of recycling should be consistent with independent geologic information linking the depositional environment to a suitable source terrane with appropriately elevated thermal maturity. Such a link is difficult to establish because of polyphase faulting and long-distance translation of terranes in northern California. To avoid data bias and increase the degree of reproducibility in the study, higher Ro values were eliminated from calculations of mean reflectance only if a data gap of a least 0.10% Ro (one sampling interval) is present or morphologic features suggested recycling.

Illite Crystallinity

Another measure of thermal maturity is the degree of crystallinity of the clay mineral illite (Weaver, 1960; Kubler, 1968). The conversion of smectite to illite involves the progressive expulsion of interlayer water and incorporation of cations (primarily K^+ and Na^+) within the clay lattice. This process is transitional, and the intermediate product is a mixed-layer/smectite clay. The final phase of illitization requires the dehydration of the last layers of water from between the clay layers and the inclusion of additional K^+ ions into the illite structure. As this reaction proceeds the degree of illite crystallinity increases (Dunoyer de Segonzac, 1970).

Perry and Hower (1970) concluded that the transformation of smectite to illite is controlled largely by temperature rather than pressure, so illite crystallinity can be correlated with thermal maturity. However, to our knowledge, crystallinity has never been calibrated directly against a temperature scale using either borehole data or experimental data. Crystallinity is measured from the morphology of the characteristic 10Å illite peak on an X-ray diffractogram. Higher crystallinity is indicated by a sharper or narrower peak, and lower crystallinity is indicated by a diffuse or broader peak (Weaver, 1960, Kubler, 1968).

As with vitrinite reflectance, several factors can bias the results of crystallinity measurements. With low-grade rocks, in particular, spurious values can be caused by detrital illite particles. Disordering of the illite is increased by the presence of interlayer smectite (Gaudette et al., 1966), and degradation may result from weathering (Dunoyer de Segonzac, 1970). Both of these factors reduce the degree of crystallinity. An increase in crystallinity can be caused by interstitial solutions in more permeable sediments, the presence of larger detrital illite particles, or the incorporation of K^+ or Na^+ into the structures of alkali-deficient illites (Dunoyer de Segonzac, 1970).

Two X-ray diffraction methods are available to measure illite crystallinity. Weaver's (1960) method, called the sharpness ratio, is the ratio of the total height of the 10Å peak to the peak height at 10.5Å (Fig. 9). Higher degrees of illite crystallinity correspond to increasing sharpness ratios.

Kubler's (1968) method was used in our study; the so-called crystallinity index (CI) uses the width of the 10Å illite reflection at half the peak height on the X-ray diffractogram (Fig. 9). Lower CI means higher crystallinity. Kubler's original values were defined in terms of millimeters, and direct comparisons of values could be made only if laboratory instruments were calibrated according to the same analytical conditions. Subsequent workers (e.g., Kisch, 1980; Duba and Williams-Jones, 1983) expressed their measurements in terms of degrees 2θ, which normalizes the differences between instruments. The crystallinity-index data presented in this report, therefore, are expressed in degrees 2θ.

Sample Preparation

Approximately forty grams of shale were crushed in a cast-iron mortar and then sifted in a 105 micron sieve. The finer fraction was dispersed in 400 milliliters of distilled water, using an ultrasonicator for four minutes. A pinch of Calgon was added prior to sonication to facilitate dispersal of floccules. Samples were allowed to settle, and after eight hours the 2-micron fraction was sampled from the uppermost 10 cm of water using a pipette. This size fraction was sampled to reduce contamination by detrital illite, which is usually larger. The clay suspension was then pipetted onto a glass slide and allowed to air dry at room temperature. Three oriented slides were prepared in this manner for each sample. One slide was left untreated, one was treated with ethylene glycol, and the other heated at 100°C for two hours.

All samples were analyzed by X-ray diffraction using a Phillips X-ray diffractometer. CuKα radiation was generated by a graphite monochromator. Samples were run at a rate of 1° per minute from 3° to 35° 2θ. The voltage was set at 35 kilovolts and 20 milliamps. The same rate and meter settings were used for all slides. All three slides (untreated, glycolated, heated) were examined to better define the 10Å illite peak and to recognize the effects of any mixed-layer clays present. Only glycolated samples were used to measure the illite crystallinity, however, because this treatment reduces the influence of mixed-layer clay minerals on the diffractogram response of illite.

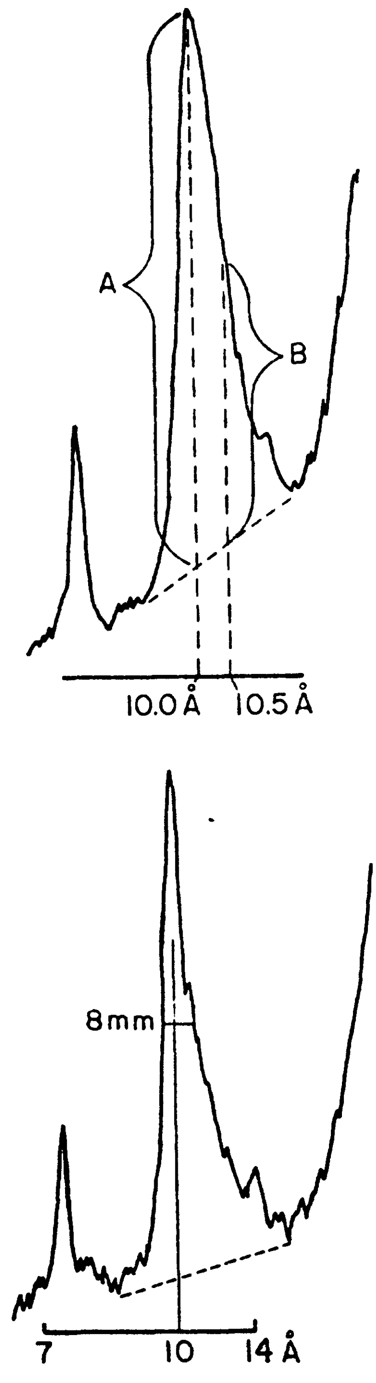
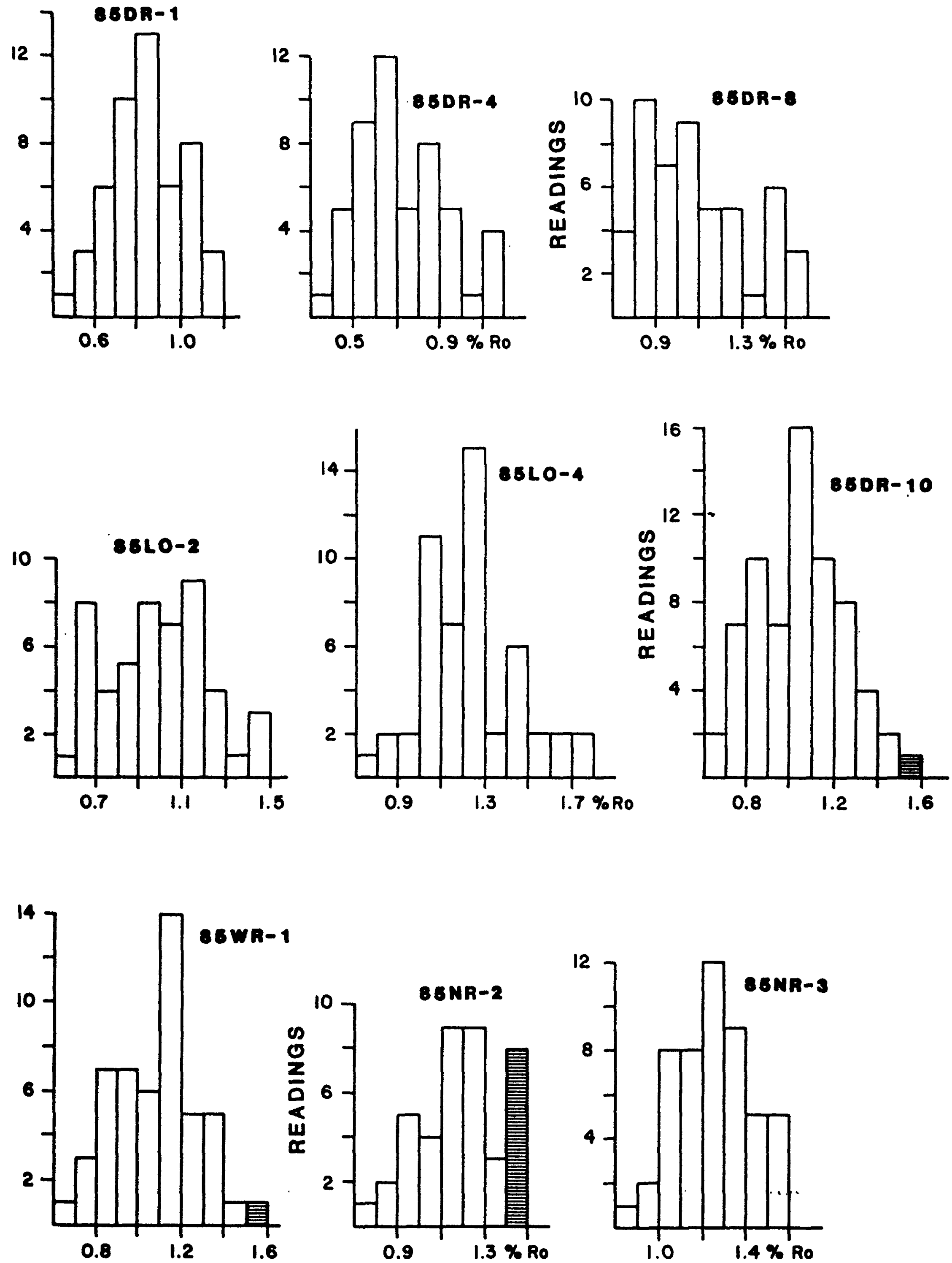


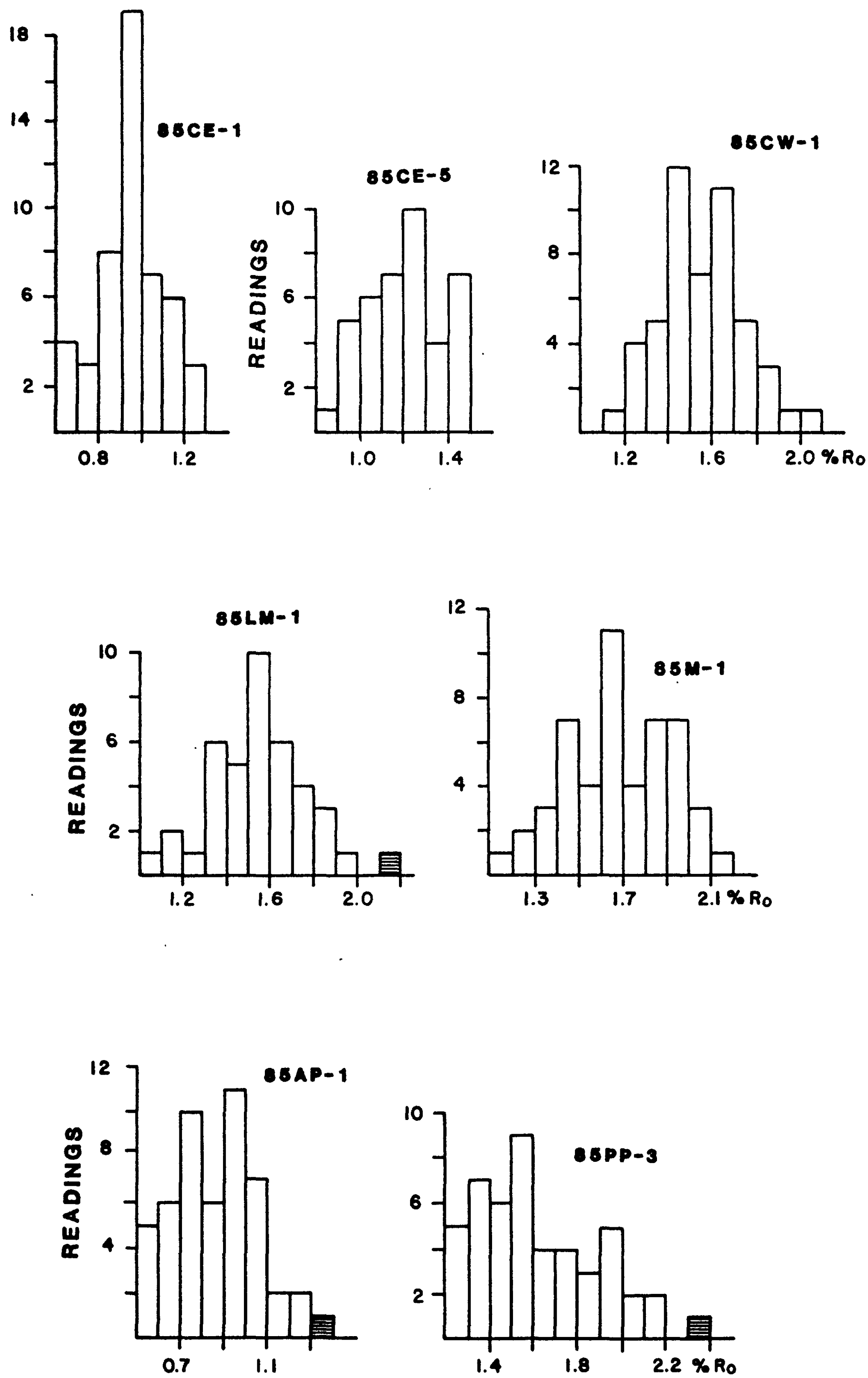
FIGURE 9. Methods used to quantify illite crystallinity. Upper diagram shows Weaver's (1960) method, termed the sharpness ratio; this parameter is the ratio of the total height of the 10 Å peak to the peak height at 10.5Å. A higher degree of crystallinity results in an increasing sharpness ratio. The lower diagram shows the Kubler (1968) method; the so-called crystallinity index uses the width of the 10Å reflection at one-half the peak height. Values (expressed in terms of °2θ) decrease with increasing crystallinity. All values reported in this study use the Kubler method.

APPENDIX B. HISTOGRAMS OF Ro VALUES FOR INDIVIDUAL SAMPLES FROM THE YOLLA BOLLY TERRANE AND FRANCISCAN CENTRAL BELT

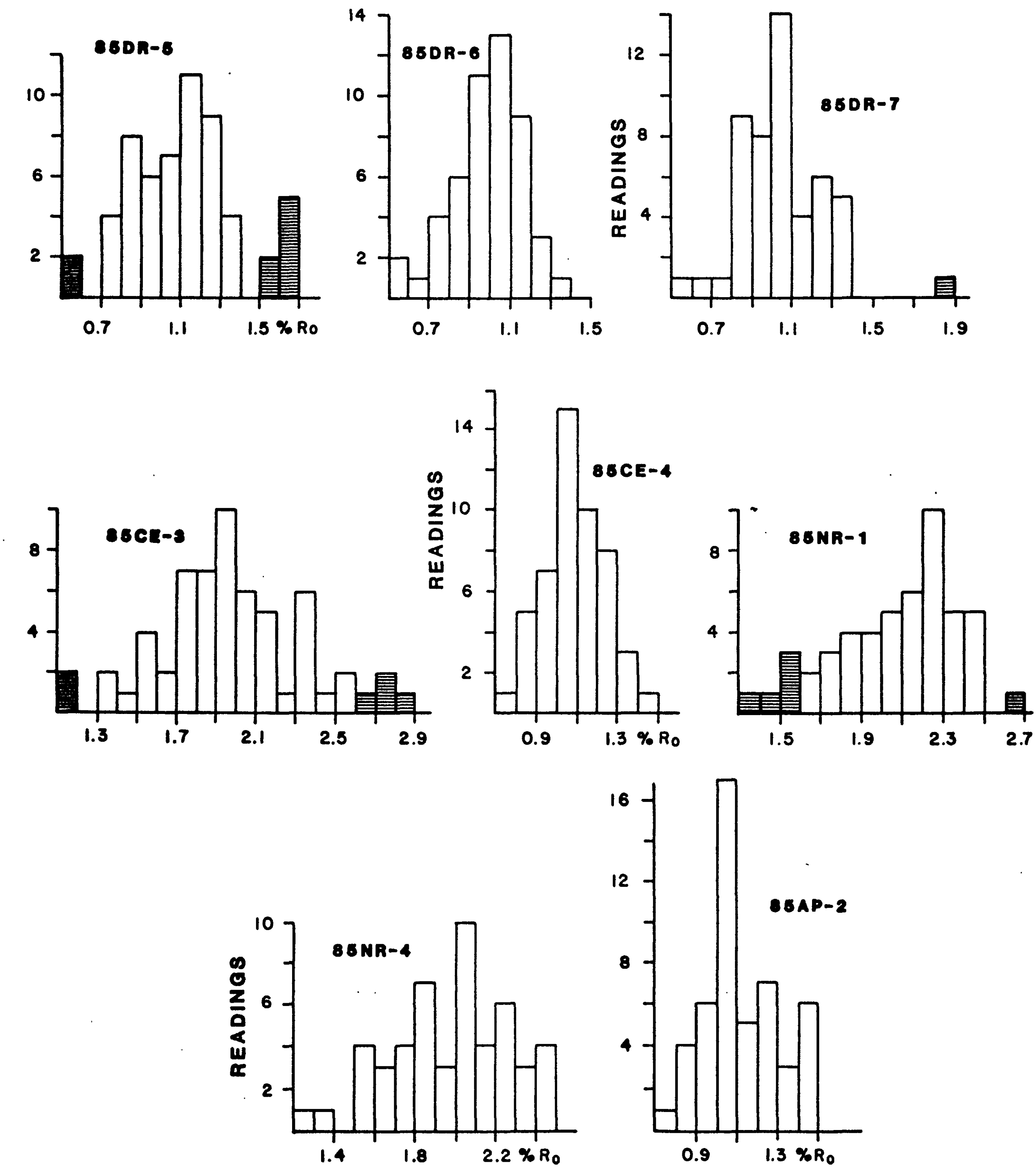


Note: Cross-hatched pattern indicates values eliminated from calculations of mean vitrinite reflectance.

APPENDIX B. (continued)



APPENDIX B. (continued) – YOLLA BOLLY TERRANE



APPENDIX C. TABULATION OF VITRINITE AND ILLITE DATA

<u>Yolla Bolly Terrane</u>

Sample	Location (TRS)	N	Rm (%)	Range	S.D.	T (°C)	CI (°2θ)
85DR-5	21N-13W-S6	50	1.08	0.75-1.45	0.19	197	0.55
85DR-6	21N-13W-S4	50	1.00	0.59-1.38	0.17	187	0.60
85DR-7	21N-13W-S3	49	1.04	0.58-1.35	0.18	192	0.70
85CE-3	23N-12W-S24	54	1.97	1.37-2.54	0.27	276	0.60
85CE-4	23N-12W-S25	50	1.09	0.73-1.45	0.15	199	0.75
85NR-1	23N-11W-S30	44	2.13	1.68-2.50	0.23	287	0.55
85NR-4	23N-11W-S13	50	1.99	1.25-2.50	0.30	278	0.50
85AP-2	3S-6E-S17	50	1.12	0.77-1.49	0.18	202	0.55

<u>Central Belt</u>

Sample	Location (TRS)	N	Rm (%)	Range	S.D.	T (°C)	CI (°2θ)
M83-87	20N-14W-S18	67	1.16	0.74-1.68	0.23	207	0.60
M83-169	2S-4E-S19	47	0.82	0.49-1.15	0.19	161	——
M83-193	1N-4E-S7*	47	0.71	0.43-1.04	0.17	142	——
M83-190	1N-3E-S15*	47	1.18	0.74-1.48	0.17	209	0.50
84MJ-1c	24N-8E-S24	118	1.21	0.90-1.48	0.15	212	——
EV15-24	4S-3E-S1	39	0.89	0.63-1.11	0.14	172	——
EV15-26	3S-3E-S36	50	0.73	0.46-1.11	0.15	146	——
EV15-28	3S-4E-S30	47	0.68	0.42-1.00	0.17	137	——
EV15-29	3S-4E-S19	49	0.90	0.55-1.35	0.21	173	——
EV15-30	3S-4E-S19	50	0.80	0.47-1.18	0.20	158	——
EV16-1	4S-5E-S8	50	0.97	0.56-1.37	0.22	183	0.80
EV16-6	4S-5E-S4	49	0.89	0.49-1.25	0.22	172	
EV16-15	3S-4E-S25	40	1.05	0.75-1.28	0.13	194	0.80
EV16-18	3S-4E-S34	49	1.11	0.71-1.40	0.19	201	0.55
EV16-22	3S-4E-S34	49	0.96	0.65-1.30	0.16	182	——
EV16-30	4S-5E-S6	50	1.14	0.90-1.47	0.15	205	0.70
EV16-32	4S-5E-S6	45	1.10	0.81-1.34	0.14	200	1.00
EV16-35	3S-5E-S5	48	0.99	0.70-1.24	0.13	186	——
EV16-38	3S-4E-S2	50	1.02	0.70-1.28	0.17	190	0.60
EV16-41	3S-4E-S29	40	0.97	0.72-1.29	0.16	183	0.90
EV21-28	4S-4E-S17	47	0.89	0.55-1.18	0.17	172	0.55
EV22-4	5S-5E-S7	50	0.74	0.43-1.06	0.14	148	——
EV22-5	4S-4E-S15	47	0.88	0.60-1.20	0.16	171	——
EV22-9	4S-5E-S18	47	1.00	0.75-1.34	0.16	187	0.60
EV22-12	4S-5E-S28	48	0.87	0.53-1.14	0.16	169	——
EV22-19	5S-4E-S11	50	0.74	0.41-1.04	0.15	148	——
EV23-6	5S-5E-S21	47	1.04	0.72-1.39	0.18	192	0.95
EV23-14	5S-5E-S2	49	0.91	0.57-1.27	0.18	175	0.70
EV23-17	4S-5E-S21	50	0.90	0.60-1.31	0.19	173	1.00
84ZJ-4	3S-7E-S32	50	1.21	0.89-1.65	0.17	212	0.90
84LMJ-1	5S-7E-S21	50	1.41	1.09-1.85	0.18	232	0.50
84LMJ-3	4S-7E-S33	60	1.27	0.92-1.55	0.17	219	0.90

*localities near Bridgeville, not shown on Fig. 3; see Underwood and Strong (1986)

84IRJ-2	5S-7E-S15	48	1.19	0.93-1.55	0.15	210	----
85LO-2	20N-14W-S27	50	0.99	0.60-1.49	0.23	186	0.65
85LO-4	20N-14W-S14	50	1.25	0.78-1.73	0.21	217	1.00
85WR-1	20N-14W-S1	49	1.08	0.68-1.43	0.18	197	0.95
85DR-1	21N-13W-S31	50	0.85	0.50-1.20	0.17	166	0.65
85DR-4	21N-13W-S6	50	0.69	0.35-1.20	0.17	138	0.90
85DR-8	21N-13W-S2	50	1.09	0.73-1.56	0.23	199	0.70
85DR-10	22N-13W-S25	66	1.04	0.65-1.48	0.19	192	1.05
85CE-1	23N-12W-S28	50	0.96	0.64-1.25	0.15	182	0.55
85CE-5	23N-12W-S25	40	1.21	0.89-1.50	0.17	212	0.60
85NR-2	23N-11W-27/22	40	1.17	0.80-1.45	0.18	208	0.70
85NR-3	23N-11W-S23	50	1.26	0.90-1.58	0.16	218	0.80
85CW-1	23N-13W-S11	50	1.56	1.21-2.03	0.19	246	0.60
85M-1	24N-13W-S6	50	1.69	1.20-2.18	0.24	256	0.50
85LM-1	5S-7E-S4	39	1.55	1.08-1.91	0.19	245	0.50
85PP-3	2S-6E-S13	49	1.60	1.25-2.17	0.27	249	0.55
85AP-1	3S-6E-S21	49	0.86	0.54-1.25	0.18	167	0.60

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