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A high $^{87}Sr/^{86}Sr$ mantle source for low alkali tholeiite, northern Great Basin

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Abstract—Olivine tholeiites, the youngest Tertiary units (about 8–11 m.y. old) at five widely spaced localities in northeastern Nevada, are geologically related to the basalts of the Snake River Plain, Idaho, to the north and are similar in major element and alkali chemistry to mid-ocean ridge basalts (MORB) and island arc tholeiites. The measured K (1250–3350 ppm), Rb (1·9–6·2 ppm), and Sr (140–240 ppm) concentrations overlap the range reported for MORB. Three of the five samples have low, unfractionated rare earth element (REE) patterns, the other two show moderate light-REE enrichment. Barium concentration is high and variable (100–780 ppm) and does not correlate with the other LIL elements. The rocks have $^{87}Sr/^{86}Sr = 0{\cdot}7052$–$0{\cdot}7076$, considerably higher than MORB ($\sim 0{\cdot}702$–$0{\cdot}703$). These samples are chemically distinct (i.e. less alkalic) from the olivine tholeiites from the adjacent Snake River Plain, but their Sr isotopic compositions are similar. They contain Sr that is distinctly more radiogenic than the basalts from the adjacent Great Basin. About 10 b.y. would be required for the mean measured Rb/Sr ($\sim 0{\cdot}02$) of these samples to generate, in a closed system, the radiogenic Sr they contain. The low alkali content of these basalts makes crustal contamination an unlikely mechanism. If the magma is uncontaminated, the time-averaged Rb/Sr of the source material must have been $\sim 0{\cdot}04$. A significant decrease in Rb/Sr of the source material (a factor $\gtrsim 2$) thus most probably occurred in the relatively recent ($\lesssim 10^9$ yr) past. Such a decrease of Rb/Sr in the mantle could accompany alkali depletion produced by an episode of partial melting and magma extraction. In contrast, low $^{87}Sr/^{86}Sr$ ratios indicate that the source material of the mid-ocean ridge basalts may have been depleted early in the Earth's history.

INTRODUCTION

BASALTS in the ocean basins exhibit a generally positive correlation between some large ion lithophile element (LIL) concentrations and $^{87}Sr/^{86}Sr$ ratio (e.g. HATERMAN and HEDGE, 1971). This presumably results from the fact that in general a more alkali-rich source mantle has a higher Rb/Sr ratio, generating in time a higher $^{87}Sr/^{86}Sr$ ratio. Least-radiogenic Sr occurs in mid-ocean ridge basalts (MORB), which contain the lowest concentrations of LIL elements.

An earlier reconnaissance study (MCKEE and MARK, 1971) indicated the presence of alkali-depleted, MORB-like olivine tholeiites with high $^{87}Sr/^{86}Sr$ ratios in northern Nevada. Similar basalt flows are the youngest rocks across a wide region of the northern part of the Great Basin in northeastern Nevada. These flows overlap a variety of older rock types typical of the Basin and Range province to the south. In a geologic sense these flows are the southern distal edge of the extensive tholeiitic provinces to the north, the Snake River and Columbia River provinces, and are not part of the Basin and Range volcanic suite.

Five petrographically similar olivine tholeiites were selected for this study from widely separated localities in northeastern Nevada (Fig. 1). Sample descriptions and locations are in the Appendix. Each sample is from the youngest unit at its locality. K–Ar ages (about 8–11 m.y., Table 1) contrast with Basin and Range volcanic rocks in central Nevada, most of which are no younger than about 18 m.y. We report Sr isotopic compositions, major and trace element concentrations to provide comparisons with basalts

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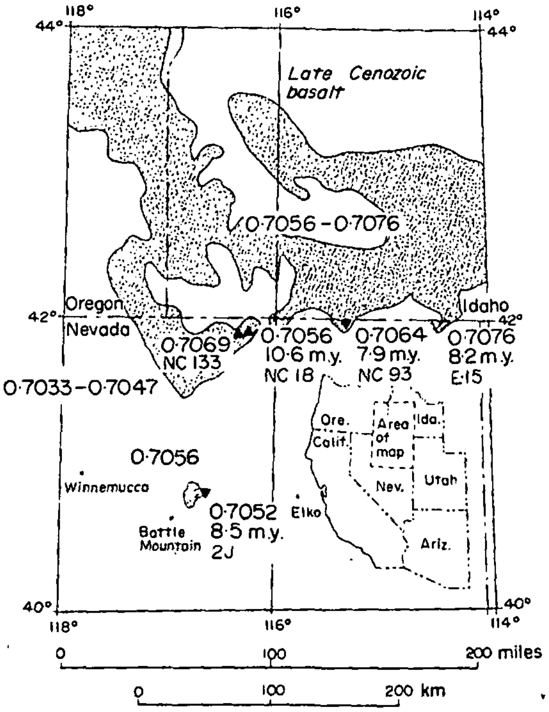

Fig. 1. Location map showing $^{87}Sr/^{86}Sr$ ratios and K–Ar ages of samples. Regional data from LEEMAN and MANTON (1971), MCKEE and MARK (1971), and NOBEL *et al.* (1973).

from other tectonic settings and constraints on petrogenetic models.

ANALYTICAL PROCEDURES

K, Rb, and Sr were measured by standard isotope dilution mass spectrometry at the University of California, Los Angeles (MARK *et al.*, 1974). Neutron activation analyses were performed at the Lawrence Berkeley Laboratory, Berkeley, California (PERLMAN and ASARO, 1969). Ar and K analyses were performed by standard procedures at the U.S. Geological Survey, Menlo Park, California (for description, see DALRYMPLE and LANPHERE, 1969).

PETROCHEMISTRY

In Tables 2, 3 and 5 we present the chemistry of the late Tertiary olivine tholeiites from northeast Nevada. Table 4 provides a comparison with other relevant basalt compositions. The samples exhibit a major-element chemistry distinct from that reported by LEEMAN and MANTON (1971) for 78 Pliocene to Holocene olivine tholeiites from the Snake River Plain. That is, they are higher in silica and lower in alkalis, TiO_2 and P_2O_5 (i.e. less alkalic). They also have more Al_2O_3 and MgO and less total Fe. The samples are also distinctly more magnesian and less alkalic than the Miocene Steens Basalt of southeastern Oregon (GUNN and WATKINS, 1970). The basalts from this study are also distinct from Hawaiian tholeiites, containing less SiO_2 and TiO_2 and more Al_2O_3. They are similar in major element chemistry to mid-ocean ridge basalts (CANN, 1971) and high-Mg Picture Gorge Basalt (WRIGHT *et al.*, 1973) and almost identical to sample No. 88 ('most primitive') from the Santa Rosa Range, Humboldt County, Nevada (LEMASURIER, 1968). The bulk of the late Cenozoic basalts from the adjacent Basin and Range province analyzed by LEEMAN and RODGERS (1970) are alkali-olivine basalts. These workers report, however, an average composition of three Basin and Range olivine tholeiites that is very similar to the alivine tholeiites from this study.

On the basis of REE contents the basalt samples fall into two groups (Fig. 2, Table 5). In one group (E-15, 6238-2J, 54NC93; referred to as 'low REE') the chondrite-normalized REE pattern shows only

Table 1. K–Ar ages and analytical data of four late Tertiary olivine basalts from northeastern Nevada

Sample number general locality	Locality (lat N) (long W)	K_2O (weight percent)	$Ar^{40}rad_X$ 10^{-12} mole per g	$Ar^{40}rad\ X/oo$ / $Ar^{40}total$	Apparent age (m.y.) ±1σ (estimated)
E-15 (Shoshone Creek)	41°57'00" 114°35'54"	0.20	2.428	13.1	8.2±0.6
54-NC-93 (Buck Creek)	41°59'48" 115°25'24"	0.19	2.196	19.7	7.9±0.5
61-NC-18 (Hat Peak)	41°54'00" 116°23'15"	0.35	5.494	6.5	10.6±1.0
6238-2J (Sheep Creek Range)	40°50'36" 116°37'15"	0.34	4.265	9.7	8.5±0.7

Constants used:

$$\lambda\epsilon = 0{\cdot}585 \times 10^{-10}\ yr^{-1}.$$
$$\lambda\beta = 4{\cdot}72 \times 10^{-10}\ yr^{-1}.$$
$$K^{40}/K\ total = 1{\cdot}19 \times 10^{-4}\ moles/moles.$$

Table 2. Major element chemistry of olivine tholeiites from northeastern Nevada

	E15	6238-2J	54NC93	61NC18	62NC133
SiO_2	48.00	47.4	48.11	47.88	48.8
Al_2O_3	16.96 (17.0)	16.7 (17.3)	16.81 (16.8)	15.68 (15.5)	15.1 (15.1)
Fe_2O_3	2.41 (ΣFeO 9.61)	1.4 (9.52)	1.36 (9.36)	2.68 (11.19)	3.0 (10.08)
FeO	7.48	8.1	8.32	8.93	7.7
MgO	8.80	9.3	9.65	8.34	8.9
CaO	12.02	11.3	11.98	10.70	11.3
Na_2O	2.09 (2.17)	2.1 (2.49)	2.13 (2.20)	2.44 (2.49)	2.2 (2.21)
K_2O	0.16	0.34	0.15	0.38	0.43
H_2O+	0.24	0.44	0.14	0.39	0.36
H_2O^-	0.21	0.21	0.08	0.21	0.38
TiO_2	1.21 (1.19)	1.2 (1.16)	0.96 (.95)	1.74 (1.80)	1.5 (1.32)
P_2O_5	0.14	0.26	0.09	0.26	0.43
MnO	0.18 (.174)	0.19 (.177)	0.18 (.183)	0.19 (.187)	0.14 (.182)
CO_2	0.01		0.00	0.01	0.05
Cl	0.01		0.00	0.00	
F	0.02		0.02	0.03	
Subtotal	99.94		99.98	99.86	
Less O	0.01		0.01	0.01	
TOTAL	99.93	98.9	99.97	99.85	100.3

Analyses of E15, 54NC93, and 61NC18 are standard rock analyses by Edythe Engleman; L. C. Peck, project leader.

Analysis 6238-2J and 62NC133 are rapid rock analyses.

Values in parentheses are neutron activation analyses calibrated against USGS standard rocks.

minor light REE enrichment and about ten times chondritic concentrations. Such a pattern overlaps those reported for mid-ocean ridge basalts (KAY *et al.*, 1970; SCHILLING, 1971), although it lacks the common depletion of light REE. The pattern is almost identical to those reported for island arc tholeiites (JAKEŠ and GILL, 1970), and for some of the transitional normal ridge-mantle blob (plume) basalts of SCHILLING (1975). The other group (61NC18, 62NC133; referred to as 'high REE') shows a marked light REE enrichment typical of continental plateau tholeiites (e.g. SCHILLING, 1971) and 'mantle plume' derived magmas (e.g. the Azores; SCHILLING, 1975). The lower Picture Gorge basalts have a pattern intermediate between the two groups (H. V. Schmincke and H. R. Bowman, unpublished data, 1973). The uranium and thorium concentrations of the low REE group are comparable to values from island arc tholeiites (JAKEŠ and WHITE, 1972). The concentrations of these elements in the high REE samples are more typical of continental tholeiites (e.g. OSAWA and GOLES, 1969; LIPMAN *et al.*, 1973). The other LIL elements generally correlate with the REE, but Ba is an exception (Fig. 3). Barium concentrations are variable, with no correlation to the other analyzed LIL elements. The Ba concentrations are much greater than those commonly reported for MORB, and some are high even for island arc tholeiites (e.g. JAKEŠ and GILL, 1970; NICHOLLS and ISLAM, 1971; PHILPOTTS *et al.*, 1971).

Table 3. K, Rb, Sr concentrations (ppm) and Sr isotopic composition of samples measured by isotope dilution mass spectroscopy

	E15	6238-2J	54NC93	61NC18	62NC133	
[illegible]	1462	2604	1246	3119	3366	
[illegible]	2.63	3.42	1.92	5.88	6.20	
[illegible]	183	231	139	239	239	
[illegible]	556	762	649	530	543	
[illegible]	0.0144	0.0148	0.0138	0.0246	0.0259	
[illegible]/^{86}Sr	0.7076±1	0.7052±1	0.7064±1	0.7056±3	0.7069±1	(±2σ)

Sr isotopic ratios are normalized to $^{86}Sr/^{88}Sr = 0{\cdot}1194$ and adjusted to a value of 0·71014 for NBS SRM 987 (0·7080 for Eimer and Amend $SrCO_3$ standard). As a result of low Rb/Sr ratios and ages, the isotopic ratios have not been corrected for growth of ^{87}Sr since eruption.

The basalts from northeastern Nevada generally contain less K, Rb, and Sr (Table 3) than do the tholeiites from the Snake River Plain (LEEMAN and MANTON, 1971). Two of the five basalts studied fall within the range of K, Rb, and Sr typical of mid-ocean ridge

Table 4. Comparison of chemical analysis of olivine tholeiites with analysis of other relevant basalts

	1	2	3	4	5	6	7	8	9
SiO_2	48.5	48.8	49.6±0.7	48.1	49.1	47.0	49.5	48.5	50.1
Al_2O_3	16.9	15.5	16.0±0.9	16.3	16.0	15.1	13.9	16.7	15.5
ΣFeO	9.5	11.0	11.5±1.3	9.8	9.7	13.5	11.2	12.6	11.2
MgO	9.2	8.7	7.8±0.9	8.5	9.1	7.6	8.4	5.9	6.7
CaO	12.1	11.1	11.3±0.6	11.1	11.8	10.0	10.3	9.4	10.6
Na_2O	2.1	2.4	2.8±0.3	2.6	2.2	2.5	2.2	3.3	2.9
K_2O	0.22	0.41	0.22±0.12	0.41	0.17	0.61	0.4	1.0	0.57
TiO_2	0.95	1.6	1.4±0.3	1.1	1.1	2.7	2.5	2.2	1.55
P_2O_5	0.15	0.35	0.14±0.07	0.17	0.09	0.58	0.3	0.40	0.22
MnO	0.18	0.17	0.18±0.04	0.15	0.19	0.20	0.2	0.18	0.20

1. Low REE group (3), olivine tholeiites, northeastern Nevada, this study.
2. High REE group (2), olivine tholeiite, northeastern Nevada, this study.
3. Ocean floor basalts, 94 selected analyses, ± one standard deviation. CANN (1971).
4. Olivine tholeiites (3), Basin and Range province, LEEMAN and ROGERS (1970).
5. Sample 88 ('most primitive'), basalt, Santa Rosa Range, Nevada, LEMASURIER (1968).
6. Olivine tholeiites (78), Snake River Plain, Idaho, LEEMAN and MANTON (1971).
7. Tholeiites and olivine tholeiites, Hawaiian lavas, MACDONALD (1968).
8. Steens Basalt, group E(16), southeastern Oregon, GUNN and WATKINS (1970).
9. High-Mg basalts, Picture Gorge Basalt, WRIGHT *et al.* (1973).

Table 5. Concentrations of Ba, REE, and other minor elements (ppm) by instrumental neutron activation analysis. Standard rock (BCR-1) is included for comparison

	E15	6238-2J	54NC93	61NC18	62NC133	Typical σ	[illegible]
Ba	781	152	105	427	373	14	[illegible]
La	6.4	6.6	5.2	13.5	16.4	0.4	[illegible]
Ce	12.8	14.8	12.2	30.1	33.9	0.7	[illegible]
Nd	10.1	8.2	10.3	20.2	19.8	1.5	[illegible]
Sm	2.43	2.72	2.37	4.50	4.61	0.02	[illegible]
Eu	1.06	1.12	0.98	1.61	1.64	0.02	[illegible]
Tb	0.48	0.52	0.50	0.91	0.73	0.03	[illegible]
Dy	3.82	4.27	4.09	5.86	5.14	0.20	[illegible]
Yb	2.36	2.81	2.77	3.15	2.68	0.05	[illegible]
Lu	0.358	0.424	0.368	0.481	0.364	0.019	[illegible]
Hf	1.64	1.83	1.90	3.32	2.77	0.11	[illegible]
Cr	342	306	427	369	539	8	[illegible]
Mn	1350	1370	1420	1480	1435	30	[illegible]
Co	50.0	44.4	53.2	50.0	48.4	0.7	[illegible]
Ni	150	120	200	105	120	25	[illegible]
Sc	40.5	45.2	47.2	39.4	38.5	0.2	[illegible]
U	0.152	0.307	0.122	0.330	0.384	0.025	[illegible]
Th	0.47	0.56	0.51	1.06	1.08	0.13	[illegible]
V	320	340	365	350	320	50	[illegible]
Ta	0.257	0.284	0.204	0.585	0.508	0.004	[illegible]
Zn	100	95	95	135	130	9	[illegible]

The typical σ involves only the precision of the measurements. The errors on the BCR-1 standard rock include the calibration errors introduced by the standards as well as the statistical errors introduced by counting radioactivity.

basalts. Two others have LIL element concentrations overlapping the low end of the range reported for the tholeiites from the Snake River Plain.

DISCUSSION

The $^{87}Sr/^{86}Sr$ range for the tholeiites from northeastern Nevada (0·7052–0·7076) is almost identical to the range reported by LEEMAN and MANTON (1971) for the tholeiites from the adjacent Snake River Plain to the north (Fig. 1). They are considerably more radiogenic than are the basalts from the adjacent Basin and Range province to the west and south (C. E. Hedge and D. C. Noble, unpublished data, 1970; LEEMAN, 1970; HEDGE and NOBLE, 1971; NOBLE *et al.*, 1973), where the Sr isotopic compositions are in the range reported for oceanic basalts (generally 0·703–0·705). High (~1200 ppm) Sr basalts from southwestern Nevada and east-central California have Sr isotopic ratios comparable to those reported here (0·706–0·707) (LEEMAN, 1970; HEDGE and NOBLE,

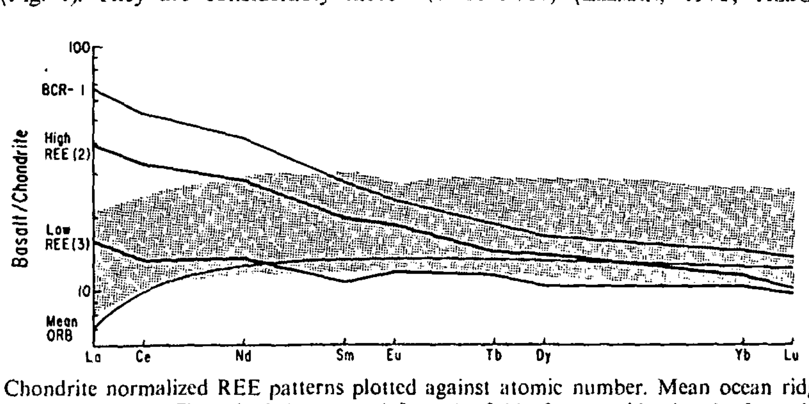

Fig. 2. Chondrite normalized REE patterns plotted against atomic number. Mean ocean ridge basalt is from SCHILLING (1971). The stippled pattern defines the field of ocean ridge basalts from the Gorda Ridge, Juan de Fuca Ridge and East Pacific Rise reported by KAY *et al.* (1970).

(1971). These basalts are also more radiogenic than the chemically similar lower Picture Gorge basalts (0·7035–0·704, McDOUGALL, in press).

HEDGE and NOBLE (1971) and LEEMAN and MANTON (1971) argue convincingly that the high $^{87}Sr/^{86}Sr$ ratios are due to a radiogenic source (mantle) rather than crustal contamination. LEEMAN and MANTON (1971) base this conclusion largely on geophysical evidence for the lack of a sialic crust, and HEDGE and NOBLE (1971) on the very high Sr contents, low Rb/Sr ratios, and lack of correlation between Sr concentrations, Rb/Sr ratios, and Sr isotopic ratios.

The scatter in Sr isotopic ratios measured for the five samples (and the tholeiites from the Snake River Plain; LEEMAN and MANTON, 1971) fall well outside the range of experimental error. Scatter of this type could be due to either crustal contamination or mantle inhomogeneity. The high Ba concentration may also indicate some form of contamination. There is a very weak correlation between Ba and $^{87}Sr/^{86}Sr$ (Fig. 3), but the lack of correlation between Sr concentration and composition (Fig. 4) argues against a contamination model, as does the lack of correlation of Ba with other LIL elements (K, Rb, REE). In addition, the low LIL element concentrations (particularly Rb, K, U, and Th) indicate that crustal contamination by LIL-rich rocks did not take place. If contamination with radiogenic ^{87}Sr did occur, however, it must have been somehow separated from its parental Rb. We have observed no petrographic evidence for crustal contamination. While some unusual form of contamination cannot be entirely ruled out, the high Sr isotopic ratios most probably reflect that of the source mantle.

Although it has been demonstrated that Rb concentration can vary widely within a single lava flow (HART *et al.*, 1971), it is important to note that the Rb/Sr ratios of the five basalts studied is such that they all plot well to the left of the 4·6 × 10^9 yr isochron (Fig. 5). It would take 6–14 × 10^9 yr for the present Sr isotopic ratios to evolve, in a source with the measured Rb/Sr ratio, from the primordial value of 0·699.

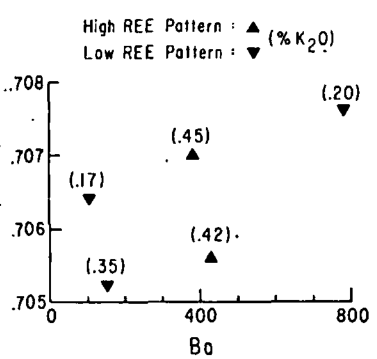

Fig. 3. Plot of $^{87}Sr/^{86}Sr$ against Ba concentration (ppm). Also indicated are K_2O concentration and REE group. Note lack of correlation of Ba with the other LIL elements.

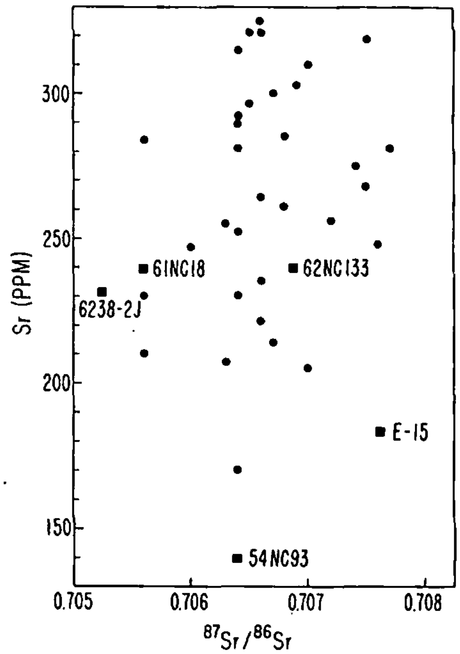

Fig. 4. Plot of $^{87}Sr/^{86}Sr$ against Sr concentration (ppm). Circles are olivine tholeiites from the Snake River Plain (LEEMAN and MANTON, 1971; adjusted to 0·7080 for the E and A standard). Squares are olivine tholeiites from northeastern Nevada (this study).

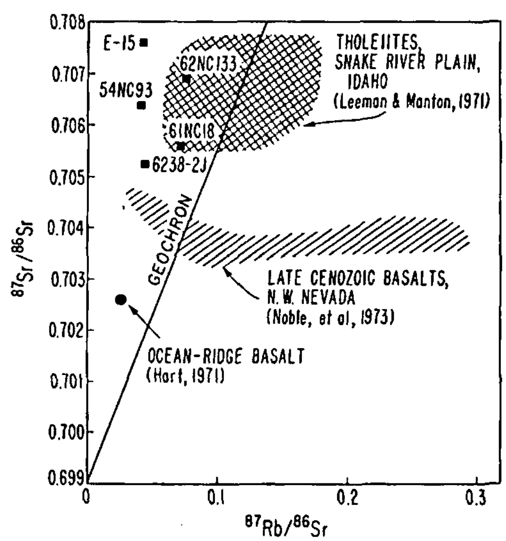

Fig. 5. Strontium isochron diagram showing that the samples studied plot well to the left of the 4·6 b.y. 'geochron'.

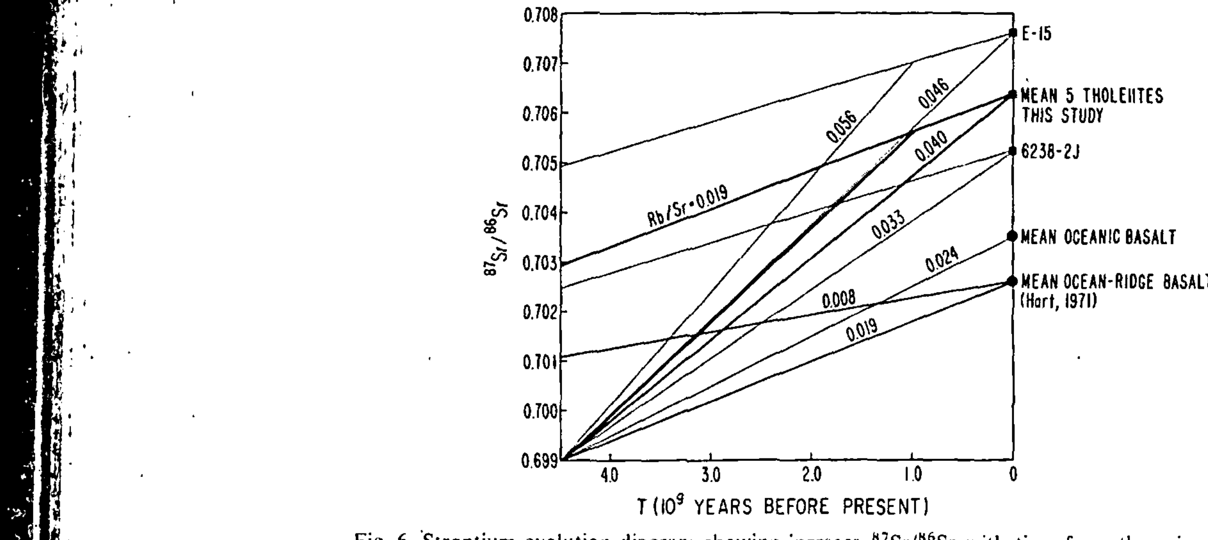

Fig. 6. Strontium evolution diagram showing increase $^{87}Sr/^{86}Sr$ with time from the primordial value of 0·699. Growth curve slopes are proportional to the Rb/Sr ratio of the systems.

The source material for these basalts almost certainly must have had a Rb/Sr ratio less than or equal to the basalts, as both partial melting (in the absence of plagioclase as indicated by the lack of an Eu anomaly) and fractional crystallization tend to increase this ratio (Gast, 1968; Hedge and Noble, 1971). In the case of low LIL tholeiites, presumably generated by a significant degree of partial melting of an ultramafic source almost all of the LIL elements will go into the melt (Kay *et al.*, 1970). Such basalts, if relatively undifferentiated, will have Rb/Sr ratios approximately equal to that of their source. In this case the source (mantle) for the samples must have had a mean Rb/Sr ratio of 0·019 when the basalts were formed. Such a Rb/Sr ratio would have evolved a $^{87}Sr/^{86}Sr$ ratio of only 0·7025 since the Earth was formed.

Single stage evolution of these basalts from an initial Sr isotopic ratio of 0·699 in $4·6 \times 10^9$ yr would have required a time-averaged Rb/Sr ratio of 0·033–0·046 (mean ~0·040) (Fig. 6). Peterman and Hedge (1971) suggest that undepleted oceanic mantle might have a Rb/Sr ratio as high as 0·04. 'Average' oceanic mantle must have a time-averaged Rb/Sr ratio ~0·024 to produce oceanic basalts with a mean $^{87}Sr/^{86}Sr$ ~0·7035. It can thus be inferred that the Rb–Sr systematics of the basalts from northeastern Nevada require at least a two-stage model to account for their Rb/Sr and $^{87}Sr/^{86}Sr$ ratios. If the source mantle were depleted in alkali elements in the relatively recent past (prior to the generation of the basalts), then the Rb/Sr ratio must have been reduced by about a factor of 2. If a single depletion episode had occurred as long ago as 1×10^9 yr ago, the time-averaged Rb/Sr ratio in the mantle during the first stage must still have been 0·039–0·056 (mean 0·046). If the depletion occurred early in the Earth's history, a greater degree of Rb–Sr fractionation is implied, requiring a mantle with a very high initial Rb/Sr ratio. If such a mantle ever did exist, it must not have survived into later Earth history. Otherwise, we would expect to find uncontaminated basalts with $^{87}Sr/^{86}Sr \gg 0·708$. Alternatively, the mantle Rb/Sr may have been gradually decreasing through time, owing to a quasi-continuous depletion process (Hart, 1971). On the basis of analogous systematics for the high-Sr basalts from southwestern Nevada and east-central California, Hedge and Noble (1971) suggest a Rb/Sr ratio as high as 0·055 for the source mantle before a Precambrian depletion. Such high Rb/Sr ratios may be indicative of alkali enrichment in the mantle.

The depletions required to produce these basalts are analogous to those required to produce mid-ocean ridge basalts (Tatsumoto *et al.*, 1965; Peterman and Hedge, 1971). In that case, however, $^{87}Sr/^{86}Sr$ ratios are low, and, therefore, the depletion must have occurred much earlier in the Earth's history (Fig. 6). To produce the high $^{87}Sr/^{86}Sr$ basalts, a depletion must have occurred late in the Earth's history, and in addition, an enrichment in LIL elements above the mean mantle concentrations possibly may have occurred at a much earlier time. The tholeiites from northeastern Nevada were then presumably produced by a large degree of partial melting of recently depleted mantle.

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APPENDIX

Sample 6238-2*J*. From the top of the Sheep Creek Range about 32 km northeast of the town of Battle Mountain (40°50′36″ N, 116°37′15″ W). It is the top flow in a series of flows that have an aggregate thickness of more than 300 m. The lower flows are basaltic andesite and are about 16 m.y. old (MCKEE and SILBERMAN, 1970). The rock is holocrystalline with porphyritic olivine (Fa_{10}) in an ophitic to subophitic groundmass. Contains augite, zoned plagioclase and opaque iron oxides.

Sample 54*NC* 93. From the uppermost flow of three flows in the cliff on the west side of the Jarbidge River, just south of the Idaho stateline (41°59′48″ N, 115°25′24″ W). The flow is about 9 m thick and is vesicular on top, with an irregular bottom caused by contemporaneous deformation. The two lower flows are respectively, 10 and 6·6 m thick. The lowest flow rests on poorly consolidated gravel. The rock is holocrystalline with less than 5% black glass. It contains olivine phenocrysts (slightly altered to iddingsite) up to 3 mm in diameter in a subophitic groundmass of pyroxene, glagioclase, granular olivine, magnetite, and ilmenite.

Sample E-15. From a flow forming the 'rimrock' on the summit of a hill on the south side of Shoshone Creek, about 6·5 km southeast of Jackpot, Nevada (41°50'00" N, 114°35'54" W). The rock is holocrystalline with porphyritic olivine. Ophitic to subophitic groundmass. Pale brown augite with 2V about 60°, plagioclase laths zoned from about An_{77} to An_{22}.

Sample 61*NC*18. From the feeder dike to the basalt flow tha forms the summit of Hat Peak about 10 km south of the Idaho stateline (41°54'00" N, 116°23'15" W). The dike is vesicular near the top. It is holocrystalline with subophitic groundmass and phenocrysts of olivine. The groundmass contains plagioclase, augite, olivine, and magnetite.

Sample 62*NC*133. From a medium-gray vesicular, 7-m thick flow on Hat Peak about 10 km south of the Idaho stateline (41°54'30" N, 116°23'45" W). The rock is holocrystalline, with ophitic groundmass and olivine phenocrysts. Groundmass is brown augite ophitically enclosing plagioclase, olivine and magnetite.

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EARTH AND PLANETARY SCIENCE LETTERS 8 (1970) 93–96. NORTH-HOLLAND PUBLISHING COMPANY

MIDDLE MIOCENE HIATUS IN VOLCANIC ACTIVITY IN THE GREAT BASIN AREA OF THE WESTERN UNITED STATES *

E.H.McKEE, D.C.NOBLE ** and M.L.SILBERMAN
U.S. Geological Survey, Menlo Park, California, USA

Received 4 March 1970

A summary of potassium-argon dates shows that a high level of igneous activity in the Great Basin and adjacent regions during middle Tertiary time (40 to 20 my ago) was followed by a period of relative quiescence in middle Miocene time that lasted for several million years (from 20 to 17 my ago). Volcanism resumed 16 my ago mainly at the margins of the region and has continued to the present.

1. Introduction

Tertiary volcanic rocks contain much varied information about the tectonic evolution of the western United States. Data accumulated over the past several years concerning the distribution, petrochemistry and age of Tertiary rocks in the Great Basin makes it clear that there are major differences in both areal distribution and petrochemistry between the volcanic rocks erupted during the middle Cenozoic (40 to 20 my ago) and those erupted during the late Miocene, Pliocene, and Quaternary (16 my ago to present). The purpose of this note is to call attention to the fact that these two periods of volcanic activity are separated by an interval of several million years during which volcanic activity was greatly reduced or nonexistent. Tectonic activity in the form of block faulting took place only during the younger episode.

2. Data

Fig. 1 shows the available potassium-argon dates for the Great Basin as outlined in fig. 2. The dates are from the references cited by Armstrong, Ekren, McKee and Noble [1] and from other recent publications (Marvin et al. [2], McKee and Stewart [3]; Gilbert et al. [4], Armstrong [5], Shilling [6], Evernden et al. [7], Kistler [8], and from other references [9–13]) and from unpublished data from a number of sources (see acknowledgements). In preparing this figure we have treated determinations on two or more phases (i.e., mineral pairs) from a single rock specimen as a single date and, if possible, two or more rocks dated from a unit have been tabulated as one date. In many cases, however, where geologic correlation is uncertain, all dates are included. In gathering data for this paper, we have paid particular attention to dates in the 15 to 20 million year interval, and undoubtedly have overlooked some dates outside of this range. Any bias so generated would only tend to increase the observed anomaly. A total of 531 potassium-argon ages are included, many of which are averages of two or more; all dates have been rounded off upward and the ± factor of analytical uncertainty disregarded.

The histogram (fig. 1) shows the marked scarcity of igneous rocks in the 17 to 20 my interval †. Only 12 ages are reported within this interval or about 2% the 500+ ages that make up the histogram. The well-known occurrence of basalt in the Late Tertiary is

* Publication authorized by the Director, U.S. Geological Survey.
** On leave from the Department of Geological Sciences, Harvard University.

† See footnote on next page.

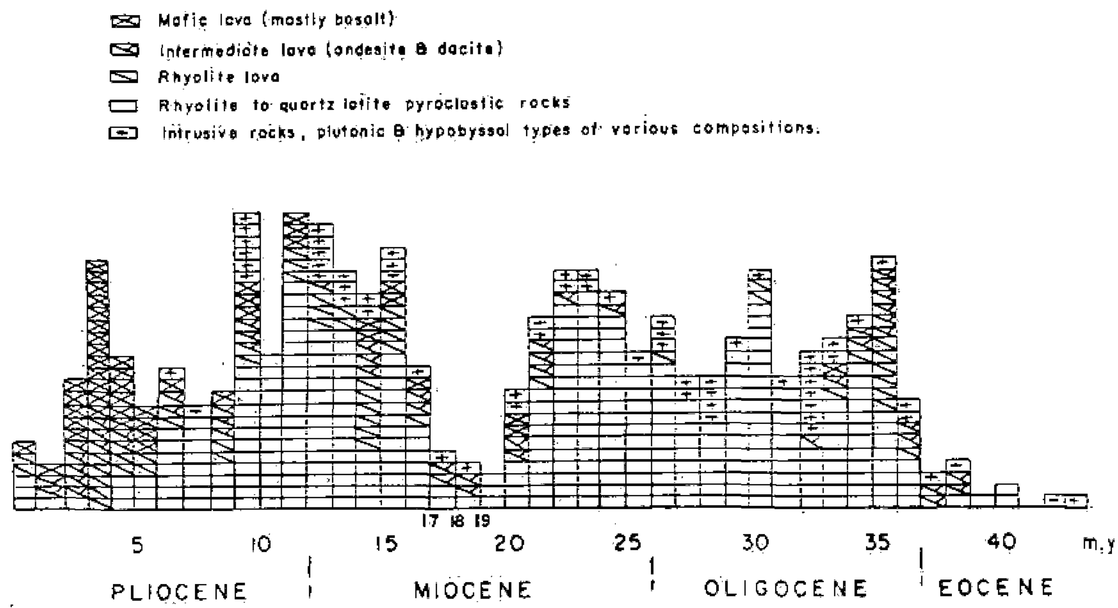

Fig. 1. Histogram of K-Ar ages of volcanic and intrusive rocks in the Great Basin. Each box represents the age of an igneous, and in some cases is the average of two or more K-Ar dates.

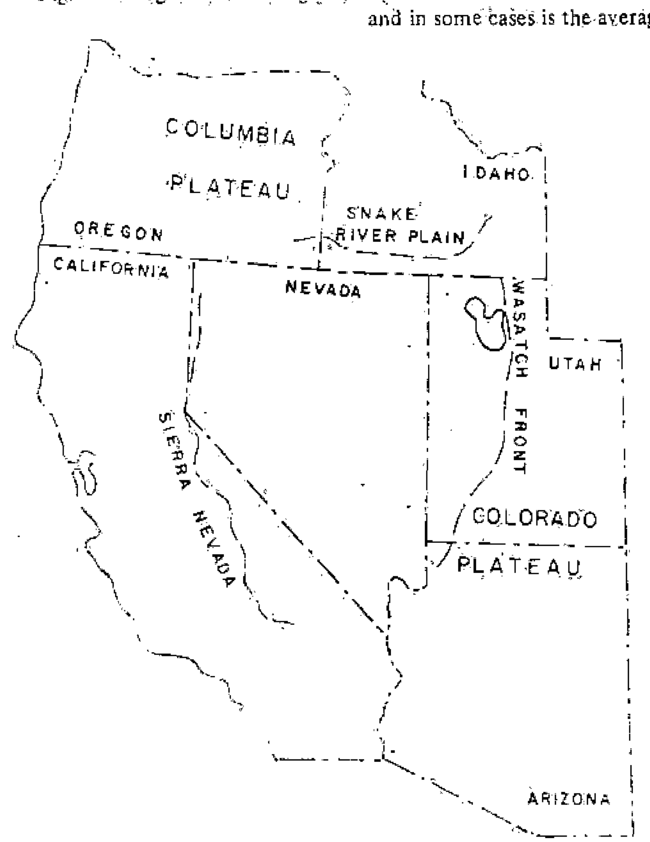

Fig. 2. Great Basin region of the Basin and Range province.

clearly reflected in the data (fig. 1) as are the w[...] spread silicic ash-flow sheets 20 to 33 my old a[...] andesitic rocks about 35 my old. The relative v[...] of Cenozoic rocks of different ages would emph[...] the paucity of rocks between 17 and 20 my old. Probably 98% or more of the igneous rocks in t[...] Great Basin were impláced during the two perio[...] of igneous activity outlined by the summary of [...] dates.

3. Discussion

Volcanic rocks of late Miocene age and your[...] in the Great Basin are mostly restricted to its m[...] (Armstrong, Ekren, McKee and Noble [11]). T[...] younger rocks include a significant percentage [...]

* Footnote from preceding page. Two of the dates in [...] to 18 my interval are ages obtained by Armstrong [...] the Hiko Tuff of southeastern Nevada (of Cook [...] have obtained an age of 19.6 ± 0.5 my on sanidine [...] the Hiko Tuff (Noble et al. [24]). Ages obtained by [...] strong tend to be slightly younger than ages on the [...] units obtained by various U.S. Geological Survey [...] and we feel that the exact age of the Hiko Tuff is [...] question.

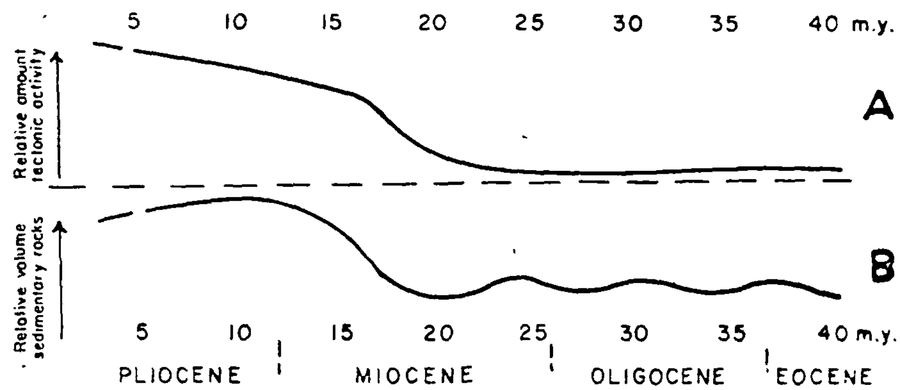

Fig. 3.

...hly differentiated silicic tuffs and lavas, both sub-...aline and peralkaline, whereas Oligocene and lower ...cene silicic rocks (the oldest Tertiary volcanic ...ks in the region) are relatively undifferentiated ...ble et al. [14]). Around the margins of the Great ...sin it can be shown that most of the high-angle ...ting is late Miocene or younger (Ekren et al. [15], ...elrod [16], Christensen [17], Noble [18]) and ...ailable data is consistent with relatively late incep-...n of basin-range faulting in the central part of the ...eat Basin as well. Fig. 3 is a generalized, graphic ...resentation of the relative amounts of tectonism ...ock faulting) and sedimentation in the Great Basin ...ring the Cenozoic. The distribution of thin but ...despread ash-flow units in the central part of the ...eat Basin indicates that little or no relief existed ...the time of their extrusion. Certainly no topo-...phy similar to present Basin and Range features ...ted prior to about 20 my ago and the amount of ...rmation in all Tertiary units suggests that most ...n and Range faulting took place late in the ...tiary. The young as well as old Tertiary rocks ...e undergone about the same amount of deforma-...n most places. Further evidence that the time ...st intense tectonism in the Great Basin was ...g the late Tertiary is reflected by the relative ...nt of sedimentary rocks in the Tertiary column ...Van Houten [19]) (curve B, fig. 2). The volumi-... deposits of lacustrine material of late Miocene ...Pliocene age (Esmeralda Formation, Truckee ...mation Humboldt Formation) are most likely ...ed to "breakup" of the region and formation of basins which trapped sediments. We believe that the major changes in the volcanic-tectonic regime here in the Great Basin during the Miocene can also be recognized over most of the rest of the western United States (see Dott [20]; McKenzie and Parker [21] and Chase and others [22] for a recent review).

Dott [20] has suggested that the inception of crustal rifting, Basin and Range faulting, and late Cenozoic volcanism resulted from a major global discontinuity in the character of sea-floor spreading. Christiansen and Lipman [25] believe that these occurrences reflect "intersection of North-America with the East Pacific Rise, mutual annihilation of sectors of the Rise and continental-margin trench, and initiation of a transform fault system in their place". If any one of these interpretations is correct, the cessation and abrupt resumption of volcanism would appear to reflect, and thus date, critical stages in the interaction of oceanic plates with the continent.

Acknowledgments

The ideas discussed in this paper were originally presented at the second Penrose Research Conference, held at Pacific Grove, California, during December 1969. We are indebted to M.C.Blake Jr., R.R.Coats, D.B.Tatlock, F.J.Kleinhampl, R.K.Hose, G.W.Walker, M.D.Crittenden Jr., and H.T.Morris for allowing us to use unpublished K-Ar determinations in preparing part of fig. 1 and to R.L.Christiansen for helpful dis-

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SPACE-TIME RELATIONS OF CENOZOIC SILICIC VOLCANISM IN THE GREAT BASIN OF THE WESTERN UNITED STATES*

RICHARD L. ARMSTRONG, E. B. EKREN, EDWIN H. McKEE, and DONALD C. NOBLE**

ABSTRACT. Physical stratigraphy supported by more than 250 K-Ar age determination demonstrates a definite space-time pattern of Cenozoic silicic volcanism within the Great Basin. Known vent areas of voluminous ash-flow units and the approximate source areas for sequences of related sheets whose original distribution is known provide the most important control points. These are supplemented by many dates on tuffs and lavas which lack more complete stratigraphic control.

Cenozoic volcanism began about 40 m.y. ago. Although locally abundant elsewhere, volcanic rocks 30 to 40 m.y. old are most abundant in east-central Nevada. The locus of pyroclastic volcanism, as defined by the time of most intense activity and the time of latest significant activity within a given area, then shifted progressively outward from east-central Nevada toward the margins of the Great Basin. Silicic volcanism had ceased by 25 to 30 m.y. ago in east-central Nevada and by 20 m.y. ago was restricted to the marginal areas of the Great Basin. The intensity of silicic volcanism has decreased progressively during the last 10 m.y.

East-central Nevada, where silicic volcanism first terminated, is less seismically active and possibly has a thicker crust than other parts of the Great Basin. The observed pattern of outwardly migrating volcanism may have been the result of convection within the mantle with a rising current centered on the east-central part of the Great Basin.

INTRODUCTION

This paper summarizes and interprets chronologic data bearing on the space-time distribution of Cenozoic volcanism in and near the Great Basin of the western United States (fig. 1). Nearby areas are included because pyroclastic rocks that erupted from vents within the Great Basin spread beyond its margins, and some rocks erupted from vents slightly outside the geomorphologically defined boundaries of the province appear to belong to this episode of volcanic activity.

The discussion is limited to the silicic volcanic rocks that constitute the bulk of the volcanic material of Cenozoic age in the Great Basin. These silicic volcanic rocks are predominantly pyroclastic material which forms voluminous and areally extensive sheets of ash-flow tuff (Gilbert, 1938; Mackin, 1960; Coats, 1964; Noble and others, 1964; Orkild, 1965; Sargent, Noble, and Ekren, 1965; Cook, 1965; McKee, 1968a; and others). The high-potash intermediate lavas present in many parts of the province are not included; available data (for example, Anderson and Ekren, 1968; Stewart and McKee, 1968) suggest that within any given area such rocks were usually erupted before the silicic rocks. Mafic volcanic rocks (mostly basalt flows) are much less common than the silicic rocks and have not yet been dated in many regions, but

* Presented at the 1967 Annual Meeting of the Geological Society of America (Armstrong and others, 1967). Publication authorized by the Director, U.S. Geological Survey.

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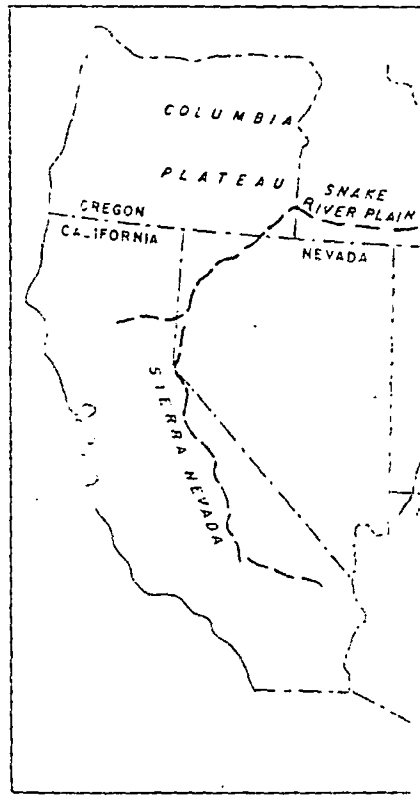

Fig. 1. Great Basin region of the Basin and Ra
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AGE AND DISTRIBUTION OF SILICIC

Previous Work

E. F. Cook (1965) was the first to rec
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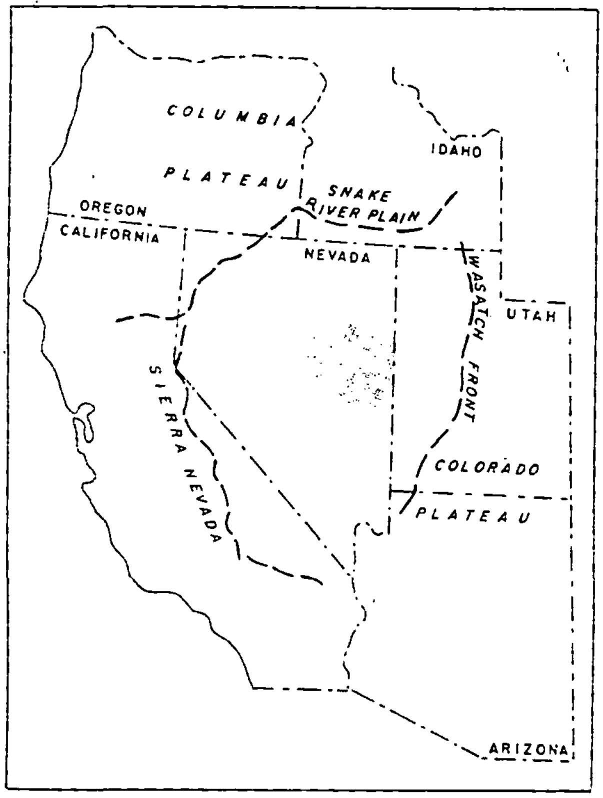

Fig. 1. Great Basin region of the Basin and Range province. Core area of silicic volcanism shaded.

where they have they usually prove to be the youngest rocks of the volcanic sequence.

This paper relies largely upon the many potassium-argon dates now available, most of them obtained from biotite and sanidine phenocryst separates, but some from whole-rock samples.

AGE AND DISTRIBUTION OF SILICIC VOLCANIC ROCKS

Previous Work

E. F. Cook (1965) was the first to recognize a systematic temporal pattern in the distribution of Cenozoic volcanism. His stratigraphic studies revealed that the volcanic section becomes progressively younger when traced from east-central Nevada south and southeastward into southeastern Nevada and southwestern Utah. All subsequent stratigraphic studies and isotopic age data (for example, Noble, 1968; Noble and others, 1967; R. L. Armstrong, E. B. Ekren, and D. C. Noble, unpub. data) have substantiated Cook's general stratigraphic framework and conclusions.

In south-central Nevada, detailed stratigraphic and isotopic work by the U.S. Geological Survey has revealed a similar pattern. In this region the Tertiary section ranges in age from 15 to more than 25 m.y. (Ekren and others, 1968; E. B. Ekren and others, unpub. data). To the south, younger rock units appear at the top of the section and older units pinch out so that in southern Nevada almost all the silicic volcanic rocks are younger than 15 m.y. (Noble and others, 1964; Orkild, 1965; Noble and others, 1967; Kistler, 1968; R. F. Marvin and others, unpub. data).

Schilling (1965) recognized a similar tendency in Cenozoic volcanic rocks to become younger toward the southwestern and western margins of Nevada. This age change has been substantiated by recent mapping and isotopic dating by various workers (for example, Robinson, McKee, and Moiola, 1968).

In northern Nevada, southeastern Oregon, and southern Idaho stratigraphic work, in conjunction with paleontologic and some isotopic data, has demonstrated the presence of large volumes of silicic pyroclastics and lavas of Miocene and Pliocene age (for example, Mapel and Hail, 1959; Willden, 1961, 1963, 1964; Malde and Powers, 1962; Carr and Trimble, 1963; Axelrod, 1964; Coats, 1964; Walker and Repenning, 1965, 1966; Noble and others, 1968). Older rocks also are present, at least locally, in northern Nevada (Coats, 1964; Axelrod, 1966). The available data are compatible with, but do not prove, a systematic northward shift in both the locus of the most intense volcanism and the cessation of silicic volcanism.

Potassium-Argon Ages

Method of presentation.—Available isotopic data, grouped into 5 m.y. intervals, are shown in figures 2 through 5. These maps summarize over 250 individual age determinations, including 80 unpublished determinations by Armstrong, 41 determinations by McKee, and approximately 80 determinations from other U.S. Geological Survey sources. Although the accuracy of the individual dates are such as to make intervals of less than 5 m.y. statistically valid, the limited number of dates in certain intervals, together with wide variations in the precision of their geologic control, do not warrant the use of a shorter time span. In addition to a breakdown by age, the data are classified to indicate their relative importance.

Distribution pattern.—Silicic volcanic rocks older than 30 m.y. (fig. 2) are concentrated in east-central Nevada, but some are present in northern Nevada, along the Wasatch front in Utah (fig. 1), and locally in the Sierra Nevada (fig. 1). Ages between 20 and 30 m.y. (fig. 3) are most prevalent immediately outside the east-central Nevada core area.[3] Ages younger than 20 m.y. are restricted to the outer part of the Great Basin area, and those younger than 10 m.y. to the margins (figs. 3 and

[3] Many of the 20- to 30-m.y. ages in the central Sierra Nevada are geographically displaced: most of the dated tuffs, which belong to the Miocene Valley Springs Formation or its equivalents, very probably had their sources in the western part of the Great Basin (Slemmons, 1966; Durrell, 1966).

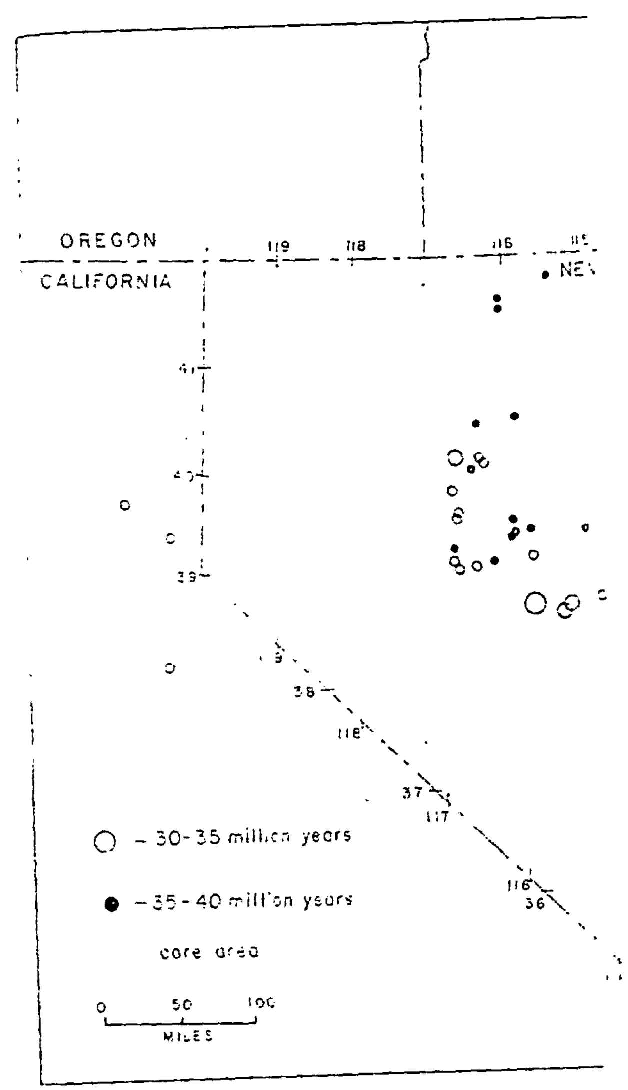

Fig. 2. Distribution of silicic volcanism in the Gr...
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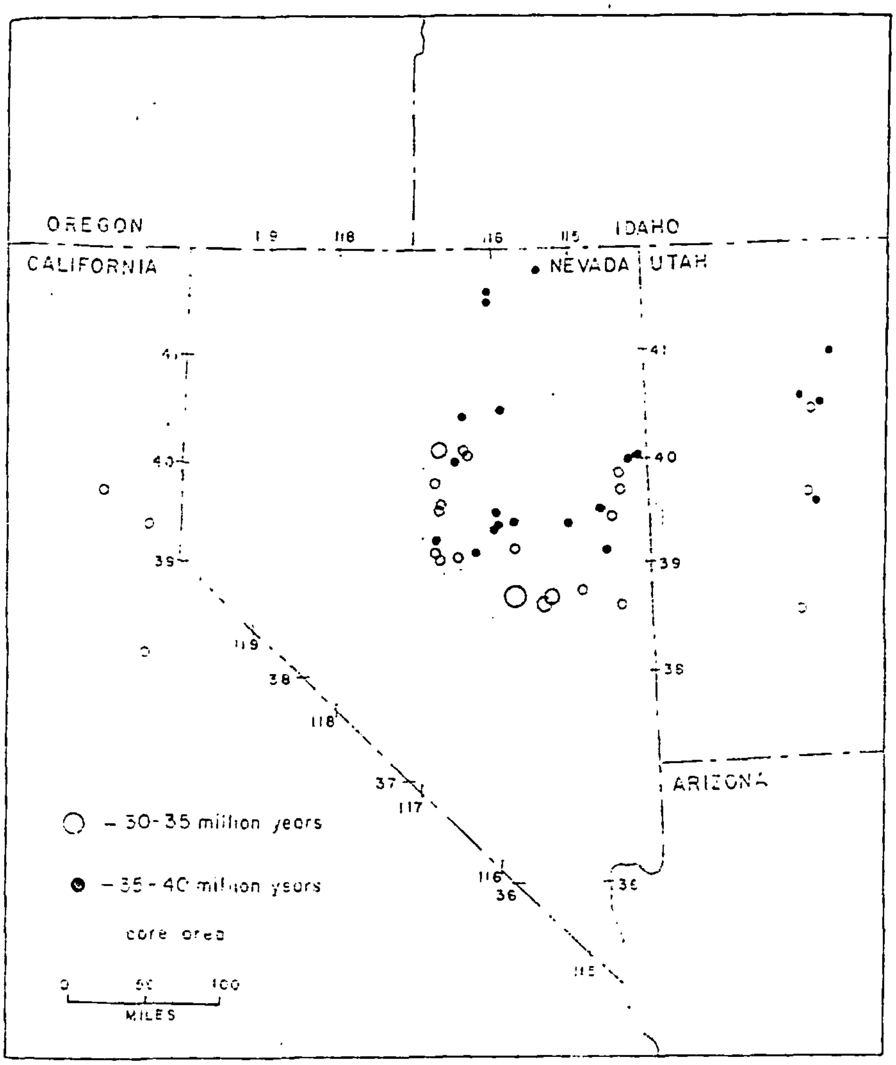


Fig. 2. Distribution of silicic volcanism in the Great Basin from 30 to 40 m.y. ago. Large symbols indicate (1) major volcanic centers of known age, or (2) the geographic centers of major ash-flow sheets or sequences of genetically related sheets for which approximate original distribution is known, but whose source is unknown. A single large symbol usually represents several, and in certain instances more than 10, isotopic dates. Medium-sized symbols show the approximate centers of major ash-flow sheets whose original distribution is partially known. Small symbols are used to represent isolated dates on ash-flow units whose areal distribution relations are uncertain, dates on lava bodies and air-fall tuffs that are not known to be genetically related to major volcanic centers, and dates on tuffaceous sedimentary rocks.

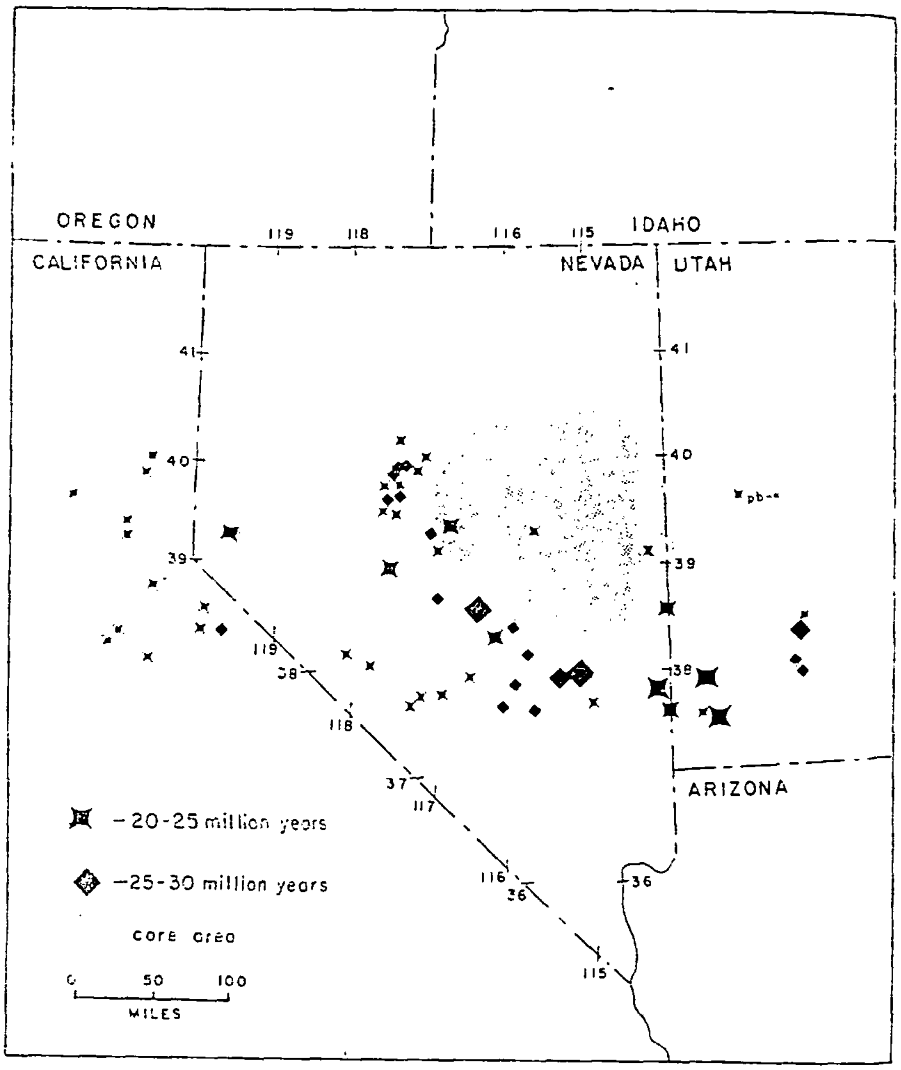
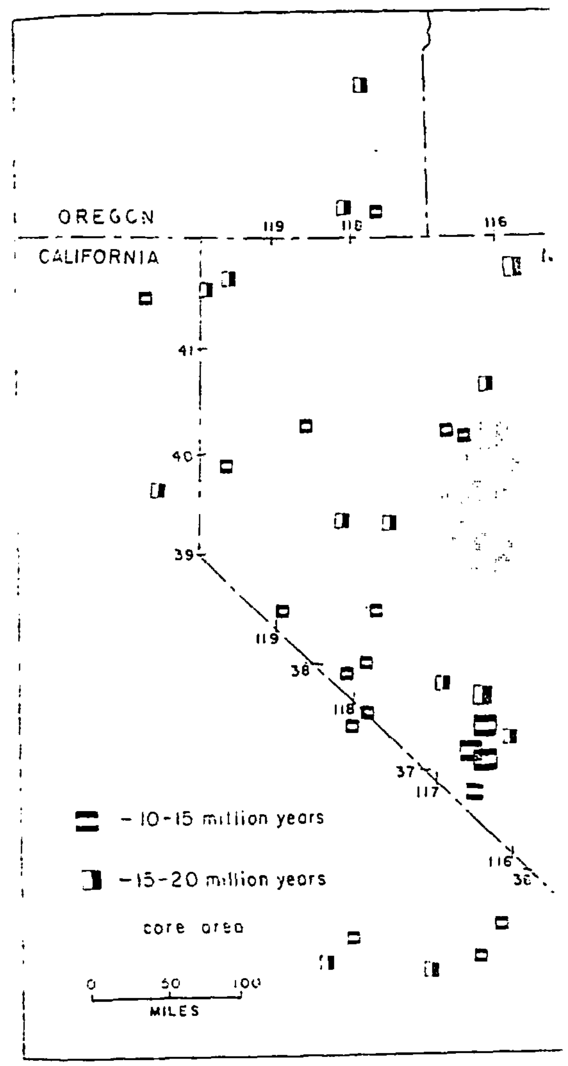


Fig. 3. Distribution of silicic volcanism in the Great Basin from 20 to 30 m.y. ago. Large symbols indicate (1) major volcanic centers of known age, or (2) the geographic centers of major ash-flow sheets or sequences of genetically related sheets for which approximate original distribution is known but whose source is unknown. A single large symbol usually represents several, and in certain instances more than 10, isotopic dates. Medium-sized symbols show the approximate centers of major ash-flow sheets whose original distribution is partially known. Small symbols are used to represent isolated dates on ash-flow units whose areal distribution relations are uncertain, dates on lava bodies and air-fall tuffs that are not known to be genetically related to major volcanic centers, and dates on tuffaceous sedimentary rocks.



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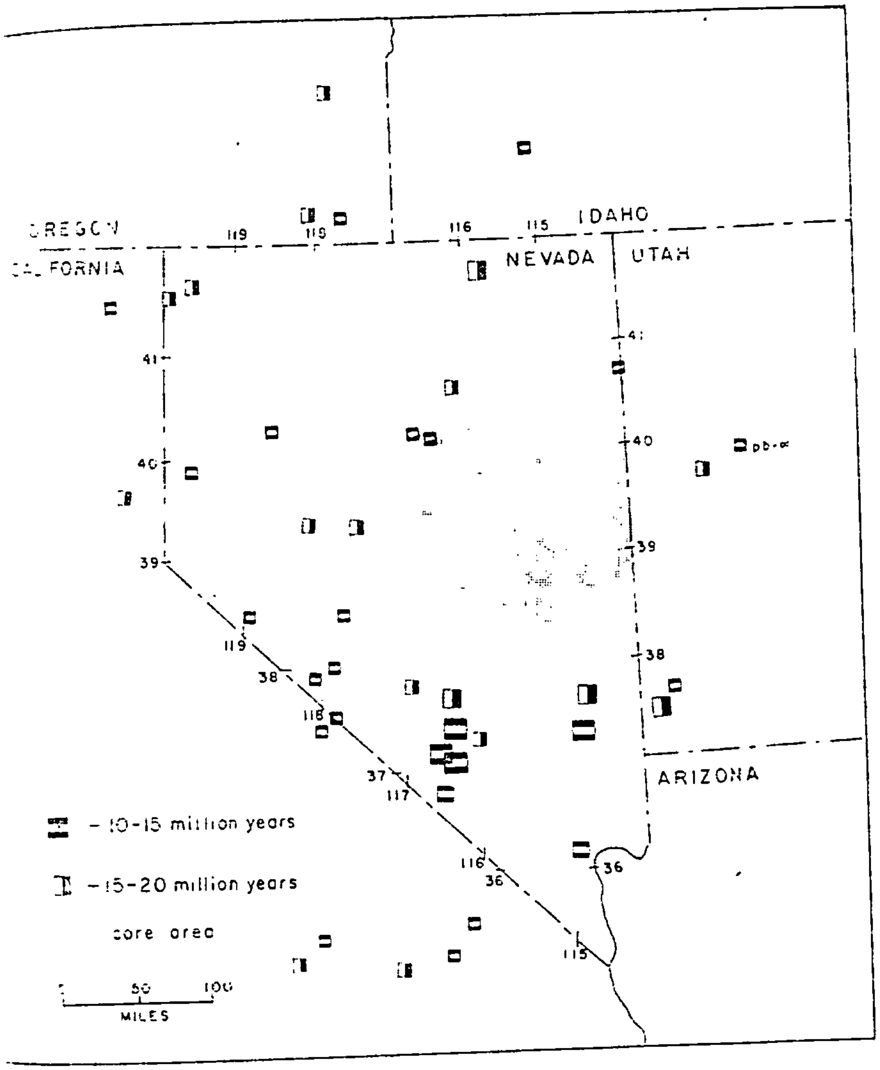

Fig. 4. Distribution of silicic volcanism in the Great Basin from 10 to 20 m.y. p. Large symbols indicate (1) major volcanic centers of known age, or (2) the geo- phic centers of major ash-flow sheets or sequences of genetically related sheets for which approximate original distribution is known but whose source is unknown. A single large symbol usually represents several, and in certain instances more than 10, topic dates. Medium-sized symbols show the approximate centers of major ash-flow sheets whose original distribution is partially known. Small symbols are used to repre- isolated dates on ash-flow units whose areal distribution relations are uncertain, dates on lava bodies and air-fall tuffs that are not known to be genetically related to volcanic centers, and dates on tuffaceous sedimentary rocks.

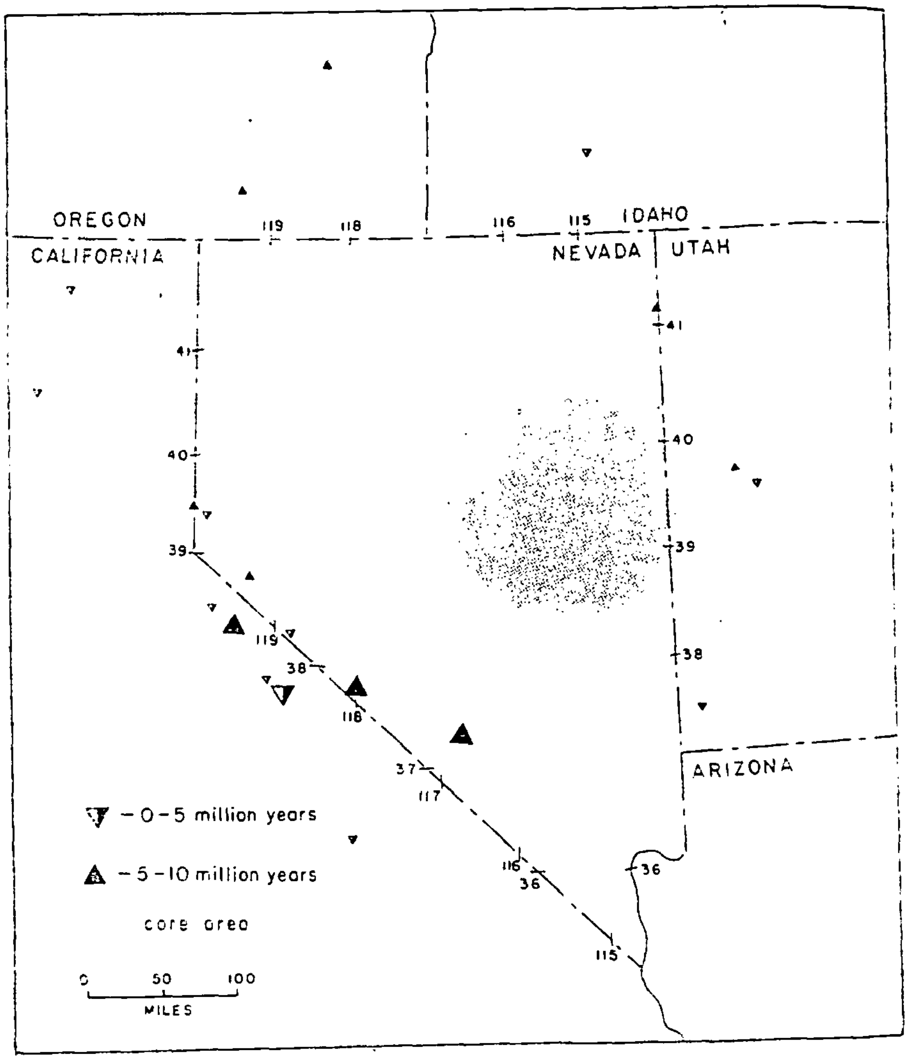

Fig. 5. Distribution of silicic volcanism in the Great Basin from 0 to 10 m.y. ago. Large symbols indicate (1) major volcanic centers of known age, or (2) the geographic centers of major ash-flow sheets or sequences of genetically related sheets for which approximate original distribution is known but whose source is unknown. A single large symbol usually represents several, and in certain instances more than 10, isotopic dates. Medium-sized symbols shows the approximate centers of major ash-flow sheets whose original distribution is partially known. Small symbols are used to represent isolated dates on ash-flow units whose areal distribution relations are uncertain, dates on laval bodies and air-fall tuffs that are not known to be genetically related to major volcanic centers, and dates on tuffaceous sedimentary rocks.

4). A striking feature of the age distribution absence of dates younger than 20 m.y. within core area[2] and the total absence of dates young most the entire State. This distribution does n bias due to removal of younger units by erosio ing the least altered or structurally involved s also tend to prevent a bias.

Summary of Volcanic His

Although not restricted to the east-centra area, more volcanic rocks older than 30 m.y. o Likewise, rocks of intermediate age are most a area and the margins. Thus, even though the Basin area was moderately active volcanicall time, there appears to have been a definite o the zone of intense volcanism. More pronoun sation of volcanic activity that followed. Sili to have ceased entirely within east-central Ne the present and then moved outward system and possibly north, of the core area. Present d of silicic volcanism was abrupt, areally system

In the eastern part of the Great Basin, t of volcanism was less systematic. Young rock the marginal areas, but older volcanics are als and near the Wasatch front. In this area no d of the cessation of volcanism is apparent.

Although mafic rocks are sporadically in canic section, most of the mafic lavas seem to rocks. In several areas in the east-central an Great Basin, isotopic data (R. L. Armstrong, the mafic volcanism occurred within 5 m.y. o activity.

The volume of silicic volcanic rocks be is distinctly smaller than that of rocks 10 Rocks less than 5 m.y. old are even less abu suggests that the intensity of silicic volcanis during the last 10 m.y.

TECTONIC SIGNIFICAN

The overall tectonic framework of th of distinctive features. These include wi faulting (for example, Nolan, 1943; Moo Mackin, 1960) and strike-slip faulting (S Myers, 1966; McKee, 1968b; and reference low upper-mantle and crustal seismic v

[2] The 10- to 15-m.y. date at lat 40°8' N, long 11 tuff associated with upper Pliocene vertebrate te material is probably at a considerable distance fro

a. A striking feature of the age distribution is the almost complete absence of dates younger than 20 m.y. within the east-central Nevada core area[2] and the total absence of dates younger than 10 m.y. from almost the entire State. This distribution does not appear to represent a bias due to removal of younger units by erosion. The practice of selecting the least altered or structurally involved samples for dating would also tend to prevent a bias.

Summary of Volcanic History

Although not restricted to the east-central part of the Great Basin area, more volcanic rocks older than 30 m.y. occur here than elsewhere. Likewise, rocks of intermediate age are most abundant between the core area and the margins. Thus, even though the outer part of the Great Basin area was moderately active volcanically during middle Tertiary time, there appears to have been a definite outward shift with time of the zone of intense volcanism. More pronounced, however, was the cessation of volcanic activity that followed. Silicic volcanic activity seems to have ceased entirely within east-central Nevada 25 to 30 m.y. before the present and then moved outward systematically to the south, west, and possibly north, of the core area. Present data indicate that cessation of silicic volcanism was abrupt, areally systematic, and final.

In the eastern part of the Great Basin, the space-time distribution of volcanism was less systematic. Young rocks appear to be restricted to the marginal areas, but older volcanics are also present in abundance at and near the Wasatch front. In this area no definite outward progression of the cessation of volcanism is apparent.

Although mafic rocks are sporadically intercalated within the volcanic section, most of the mafic lavas seem to overlie the silicic volcanic rocks. In several areas in the east-central and southeastern part of the Great Basin, isotopic data (R. L. Armstrong, unpub. data) indicate that the mafic volcanism occurred within 5 m.y. of the end of silicic volcanic activity.

The volume of silicic volcanic rocks between 0 and 10 m.y. in age is distinctly smaller than that of rocks 10 to 20 or 20 to 30 m.y. old. Rocks less than 5 m.y. old are even less abundant. This change strongly suggests that the intensity of silicic volcanism has progressively decreased during the last 10 m.y.

TECTONIC SIGNIFICANCE

The overall tectonic framework of the Great Basin has a number of distinctive features. These include widespread large-scale normal faulting (for example, Nolan, 1943; Moore, 1960; Thompson, 1960; Mackin, 1960) and strike-slip faulting (Shawe, 1965; Hamilton and Myers, 1966; McKee, 1968b; and references cited therein), thin crust, low upper-mantle and crustal seismic velocities and densities, and

[2] The 10- to 15-m.y. date at lat 40°8′ N, long 116°47′ W, is on a shard-rich bedded tuff associated with upper Pliocene vertebrate remains. The source of the volcanic material is probably at a considerable distance from the sample site.

severe P_n wave attenuation (Pakiser and Zietz, 1965; James and Steinhart, 1966; Hill and Pakiser, 1966; Pakiser and Robinson, 1966; Woollard, 1966), continuing seismic activity (Ryall, Slemmons, and Gedney, 1966), and high heat flow (Lee and Uyeda, 1965; Roy and others, 1968). Viewed as a whole, these features emphasize the uniqueness of the Basin and Range tectonic province. Moreover, it seems likely that many of these features may be related to the Cenozoic volcanism, and indeed some of them show a pattern similar to that defined by the distribution of volcanic rocks. For example, the core area is relatively inactive seismically (Ryall, Slemmons, and Gedney, 1966; Woollard, 1958) and seems to have a slightly thicker crust (Eaton, 1963; Pakiser and Zietz, 1965; Hill and Pakiser, 1966; 1967) compared to surrounding parts of the Great Basin.

The outward shift of intense volcanic activity may have been paralleled by an outward expansion of a zone of normal faulting within the Great Basin. This faulting may be reflected by Basin and Range structures that postdate the silicic volcanic activity in most regions (Ekren and others, 1968). Such systematic volcanic migration (at a rate of approximately 1-2 cm per yr) across hundreds of miles, must reflect som... primary motivating force located within the mantle. Menard (196... 1964) has suggested that the Basin and Range region represents the e... tension beneath the continent of the East Pacific Rise, resulting in th... uplift or distention of a zone of the crust at a rate of several centime... per year. In the models of ocean-floor spreading (Dietz, 1961; He... 1962; 1965; Vine and Matthews, 1963; Vine, 1966), the distention is du... to the effects of a rising column of mantle material which is part ... the overall convection system in the mantle. In the Great Basin, ... upwelling of mantle material that began in the core area of east-cent... Nevada and spread asymmetrically outward, has been suggested by ... L. Cook (1962; 1968). Magma may have resulted from direct heating ... the lower crust or upper mantle by the rising hot material or from ... overall rise of temperature resulting from deep-seated convective mo... ments.

A slightly different hypothesis suggests that the convection curre... or some other type of mantle disturbance—triggered the rise of dia... of mantle material (Green and Ringwood, 1967). Magmas might h... resulted (1) from the partial fusion of the diapir on release of press... (2) indirectly, by fusion of crustal or uppermost mantle material by ... hot diapir, or (3) by a combination of the two. This mechanism w... explain the common occurrence within the Great Basin of axially ... metrical volcanic centers of the collapse-caldera type, each characte... by a chemically mineralogically, and otherwise lithologically cohe... ...ence of tuffs and lavas distinct from those of neighboring volc... ...oble and others, 1965). The generation and eruption of ma... ...irectly related to preexisting tectonic features, su... ...t extend to deep crustal or subcrustal depths. ... a third and somewhat different mechanism ... antle material began to rise in the core are...

...rust was progressively distended and fractured. These ...rated to ever increasing depths, tapping magma sou... lower crust and upper mantle. Release of confining press... ...ures would result in partial melting of hot material. H... ...elatively shallow depth in the crust would have been pre... ...onsequence of the Mesozoic orogenies that produced the ...igh-grade metamorphic Paleozoic rocks now exposed ... ...reat Basin. The metamorphic rocks do not seem to have ...mperatures favorable for argon retention in minerals ... ...me (Armstrong and Hansen, 1966; Armstrong and Hills, ...ortions of the crust must also have remained at elevated ...er the Mesozoic metamorphism and were thus pote... ...urces. Generation and upward movement of magma wo... ...s of considerable heat; the residue from partial melti... ...able to yield additional magma, so that the fractures w... ...continually deeper sources, eventually sources within ...elf.

The observation that basalts are commonly erupted ...cic volcanic rocks, in any given area, is consistent with ... the tapping of ever-deeper sources of magma. In this mod... ...tion of magma types would reflect original heterogeneities ... upper mantle and regional differences in thermal gradie... ...lting. Partial melting under varying pressure-temperature ...d result. The progressive outward shift of volcanic activi... ...crustal fracturing began in the core area—an area that coin... ...belt of highest grade Mesozoic regional metamorphism—a... ...ly outward toward the margins of the Great Basin. Ce... ...anic activity reflects the exhaustion of the magma sources.

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crust was progressively distended and fractured. These fractures penetrated to ever increasing depths, tapping magma sources within the lower crust and upper mantle. Release of confining pressure by the fractures would result in partial melting of hot material. Hot material at a relatively shallow depth in the crust would have been present as a direct consequence of the Mesozoic orogenies that produced the medium- and high-grade metamorphic Paleozoic rocks now exposed in the eastern Great Basin. The metamorphic rocks do not seem to have cooled below temperatures favorable for argon retention in minerals until Tertiary time (Armstrong and Hansen, 1966; Armstrong and Hills, 1967). Deeper portions of the crust must also have remained at elevated temperatures after the Mesozoic metamorphism and were thus potential magma sources. Generation and upward movement of magma would result in loss of considerable heat: the residue from partial melting would be unable to yield additional magma, so that the fractures would have to tap continually deeper sources, eventually sources within the mantle itself.

The observation that basalts are commonly erupted later than silicic volcanic rocks, in any given area, is consistent with this concept of the tapping of ever-deeper sources of magma. In this model the localization of magma types would reflect original heterogeneities of the crust and upper mantle and regional differences in thermal gradient prior to faulting. Partial melting under varying pressure-temperature conditions would result. The progressive outward shift of volcanic activity suggests that crustal fracturing began in the core area—an area that coincides with the belt of highest grade Mesozoic regional metamorphism—and moved slowly outward toward the margins of the Great Basin. Cessation of volcanic activity reflects the exhaustion of the magma sources.

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AGE OF ADULARI
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MANUEL N. BASS
Scripps Institution of O

ABSTRACT. Adularias from quartz
ages that bracket the time of crystalli
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suggest deposition in Late Pennsylva
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AGE OF ADULARIA AND METAMO

Quartz veins in the Ouachi
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ogies of most veins faithfully re
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were derived by lateral secretion
232-233). The veins are thus typ
low-grade metamorphic rocks (Ho
ing veins are found in shale and
stone (Engel, 1951, p. 227) and
cleft veins. Chlorite as a vein
especially common in veins in the
shale (Engel, 1951, p. 229, 233).

DATE

The two dated specimens ar
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of the dated specimens.

Specimen 1 is a breccia of
Early(?) to Middle Ordovician W
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pink, the pink occurring as distin
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GEOLOGIC HISTORY OF ROCKY MOUNTAIN REGION[1]

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ABSTRACT

During late Precambrian time, sedimentary rocks were deposited in a geosyncline in the Cordilleran region. Eastward extensions of this geosynclinal sea occupied parts of the Rocky Mountain region. After gentle deformation and erosion, the sea spread eastward during the Cambrian and Ordovician Periods. Discontinuous Ordovician, Silurian, and Early Devonian rocks indicate short intervals of marine invasion interrupted by periods of erosion. A major invasion of the sea over the craton is recorded by the onlap of Devonian and Mississippian carbonates and Devonian evaporites which rest on rocks ranging in age from Precambrian to Early Devonian.

The pattern of widespread shallow seas of the Mississippian Period was interrupted during the Pennsylvanian and Permian Periods by significant tectonic activity (Ancestral Rockies). Parts of the uplifts remained positive until Triassic or Jurassic time and supplied coarse clastic sediments to late Paleozoic basins in adjacent areas. At greater distances from land, sandstone, red shale and siltstone, evaporites, and carbonates accumulated. Marine Triassic sediments were deposited in southeastern Idaho and adjacent areas. Triassic and Early Jurassic continental deposits accumulated throughout much of the region.

A series of Jurassic marine invasions from the Arctic initiated another major sequence of events. The boreal sea extended southward into the northwestern and western parts of the region in Middle Jurassic time, and successive transgressions reached as far southeast as northern Colorado by Late Jurassic time. After withdrawal of the Jurassic sea, the pattern of overlap was continued by deposition of non-marine Jurassic and Cretaceous sediments. During the Early Cretaceous a sea again invaded from the north and in late Early Cretaceous time joined one from the south, forming a seaway which persisted throughout the remainder of the Period. During Early Cretaceous time, clastic sediments were derived from the craton on the east and from the Cordilleran region on the west. During Late Cretaceous time, the western source area predominated.

The present tectonic framework began to form during the Late Cretaceous and early Tertiary with the development of uplifts and intermontane basins (Laramide orogeny). Extensive thrust faulting occurred in the western part of the region. Lacustrine and fluviatile sediments, derived from surrounding uplifts, were deposited within intermontane basins.

Volcanic activity was moderately important on the west during the Cretaceous Period, but igneous intrusion and volcanic activity became widespread throughout the Rockies in the Tertiary. The present drainage system was largely developed as the intermontane basins filled. Subsequent stream erosion, accompanied by Pleistocene glaciation and regional uplift, shaped the present topography.

INTRODUCTION

The area considered in this report is generally regarded by the petroleum industry as the Rocky Mountain region. It includes the middle and southern Rocky Mountains, a large part of the Great Plains, and the Colorado Plateau. The western Montana disturbed belt (northern Rockies) is not included.

Much of this compilation is based on the extensive compilations of other workers that are, in turn, based on the publications of many hundreds of geologists. Maps published by Eardley (1962), Sloss *et al.* (1960), and in numerous guidebooks were especially useful. We appreciate the permission to study unpublished maps of Ogden Tweto, J. A. Barlow, Jr., C. E. Jenkins, and B. D. Rea.

Most of the isopachous maps have been reconstructed to show probable thicknesses before Laramide and post-Laramide erosion. In addition, some of the maps have been reconstructed to show probable original areal extent of the units considered. Construction of paleogeographic maps is always made difficult by the impossibility of establishing the true former extent of eroded stratigraphic units. A chance discovery may establish that there were normal marine carbonates deposited in the center of what was previously considered to be a land area! The various kinds of maps and cross sections have been selected to provide an outline of the major events in the tectonic and sedimentational history of the Rocky Mountain region.

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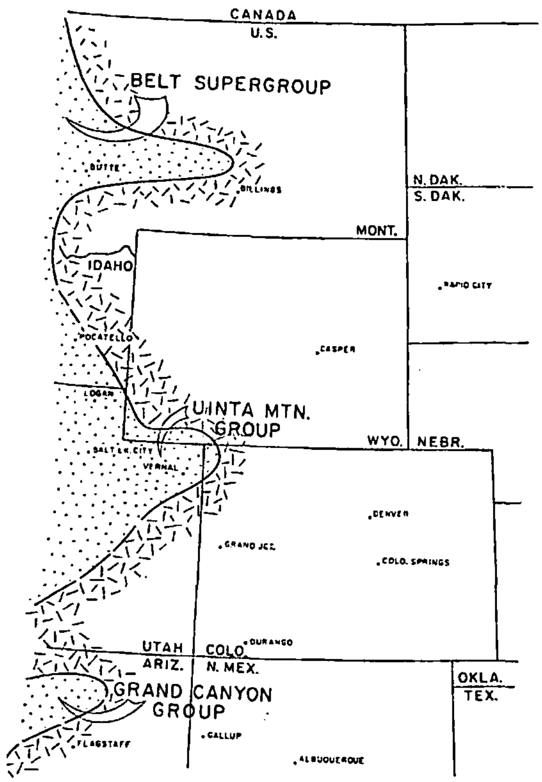

Fig. 1.—Late Precambrian paleogeologic map showing Precambrian sedimentary rocks (dots) west of more ancient igneous and metamorphic rocks (after Blackwelder, 1946; Lochman-Balk, 1956; Sloss, 1950; Williams, 1953).

Precambrian

There were 15,000 to perhaps as much as 50,000 feet of Precambrian sediments deposited in western parts of the region, including the Grand Canyon Group in Arizona, the Uinta Mountain Group centered in northern Utah, and the Belt Supergroup in Montana (Fig. 1). Belt rocks are about one billion years old. A recently determined age of 1,070 million years (m.y.) is based on potassium-argon and rubidium-strontium analysis of glauconite from the upper part of the Beltian Missoula Group (Gulbrandsen, Goldich, and Thomas, 1963). Other previously determined ages are as much as several hundred million years older or younger.

Northwest and southwest of the region there may have been continuous deposition from Precambrian into Cambrian time. At the top of the eastward projections of these ancient sediments, however, there is probably an unconformity of considerable magnitude. The original maximum extent, except possibly in local areas (*e.g.*, La-Hood Formation of McMannis, 1963), is unknown, and the eastward projections may bear little relation to the original depositional pattern.

The three eastward projections of Precambrian sedimentary rocks had different structural histories throughout post-Precambrian time. The area of Belt sedimentary rocks in Montana was the locus of deposition of the central Montana trough (Big Snowy basin) which provided a connection between the Cordilleran geosyncline and the Williston basin, especially during parts of Paleozoic time. It was the site of mountain building during the Laramide orogeny. The area of deposition of the Uinta Mountain Group was a seaway during the Pennsylvanian, but was not orogenically active until Laramide uplift. The Grand Canyon Group was tilted during late Precambrian time, but the region was one of relative stability and positive movements in later eras.

East of the region of Precambrian sedimentary rocks, the older basement complex consists of metamorphic and igneous rocks. A northeast-southwest-trending band of older rocks (2,300-2,700 m.y.) crosses Wyoming. Northwest and southeast of these more ancient rocks are younger basement rocks (1,300-1,800 m.y.) (Blackstone, 1963; Eardley, 1962; Engel, 1963). In Colorado and in southern and northwestern Wyoming the dominant trend of foliation and bedding is northeast, and in the remainder of Wyoming the dominant trend is northwest (King, 1959, p. 99).

Tectonic trends within visible basement rocks in some areas are parallel with Paleozoic and later structures, but in much of the region there is little obvious relation between visible basement structure and later structure. Although most structural development in the region probably is related to vertical movements of basement blocks, the source of energy for movement was deep within the crust or mantle, and the orientation of forces is not reflected in the visible basement rocks.

In some areas, such as the Williston basin, Precambrian ancestral structural features were intermittently active throughout geologic time. In other areas, such as the Ancestral Rocky Mountains, late Paleozoic tectonic elements were reactivated during the Laramide orogeny but not necessarily with the same orientation, and post-Laramide structural developments cross-cut previous structural trends. In still other areas, such as the Wyoming basins and ranges, there is no record of major pre-Laramide structural activity of elements corresponding with Laramide structures.

Cambrian

During the Cambrian Period there was progressive spreading of a shallow epicontinental sea eastward and southeastward from the Cordilleran geosyncline (Lochman-Balk, 1956). Lower Cambrian rocks are confined to the geosynclinal area. A generalized east-west diagram (Fig. 2) showing the overlap of Cambrian rocks on basement is representative of most of the region, from north to south. In eastern Colorado the Cambrian sea came from the east (MacLachlan, 1961). It is probable that the northeast-southwest-trending transcontinental arch (Siouxia and Sierra Grande) was not covered in its southwest part until the Ordovician (Fig. 3). Clastic sediments were overlain by carbonates as the sea moved toward the arch.

Figure 3 illustrates the progressive age of rocks resting on basement. In an area in central Colorado the western sea may have joined the southeastern sea during Late Cambrian. This has been called the Colorado sag and was a structurally low area on the transcontinental arch. Early Ordovician deposition was essentially a continuation of Late Cambrian deposition, with no obvious lithologic or faunal break, and was a part of the first cycle of marine sedimentation.

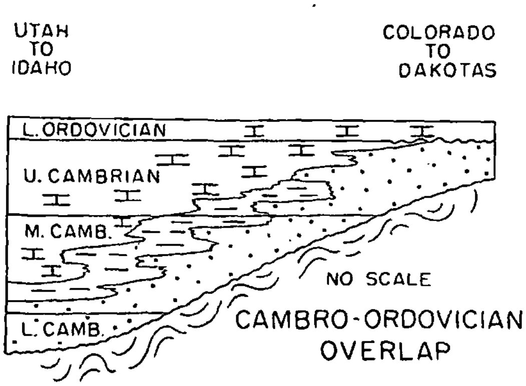

Fig. 2.—West-to-east restored diagrammatic cross section of Cambro-Ordovician overlap. Basal sandstone (dots) is laterally equivalent to shale (horizontal lines) and carbonate (limestone symbols).

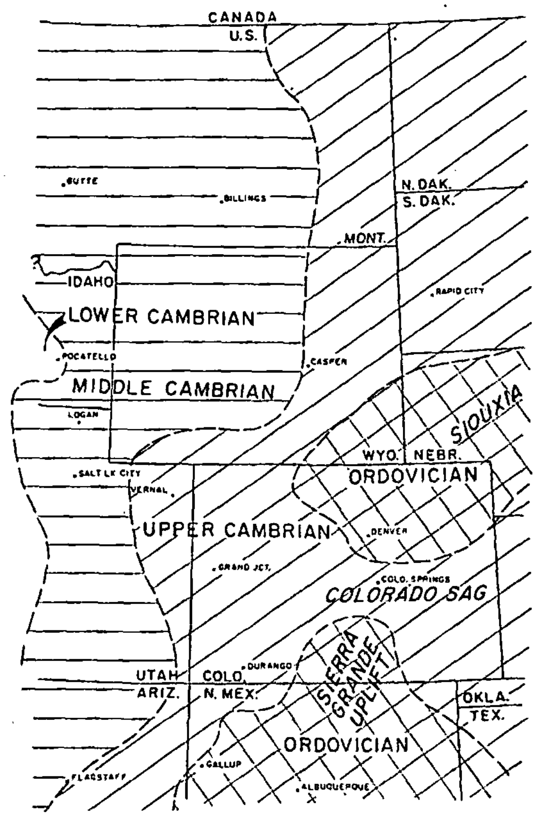

Fig. 3.—Restored worm's-eye map of Cambrian and Lower Ordovician rocks on Precambrian rocks at end of Early Ordovician (after Berg, 1960; Christiansen, 1963; Eardley, 1963; Lochman-Balk, 1956; McKee, 1951; Scopel, 1964; Sloss, 1950; Sloss *et al.*, 1960; Stevens, 1961; Wheeler, 1947).

Ordovician

Middle or Upper Ordovician rocks unconformably overlie Lower Ordovician to Precambrian rocks in the region. The unconformity resulted from withdrawal of the sea to the geosyncline in late Early Ordovician time. Return of the sea to the cratonic area in Middle and Late Ordovician, the second cycle of sedimentation, is indicated by basal clastic sediments overlain by carbonates and could be diagrammed in a manner similar to that of the Cambrian overlap. Post-Ordovician periods of erosion have removed much of the record, but Upper Ordovician carbonates indicate that clear marine waters probably occupied most of the region. Thickest sedimentary sequences occur in the geosynclinal area and in the Williston basin. Middle Ordovician sediments indicate the first development of a depositional Williston basin

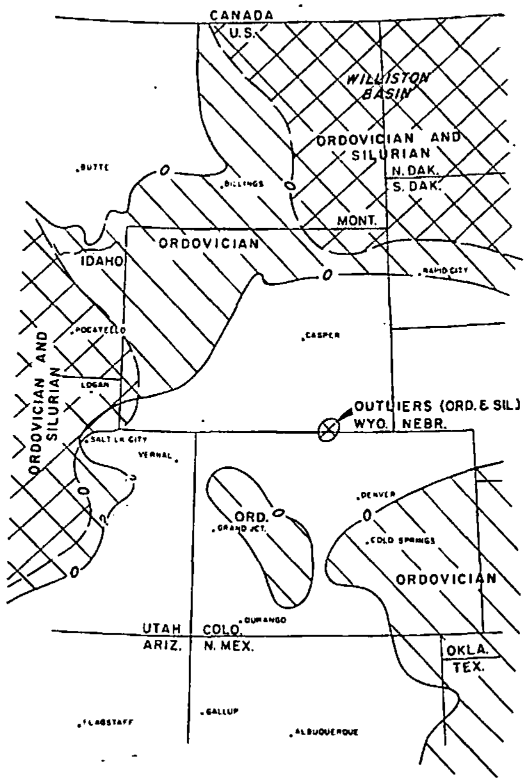

FIG. 4.—Ordovician-Silurian distribution map (after Chronic and Ferris, 1961, 1963; Hintze, 1959; Rush, 1963; Sandberg and McMannis, 1964; Sloss *et al.*, 1960; Stoyanow, 1936).

(Sandberg and Hammond, 1958, p. 2329). Restricted circulation in the Williston basin is indicated by the occurrence of evaporites in Middle and Upper Ordovician rocks and in the rocks of subsequent periods (Sandberg, 1962).

The discovery of Cambrian (?), Ordovician, and Silurian rocks in outliers (Fig. 4) just north of the Wyoming-Colorado boundary (Chronic and Ferris, 1963), in an area previously mapped as Precambrian, has resulted in drastic revision of early Paleozoic paleogeographic maps. These rocks are an additional indication that the area previously considered to be a part of the positive transcontinental arch actually was covered by the sea. Later uplift of the arch and subsequent erosion led to development of the present limits of Ordovician sediments. Additional evidence of former extent of Ordovician sediments was found in 1964 in a third outlier in northern Colorado, about 10 miles south of the previously described southern Wyoming outliers. The newly discovered outlier has yielded a fauna of Late Ordovician age (John Chronic, personal communication).

Silurian

The record of Silurian deposition is the most fragmentary part of regional stratigraphic history. The Williston basin carbonates and evaporites comprise the thickest Silurian section in the region. In addition a varied and unquestioned Silurian fauna has been collected from the southeastern Wyoming outliers (Cronic and Ferris, 1963). The fauna and rock types from these localities indicate a marine environment of deposition far removed from a shoreline. It is probable that deposition was continuous from Late Ordovician through Silurian time and that the region was completely covered by the Silurian sea. Present limits of Silurian rocks in the Cordilleran geosyncline and the Williston basin are probably the result of pre-Devonian and subsequent periods of erosion.

Devonian

The sea withdrew from the craton during Early Devonian and the period of erosion that followed was one of the most extensive in the region. Limits of pre-Devonian formations on the northern Montana uplift (Alberta shelf) are in doubt primarily because of this unconformity. The pattern of Devonian erosion also indicates that the transcontinental arch was positive. When the sea returned during Middle and Late Devonian, a third cycle of deposition was initiated. The sea transgressed from northern Alberta into the Williston basin and in it were deposited thick evaporites and carbonates. In parts of the region the transgression again was characterized by clastic deposition.

Middle Devonian rocks occur only in the Cordilleran geosyncline and the Williston basin and indicate the slow progress of Devonian overlap. The present southeastern limit of Upper Devonian rocks is indicated by the zero isopach in Figure 5. Conservatively estimated maximum limits of Devonian deposition are indicated by dotted lines on the map. The region was probably not completely covered by the sea until Mississippian time.

Mississippian

In much of the region there apparently is a disconformity between Devonian and Mississippian formations. Clastic sediments in basal Mississippian beds indicate uplift of the northern part of the ancestral Front Range. Uplift may have occurred also in other elements of the Ancestral Rockies (Fig. 6). Some Devonian sediments probably were removed during this period of erosion, and in areas beyond the limits of Devonian deposition, Mississippian rocks rest on pre-Devonian Paleozoic and basement rocks. In western Montana and northwestern Wyoming, transitional Devonian-Mississippian strata ("dark shale unit" of Sandberg, 1965) unconformably overlie older Devonian beds. The time represented by pre-Mississippian or Early Mississippian erosion, however, does not appear to be very long, and the total aspect is one of continued transgression and completion of the cycle of sedimentation that began in Devonian time.

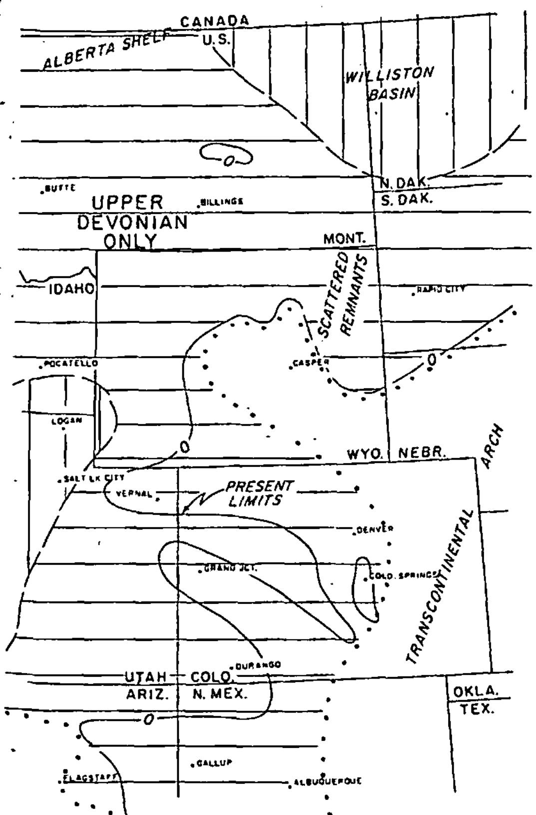

FIG. 5.—Devonian distribution map. Dotted lines indicate possible maximum extent, vertical lines show limits of Middle Devonian rocks, and horizontal lines show limits of Upper Devonian rocks (after Eardley, 1963; McKee, 1951; Rothrock, 1960; Sandberg and Hammond, 1958; Sloss *et al.*, 1960).

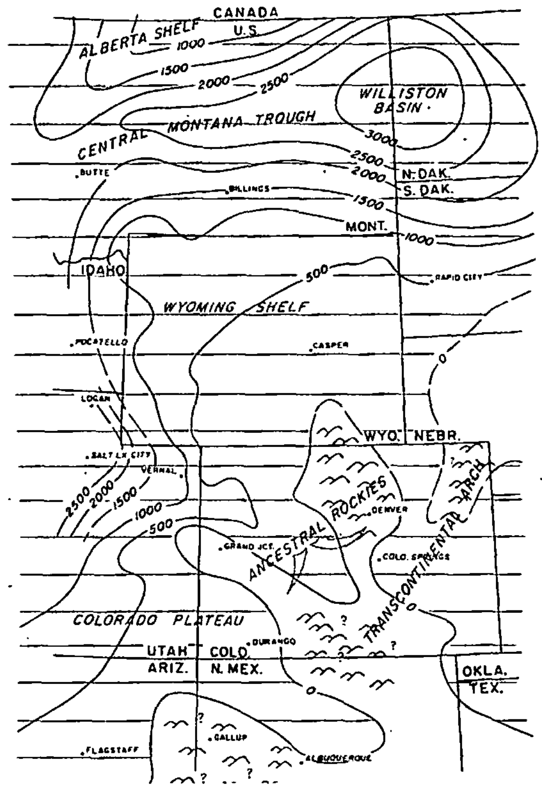

FIG. 6.—Mississippian isopachous map; isopach interval 500 feet (after Carlson, 1963; Eardley, 1963; Maughan, 1963; McKee, 1951; Rothrock, 1960; Sandberg, 1962; Sloss *et al.*, 1960).

The Mississippian deposits are predominantly carbonates, but in the Williston basin thick evaporites were deposited (part of the Charles Formation). Late Mississippian (Chesterian) sediments are not common in the region and may have been removed by pre-Pennsylvanian erosion. The dominantly clastic Chesterian Big Snowy Group is conformable with the underlying Charles Formation in the Williston basin (Sandberg, 1962), but around the margins of the basin and in central Montana the contact is disconformable (Sloss, 1950, p. 444). Mississippian rocks probably once covered the entire region, but were thinnest over the transcontinental arch and the incipient Ancestral Rockies. The isopachous map (Fig. 6) tends to confirm this pattern, although the thickness was modified an unknown amount by post-depositional, largely pre-Pennsylvanian, erosion. During Late Mississippian time the sea apparently withdrew from the region and then began an advance which started the fourth cycle

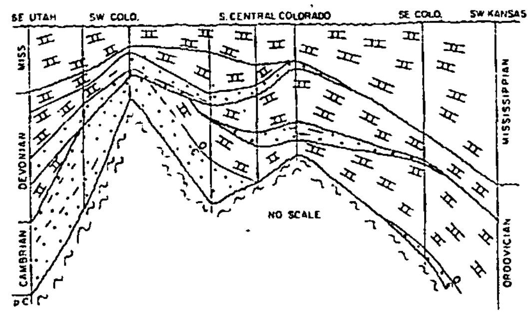

FIG. 7.—Schematic lower and middle Paleozoic stratigraphic diagram (modified from Rold, 1961). Symbols as on Figure 2.

of deposition. Faunal evidence in northwestern Colorado, western Wyoming, and western Montana indicates that this next sedimentation cycle began in latest Mississippian time.

EARLY AND MIDDLE PALEOZOIC TECTONIC FRAMEWORK

The isopachous map (Fig. 6) emphasizes the tectonic framework of the region, a framework which was partly revealed in earlier periods and which continued into late Mesozoic time. On the north, extending southward into northern Montana, is the Alberta shelf that was stable throughout its history and was positive throughout much of geologic time. South of this shelf is the central Montana trough (Big Snowy basin) that was a negative structural element throughout Beltian deposition and was a seaway during much of Paleozoic time, but was an area of uplift during the Laramide orogeny (central Montana uplift). The Williston basin (southeast of the Alberta shelf in Montana and North Dakota) was the site of deposition for 17,000 feet of sediments, mostly of Paleozoic age. South of the Williston basin and the central Montana trough, the Wyoming shelf was an area of great stability until the Laramide orogeny. The southern Rockies of Colorado and New Mexico form another distinctive region of relative instability, especially during late Paleozoic and Laramide orogenies. On the southwest the Colorado Plateau, including parts of Colorado, New Mexico, Utah, and Arizona, was stable during its entire history and was only moderately deformed during the Laramide orogeny. West of this entire region is the Cordilleran geosyncline, which is arcuate, convex toward the east, and was relocated eastward with time.

Lower and middle Paleozoic correlations and positions of unconformities across southern Colorado are diagrammed in Figure 7. The stratigraphic diagram illustrates the effects of regional uplifts which were especially pronounced along the transcontinental arch.

PENNSYLVANIAN

The pre-Pennsylvanian unconformity is one of the most significant in the region. Pennsylvanian strata rest on Precambrian basement along the flanks of the Ancestral Rocky Mountains and over the crest of the southwestern end of the transcontinental arch (Levorsen, 1960, p. 118). The pre-Pennsylvanian unconformity is the result of both orogenic and epeirogenic uplift. The Ancestral Rocky Mountain trend is the continuation of the Wichita-Amarillo system on the southeast (Hills, 1963). Structural relief developed in Desmoinesian time alone was at least 5,000 feet (Mallory, 1960, p. 26). Total structural relief that developed during Pennsylvanian and Permian deposition along the southwestern flank of the Uncompahgre uplift was greater than 15,000 feet. The tremendous volumes of coarse clastics shed from the narrow, elongate Front Range and Uncompahgre uplifts (Fig. 8) indicate the amazing potential of island areas to supply large amounts of sediment.

Figures 8 and 9 illustrate regional relation of dominant facies in Pennsylvanian rocks. Thick evaporite deposits occur in the Paradox basin and minor amounts in the central Colorado trough. North of the Ancestral Rockies (Front Range and Uncompahgre uplifts), fine clastic sediments were deposited on the Wyoming shelf in shallow marine and continental environments. A northwest-trending area of thin Pennsylvanian rocks in Wyoming has been mapped by Love (1954), and along this arch younger Pennsylvanian rocks flank older rocks beneath the pre-Permian unconformity. Beyond the areas of clastic and evaporite deposition, the carbonate facies becomes more significant. The extent of Pennsylvanian and Permian rocks in northern Montana prior to pre-Mesozoic erosion is unknown.

PERMIAN

The Pennsylvanian-Permian boundary is difficult to define in the southern part of the region, but in much of Wyoming a disconformity exists at this boundary. Permian rocks were deposited in the miogeosyncline that extended into Utah, Idaho, and western Wyoming. From time to time seas covered the western and southeastern parts of the region. The Ancestral Rocky Mountains were still positive and shed variable amounts of arkosic clastics into adjoining troughs and basins.

Dark shale, phosphorite, and chert were deposited in eastern Idaho and parts of adjoining States (Sheldon, 1963). Carbonate deposition dominated in a band on the east and south (Fig. 10). Farther east, shale and siltstone of the redbed facies contain thin carbonate and evaporite tongues. Coarse arkosic sediments surrounding the Ancestral Rockies intertongue with redbeds, sandstone, limestone, and evaporites. The Zuni and Front Range uplifts were less important sources of clastics than the Uncompahgre uplift. Significant thicknesses of evaporites formed, especially in western Nebraska and northeastern Colorado.

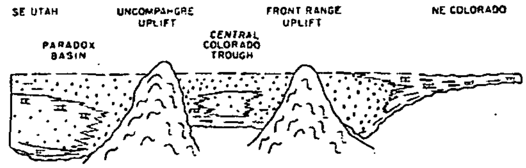

FIG. 9.—Diagrammatic restored section of Pennsylvanian deposits, SW.-NE., across Colorado. Symbols are same as for Figure 8 (after Mallory, 1960). No scale.

Cyclic deposits are present throughout much of the region and are most numerous in the Denver basin. Wolfcampian carbonates and sandstone of the eastern part of the region are not reflected in

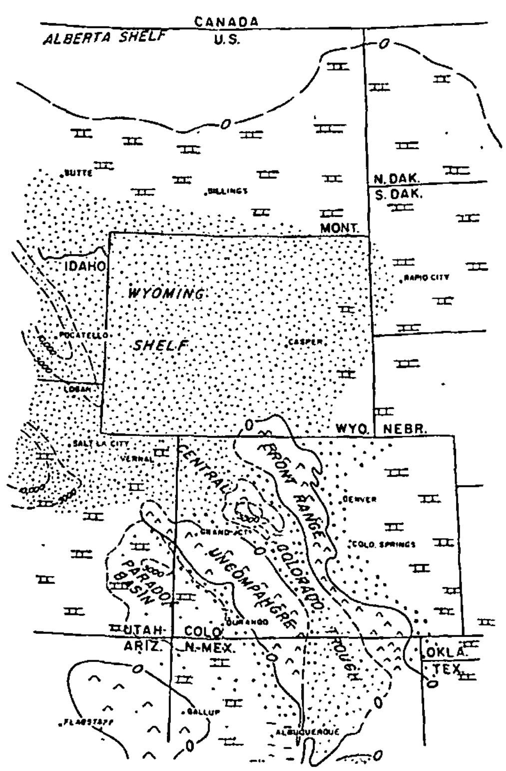

FIG. 8.—Dominant facies in Pennsylvanian rocks: conglomerate (circles), sandstone (dots), shale (dashed lines), carbonate (limestone symbols), evaporite (plus signs). Isopachous interval 5,000 feet. Ancestral Rockies are within zero isopachous lines in southern part of map (after Eardley, 1963; Mallory, 1960; McKee, 1951; Sloss, 1950; Sloss *et al.*, 1960).

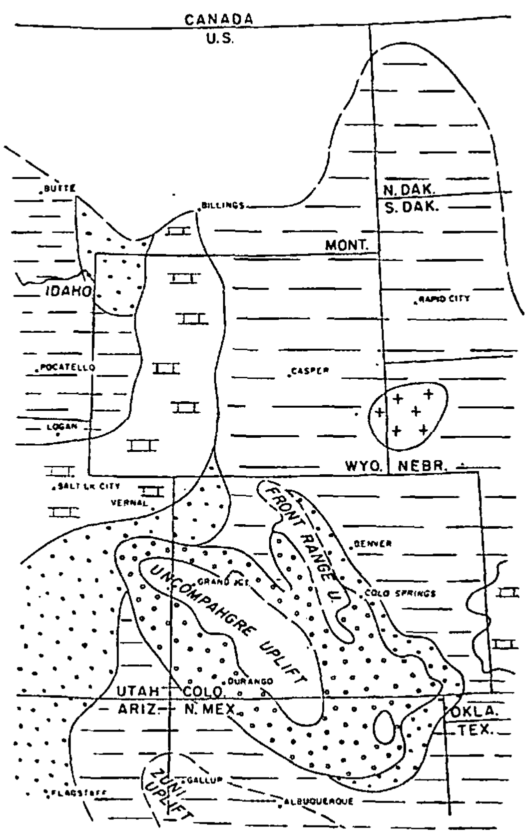

FIG. 10.—Dominant facies in Permian rocks (largely Leonardian and Guadalupian). Wolfcampian rocks not included in the east, but are included in southern part of map. Symbols same as for Figure 8 (partly based on maps by Sheldon, 1963; Peterson, 1959; Momper, 1963).

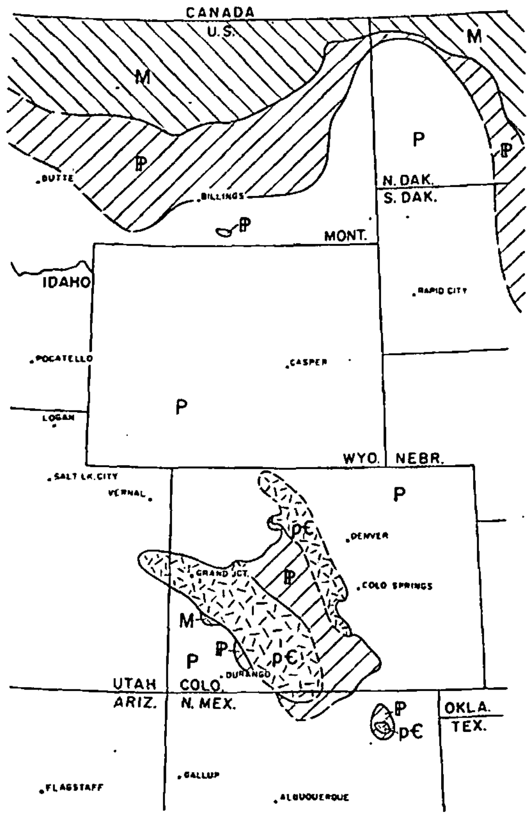

FIG. 11.—Pre-Mesozoic paleogeologic map: Precambrian (pЄ), Mississippian (M), Pennsylvanian (IP), and Permian (P) (modified from McKee *et al.*, 1956, 1959).

the Permian facies map (Fig. 10). Wolfcampian sediments, however, have been included in the southern part of the map because it is not possible to separate them from other Permian deposits.

Paleozoic-Mesozoic Relations

The pre-Mesozoic paleogeologic map (Fig. 11) illustrates the distribution of geologic units prior to deposition of Mesozoic rocks. Mississippian rocks are present along the northern part of the region and are paralleled on the south by Pennsylvanian and Permian rocks. Limits of Paleozoic formations in the northern part of the region are influenced by pre-Middle Ordovician, pre-Upper Devonian, pre-Upper Mississippian, and pre-Middle Jurassic erosion. Various Permian formations are present in the central part of the region and, if depicted, would make the paleogeologic map more complicated than is indicated. Remnants of the Ancestral Rockies were present in Colorado during the early Mesozoic, but contributed little sediment to Mesozoic deposits.

In much of the region a disconformity exists between Triassic and Permian rocks, but throughout most of Wyoming and southeastern Idaho (Figs. 11, 12) there was probably continuous deposition from latest Permian through earliest Triassic time. In the southwestern part of the region successively younger Triassic rocks onlap progressively older rocks from west to east toward the Uncompahgre uplift.

Figure 12 illustrates the various Mesozoic units that rest on the Paleozoic and Precambrian rocks of Figure 11. Triassic rocks were deposited throughout most of the area, were partly removed in the Jurassic, and then were overlapped by Jurassic deposits. Prominent areas of Jurassic overlap are in Montana, the Great Plains, and

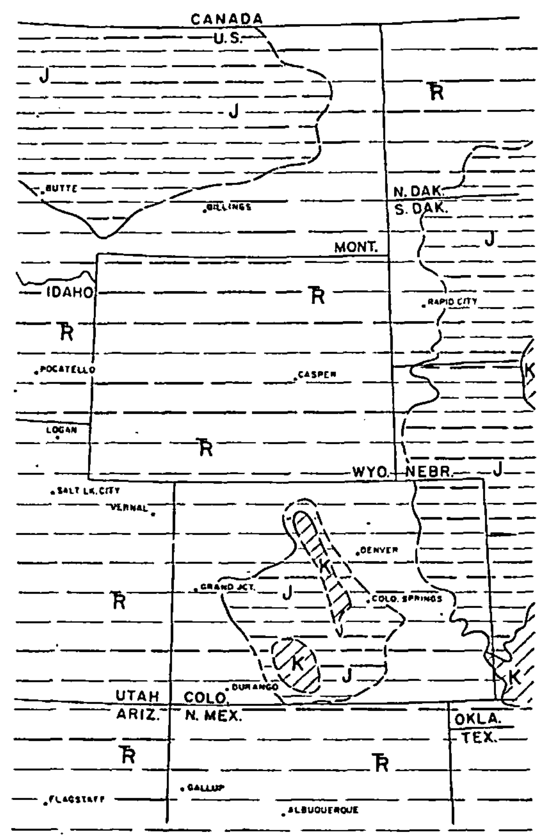

FIG. 12.—Worm's-eye map of Mesozoic rocks on older rocks: Triassic (Tr), Jurassic (J), and Cretaceous (K) (modified from McKee *et al.*, 1956, 1959).

central Colorado. Cretaceous rocks finally covered remnants of the Ancestral Rockies and other areas on the east.

Triassic

During Early Triassic time the miogeosyncline extended into eastern Idaho, southwestern Montana, and westernmost Wyoming (Fig. 13); the remaining parts of the region were shelf areas. Thickest sediments, as during much of the Paleozoic, were deposited in the miogeosyncline where thick carbonates (Dinwoody and Thaynes Limestones) were deposited. Thin tongues of carbonates, for example, the Alcova Limestone, extended toward the east. The Zuni and Defiance positive elements were elevated areas during Early Triassic, but were buried by Late Triassic sediments. The northwestern part of the Uncompahgre uplift also was covered by sediments during Late Triassic, but central Colorado was a positive area. Many local basins of deposition and uplifted areas do not correspond with Laramide tectonic features.

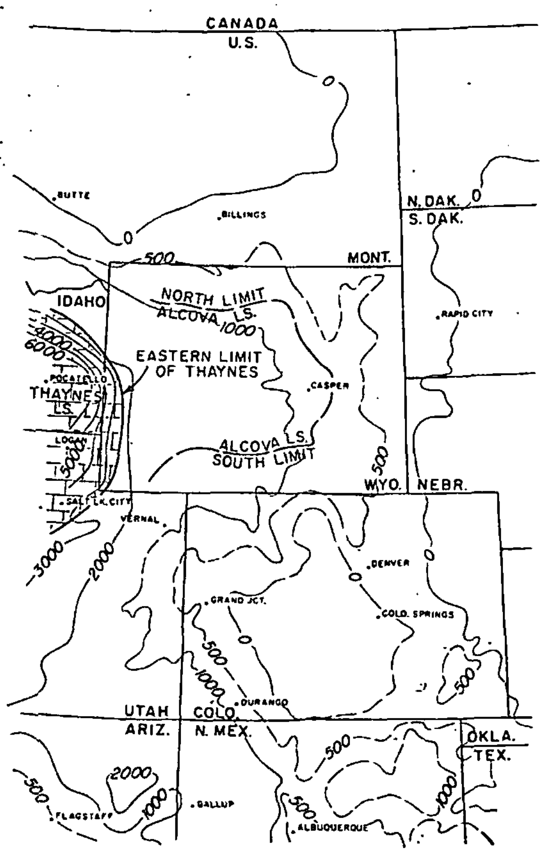

Fig. 13.—Triassic isopachous map; isopachous interval 500 and 1,000 feet (modified from McKee *et al.*, 1959). Alcova Limestone present only in western and central Wyoming.

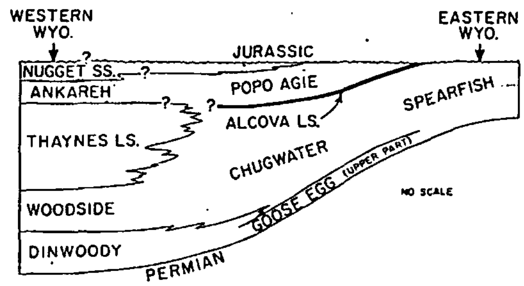

Fig. 14.—Stratigraphic diagram of Triassic rocks across Wyoming (modified from Thomas, 1949).

A disconformity at the base of the Chinle Formation (and/or Shinarump Conglomerate) in the southwestern part of the region separates Lower from Upper Triassic rocks. This disconformity may be present throughout a large part of the region, but its existence has not been established in Wyoming. The stratigraphic diagram (Fig. 14) does not show the disconformity, although the hiatus is supposed to represent most of Middle Triassic time. The relation of the Alcova Limestone to the Thaynes is questionable and the age of the Nugget Sandstone also is in doubt (discussion by Oriel, in McKee *et al.*, 1959, p. 23).

Figure 15 illustrates stratigraphic relations on the northeastern flank of the Uncompahgre uplift prior to Late Triassic sedimentation. Major unconformities and names of Paleozoic formations are shown. The stratigraphic history of the central Colorado trough is summarized in this diagram.

Jurassic

In the southwestern part of the region, Upper Triassic rocks are conformable with Lower Jurassic rocks. Toward the east and north, younger Jurassic formations overlap Triassic and older rocks. Along the eastern margin of Triassic rocks, several hundred feet of Triassic sediments were removed by pre-Late Jurassic erosion.

During Jurassic time, thickest marine deposition was centered in the Twin Creek trough along the western boundary of the region. Twin Creek (and equivalent) sedimentation is the last significant carbonate deposition in the Rocky

Mountain region. A Middle Jurassic paleogeographic map (Fig. 16) shows the regional northeast trend of depositional environments: normal marine (Sawtooth Formation) at the northwest, separated from a restricted environment at the southeast. This depositional strike continued into Late Jurassic and was controlled by the transcontinental arch.

There were several Middle and Late Jurassic invasions by the Arctic sea, the most extensive of which are represented by the shallow marine and transitional sediments of the Sundance Formation and Todilto Limestone. Maximum limit of the sea is shown on Figure 17. Thickest sedimentation was in the same general area as Triassic and earlier deposition. The source area for most of the Jurassic clastics was on the west, along a north-south-trending uplift which formed in the Cordilleran trough during the Nevadan orogeny. After northward withdrawal of the Sundance (Swift) sea, non-marine variegated shales and coarser clastics of the Morrison Formation were deposited. Wyoming formation nomenclature and stratigraphic relations are illustrated in Figure 18.

Through much of the region, the Jurassic-Cretaceous boundary is indeterminate or questionable. The boundary may be within the non-marine Morrison Formation. There is no regional unconformity at the base of Cretaceous rocks except where they onlap areas not previously covered by the Morrison Formation (Fig. 12).

Cretaceous

During Early Cretaceous the Arctic sea again

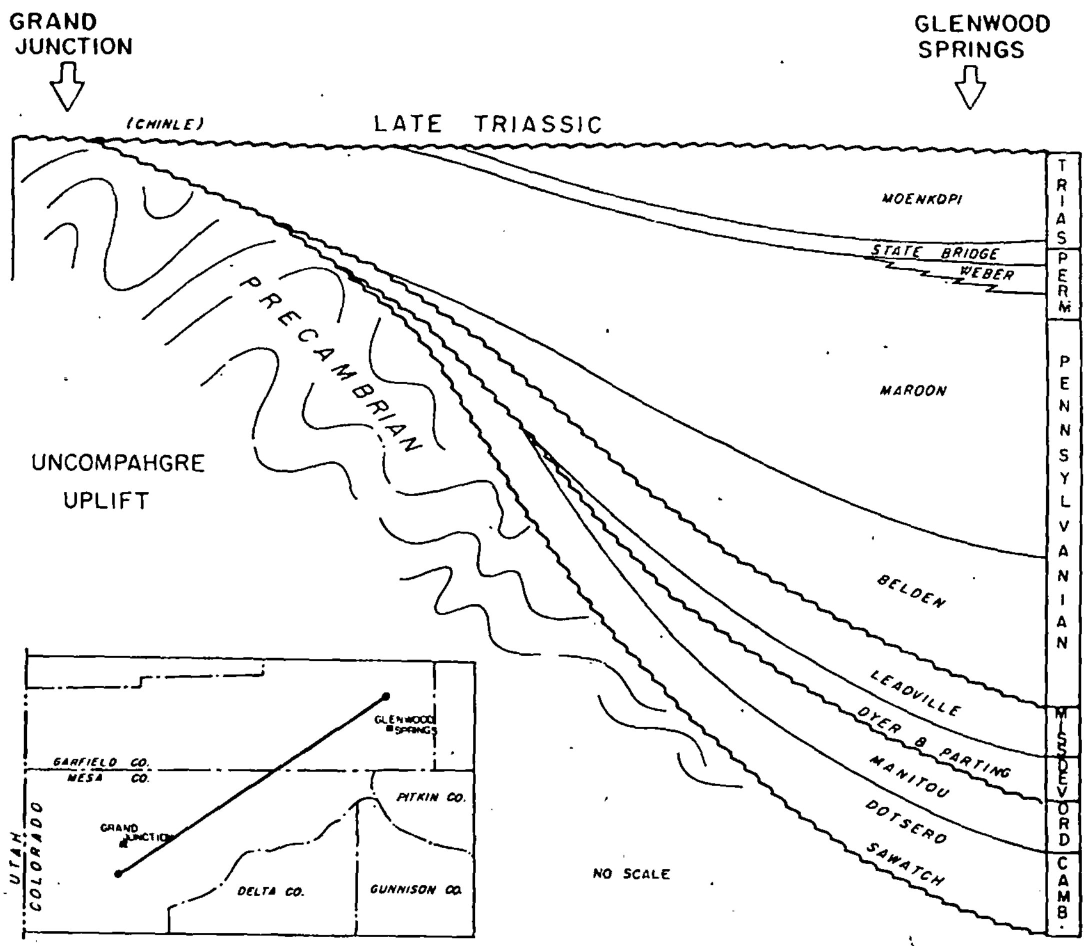

FIG. 15.—Stratigraphic diagram showing thick sedimentary section in central Colorado trough thinning toward Uncompahgre uplift (from Haun, 1962).

invaded the Rocky Mountain region. The Dakota Group, Cloverly, and associated formations, become younger southward and were deposited in the transitional environments near the margins of this sea. The Skull Creek Shale and equivalent marine sediments were deposited when the Arctic sea had joined, over the transcontinental arch, a seaway that extended northward from the Gulf of Mexico (Haun, 1963). The seas were separated for a short time by the joining of deltaic deposits from east and west, but were reunited in Late Cretaceous. The southward movement of the sea caused the Dakota Group and its lithogenetic equivalents to become progressively younger toward the southern and eastern margins. The sea did not reach northwestern New Mexico until Late Cretaceous time. Major sources of clastics were in areas west and east of the seaway in Early Cretaceous (Figs. 19, 20), but in Late Cretaceous the dominant source area was on the west. Thick deposits on the west (Fig. 19) reflect nearness of clastic source, as well as major down-

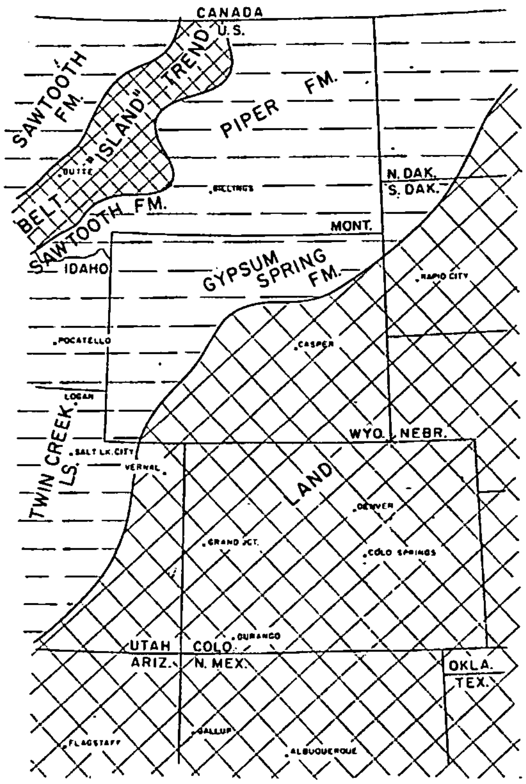

FIG. 16.—Paleogeographic map of Middle Jurassic (after Peterson, 1957).

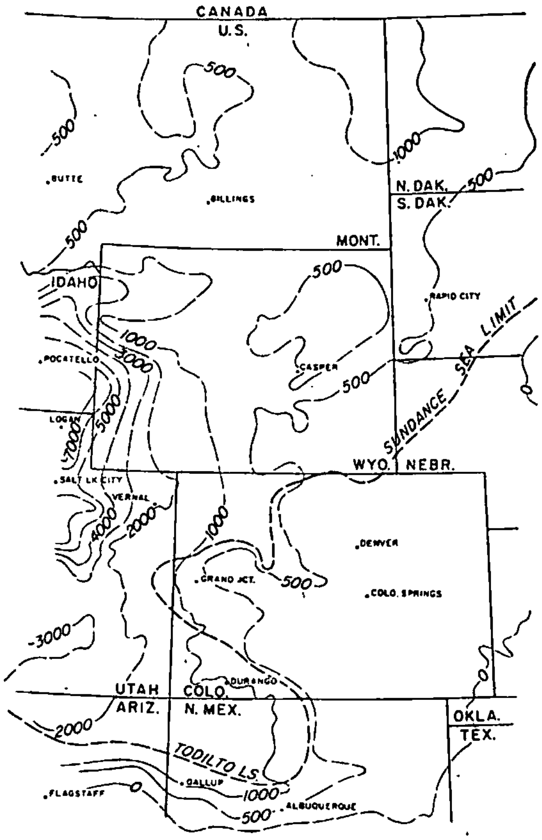

FIG. 17.—Jurassic isopachous map; isopachous interval 500 and 1,000 feet (modified from McKee *et al.*, 1956).

warping, and are slightly east of thickest deposits of earlier periods. Figure 20 illustrates formation nomenclature and stratigraphic relations of Cretaceous and early Late Cretaceous rocks

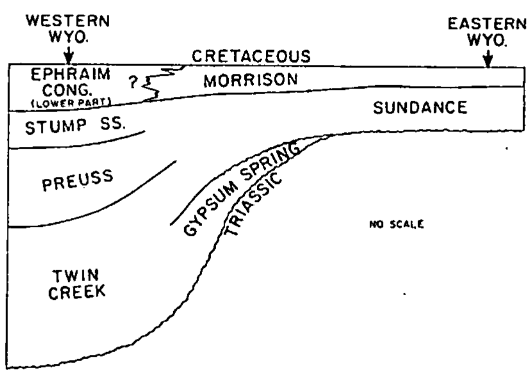

FIG. 18.—Stratigraphic diagram of Jurassic rocks across Wyoming (modified from Thomas, 1949).

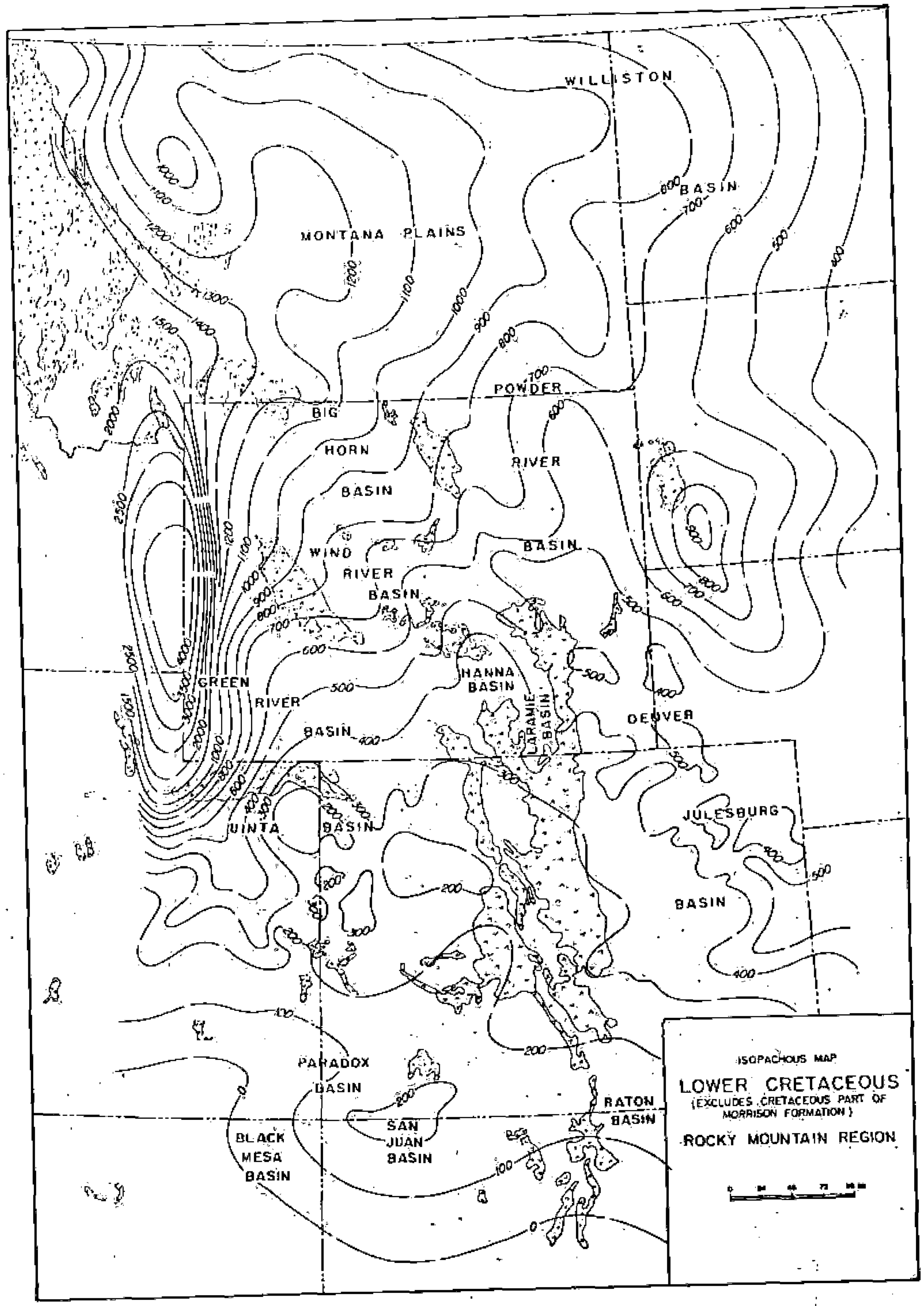

FIG. 19.—Lower Cretaceous isopachous map (from Weimer and Haun, 1960; Haun and Barlow, 1962)

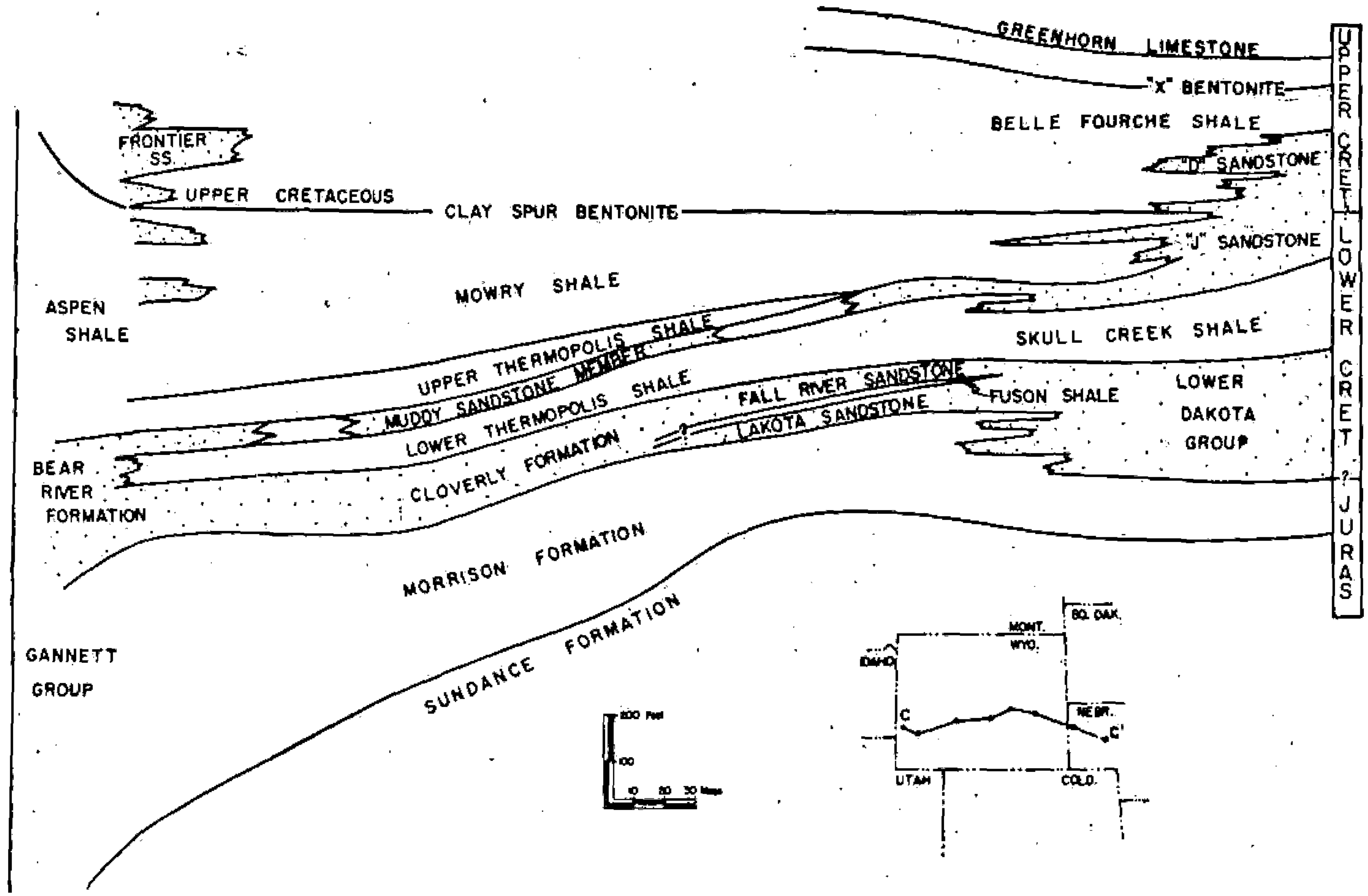

FIG. 20.—Stratigraphic diagram of Late Jurassic and Early Cretaceous rocks across south-central Wyoming (from Haun and Barlow, 1962). Scale: horizontal, 0.5 inch = 30 miles; vertical, 0.5 inch = 200 feet.

across south-central Wyoming and western Nebraska.

The west-to-east regression of the Late Cretaceous sea was periodically interrupted by transgressions that resulted in intertonguing of marine and non-marine sediments (Weimer, 1960). The thick non-marine and transitional deposits of the Mesaverde Formation accumulated in coastal-plain and deltaic environments along the western margin of the sea. The eastern marine shales and carbonates, 3,000 to 7,000 feet thick (Figs. 21, 22), were deposited contemporaneously with non-marine sediments on the west, more than 15,000 feet thick (Weimer and Haun, 1960). The source area was in the former position of thick Paleozoic and early Mesozoic miogeosynclinal deposition and is the area on the map (Fig. 21) where Upper Cretaceous is absent. Areas of thin sediments in Figure 21 reflect pre-Tertiary erosion. Areas of thickest deposition (Fig. 22) changed with time, becoming located progressively farther eastward.

During the Cretaceous, and especially during latest Cretaceous, early phases of Laramide tectonic activity began. Growth of Laramide mountains and basins, as well as minor tectonic features, influenced depositional patterns. In some parts of the region igneous activity accompanied Late Cretaceous deposition.

Cenozoic

The Laramide orogeny began in latest Cretaceous (mid-Maestrichtian) time and lasted until the end of the Eocene. This is an arbitrary definition, because the writers recognize the fact that there was orogenic activity in the Cordilleran area at various times beginning with the Jurassic Nevadan orogeny and continuing, with several maxima, until the Laramide. Each succeeding orogenic pulse was in a more eastward position. An early Late Cretaceous uplift in south-central Utah, and probably on the north, has been named the Cedar Hills orogeny (Eardley, 1962, p. 293). In the major part of the region under consideration, the Laramide, as defined here, has specific meaning. During the Laramide there developed vertical uplifts and basins, folds, reverse and thrust faults, and tremendous thicknesses of non-marine sediments. Thrust faulting was dominant in the western area of thick miogeosynclinal deposition. During the Laramide orogeny 15,000 to 45,000 feet of structural relief developed. Post-Laramide tectonic activity was of a different character and involved regional uplift and normal faulting.

Figure 23 shows the present thickness of Paleocene and Eocene sedimentary rocks within the different structural and depositional basins and outlines the present tectonic framework of the region. In the westernmost basins more than 10,000 feet of sediments were deposited. The western basins of Wyoming, Colorado, and Utah contain the valuable oil-shale deposits of the Green River lake beds. Lake beds are also present in the Wind River, Big Horn, and possibly other basins. Oligocene, Miocene, and Pliocene sediments almost completely buried the mountain ranges of Wyoming and adjacent areas (Love *et al.*, 1963) and were largely removed by later erosion. Igneous activity, both intrusive and extrusive, is confined mainly to the southern and northwestern parts of the region (Fig. 24). Most of the Wyoming shelf, with the exception of the Yellowstone region of northwestern Wyoming, was not involved in igneous activity, but volcanic ash made a large contribution to the late Tertiary sediments. Normal faulting, regional uplift, mountain glaciation, and development of the present drainage system characterize the late Tertiary-to-Recent history of the region.

Summary

The depositional history of the region is summarized in Figure 25. The vertical scale represents geologic time as determined by Kulp (1961). The horizontal scale represents the part of the Rocky Mountain region in which sediments were deposited. The farther toward the right that the line extends, the greater is the area covered by sediments at any given time. Conversely, the leftward projections indicate major unconformities. The part containing limestone symbols represents marine deposits, and the part containing the dotted pattern represents non-marine deposits. The sequences listed on the right side of the diagram are those of Sloss (1963). A question mark has been added to Tejas because there is general lack of definition of the Tejas-Zuni boundary. Perhaps Tejas should be removed from the list of sequence names. It should be emphasized that the sequence names are rock units, not time units, and refer only to those rocks de-

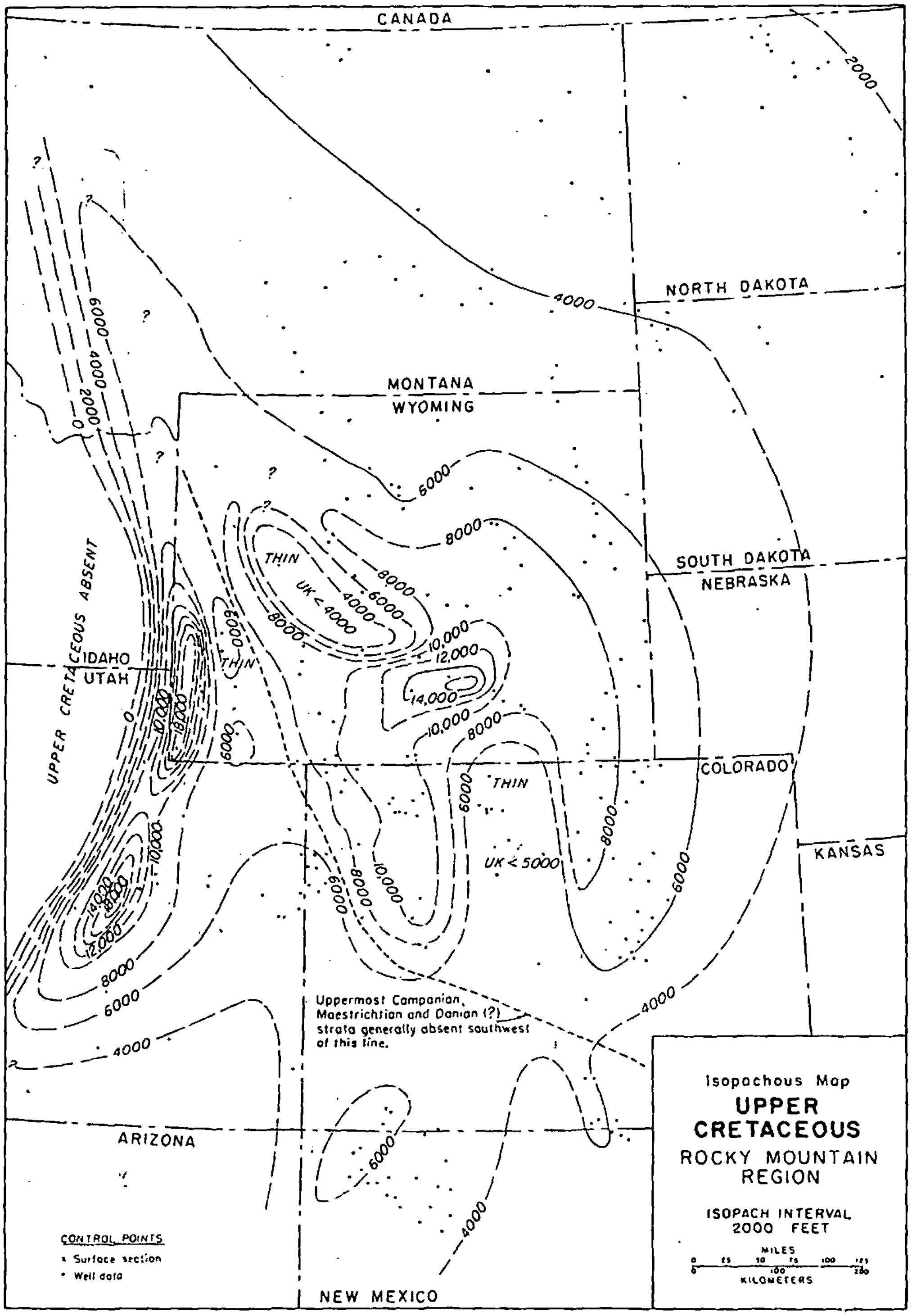

FIG. 21.—Upper Cretaceous isopachous map (from Weimer and Haun, 1960).

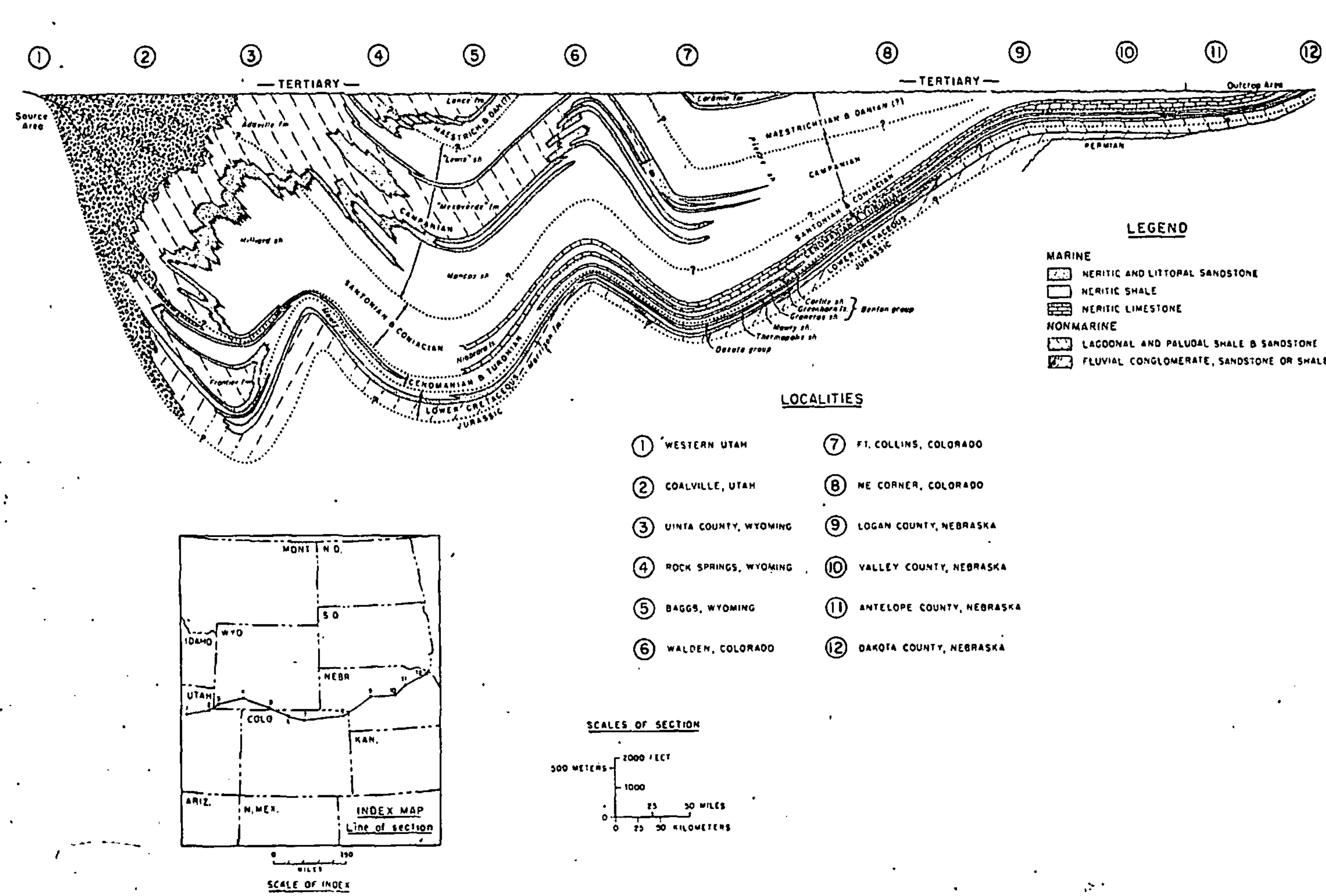

FIG. 22.—Diagrammatic restored section of Cretaceous from western Utah to eastern Nebraska (from Weimer and Haun, 1960).

posited within the wedges of sediments diagrammed at the left. The sequences are bounded by unconformities which differ, from place to place, in the length of the erosional interval. The sequence concept simplifies visualization of the position of major unconformities and periods of maximum deposition.

The most significant events, since the Precambrian, in the geologic history of the Rocky Mountain region are the following.

1. Transgression of the sea in Cambrian-Early Ordovician.

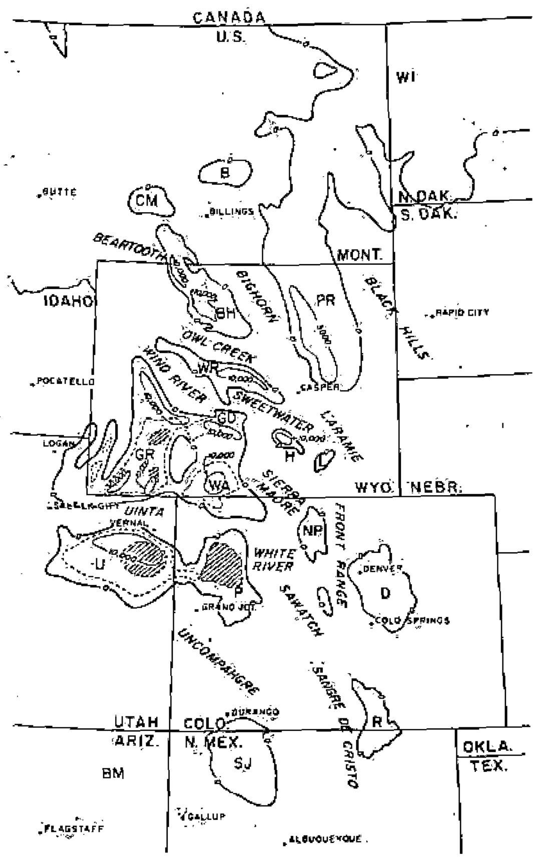

FIG. 23.—Early Tertiary tectonic framework emphasized by Paleocene and Eocene sedimentary rocks. Isopachous contour interval 5,000 and 10,000 feet. Eocene oil-shale areas outlined by dashed lines; high-grade oil shale shown by diagonal lines. Early Tertiary structural and depositional basins: Williston (WI), Bull Mountains (B), Crazy Mountains (CM), Powder River (PR), Big Horn (BH), Wind River (WR), Great Divide (GD), Green River (GR), Washakie (WA), Hanna (H), Laramie (L), Uinta (U), Piceance (P), North Park-Middle Park (NP), Denver (D), Raton (R), and San Juan (SJ).

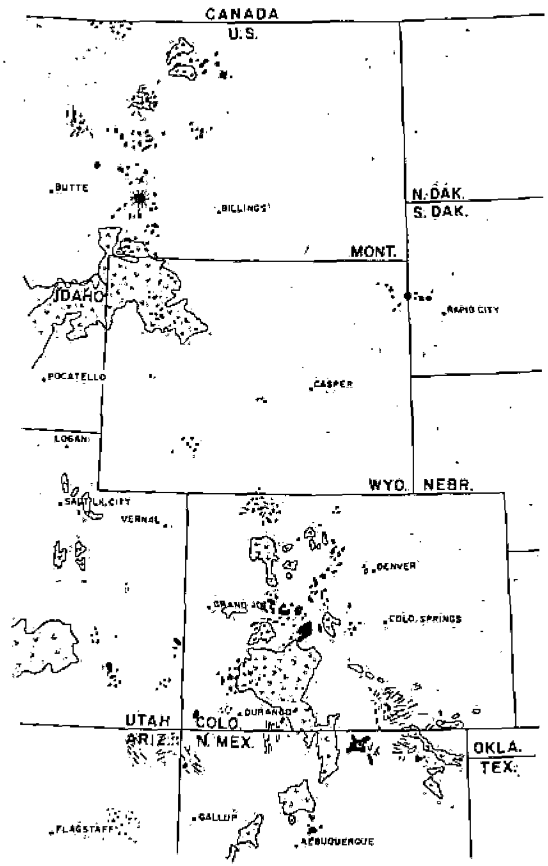

FIG. 24.—Cenozoic igneous rocks: major intrusions (solid black), dikes (lines), and extrusives (Vs). Some of these areas became active during Late Cretaceous.

2. Transgression of the sea in Middle to Late Ordovician and Silurian. This is poorly documented.

3. Regression and transgression of the sea in Late Devonian to Mississippian, with a minor withdrawal in Late Devonian.

4. Uplift of some of the elements of the Ancestral Rockies, especially the northern ancestral Front Range, in Early Mississippian.

5. Ancestral Rocky Mountain orogeny in Pennsylvanian and Permian, accompanied by invasions of the sea into trough and basin areas, and deposition of first major non-marine sediments.

6. Shift from more westerly seas of the Triassic to the Arctic seas of the Jurassic and Cretaceous, influenced by the Nevadan orogeny on the west.

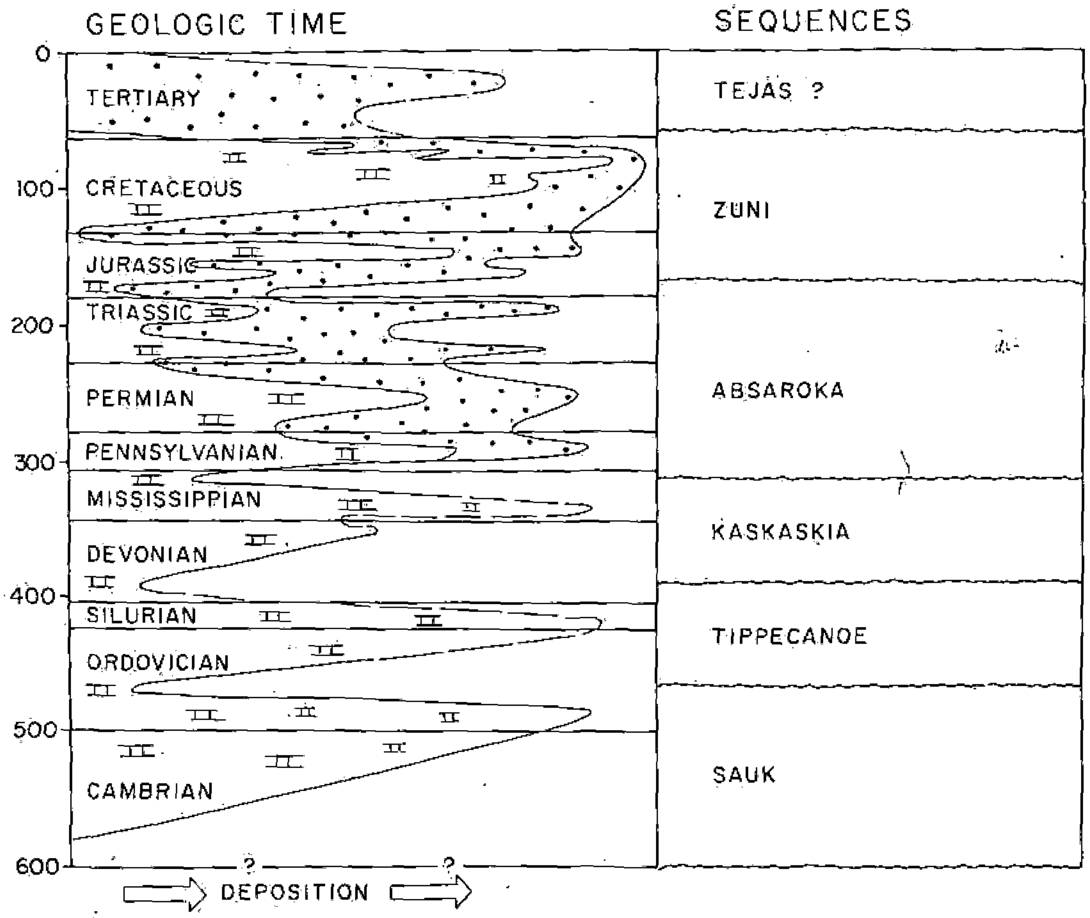

FIG. 25.—Summary diagram. Vertical scale in 100 million years (Kulp, 1961), horizontal scale represents percentage (0 to 100 per cent from left to right) of region in which marine (limestone pattern) and non-marine (dots) deposits originally accumulated; sequence names are from Sloss (1963).

7. Marked eastward shift of uplifted clastic source areas in Utah and Idaho during the Cretaceous.

8. Extensive invasion of Cretaceous seas from Arctic and Gulf, with construction of major deltas in eastern and western areas.

9. Laramide orogeny, with vertical uplifts, compressive folds and faults, thick continental deposits, and volcanism.

10. Late Tertiary basin filling and re-excavation, normal faulting, volcanism, and establishment of present drainage pattern and geomorphic features.

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RÉSUMÉ OF DEPOSITIONAL AND STRUCTURAL HISTORY OF WESTERN MONTANA[1]

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ABSTRACT

The western part of Montana is not a depositional basin in the sense used in this symposium, but its depositional and structural history is related to events of nearby areas. The area discussed lies partly in the shelf region and partly in the marginal area of the Cordilleran geosyncline. The decipherable part of its history begins with late Precambrian (Belt) sedimentation, during which the fundamental structural framework of western Montana evolved. Thick Belt strata are present in the western extremities and in an eastward-projecting embayment. Subsequent depositional patterns and present structural configuration are closely related to distribution of that thick sedimentary wedge. Coarse arkosic conglomerate was deposited along the southern fault-controlled margin of the Belt embayment. Cambrian through Mississippian formations and parts of the Cretaceous section are typically thicker in east-west zones, essentially coincident with the old Belt embayment, than they are north or south of the embayment.

Along the southwestern Montana and Idaho border a positive arch existed against which Cambrian through Devonian formations thin or disappear. This positive element became strongly negative during Mississippian and later depositional intervals as geosynclinal subsidence encroached on the cratonic margin.

Important facies changes take place in stratigraphic units across the northeast-trending Greenhorn fault in the Greenhorn-Snowcrest Range. These changes, which occur in short distances, suggest faulting or strong flexure along this zone during post-Ordovician to pre-Late Devonian and during Mississippian times. Pennsylvanian, Permian, and Triassic thicknesses also seem to be mildly influenced by relatively negative movements in this area.

Other northeast-striking thickness trends in several stratigraphic units are apparent in the Sweetgrass arch area, where they seem to coincide with known present-day subsurface faults. Northeast-striking structural trends apparently also control the thickness of Upper Cretaceous and Paleocene strata in the Crazy Mountains basin.

In general, Triassic, Permian, Pennsylvanian, and Mississippian formations successively underlie Jurassic beds from south to north, a relationship that has been explained by southward tilt and beveling during pre-Jurassic erosion. Irregularities in the truncational pattern and general thinning of each formation beneath the next younger unit indicate that much of the northward pinch-out is related to depositional thinning on which southward tilt was superimposed. During deposition of the marine Jurassic several large "islands" remained above for part or all of that interval.

Late in Jurassic time the western seaway along which earlier seas had transgressed the region was destroyed by increasing tectonism in the area west of Montana, and a flood of débris was carried eastward to form the non-marine Morrison Formation. The basal conglomerate of the Kootenai Formation (Lower Cretaceous) indicates a particularly strong uplift in areas that could not have been far west of Montana. When the seas returned to this region, they came from the north and south and spread westward, inundating western Montana.

In the eastern part of the area, Cretaceous and Paleocene rocks are generally separable into rock and time-rock units; however, on the west the corresponding sequence is almost entirely non-marine, sparsely fossiliferous, and exceedingly diverse in lithologic character.

Four major westward advances of the sea punctuated Cretaceous deposition in an increasingly unstable tectonic setting. Locally, volcanic debris is very abundant in the Colorado Group, and strong increase in thickness westward attests to further encroachment of geosynclinal downwarping onto the cratonic margin.

Laramide orogeny began in the Montana area coincident with deposition of the Eagle-Claggett and correlative units. Local areas of strong uplift, erosion, and volcanism, and the large influx of andesitic volcanic débris in these stratigraphic units, are evidence of the initial stages of orogeny. Accumulation of very thick volcanic sequences in at least two separate fields during Judith River time attests to increasing intensity of orogenic processes. Strong deformation and erosion, followed by deposition of coarse erosional products, and volcanism in the southwestern and central parts of the area, intrusion of granitic plutons in the west-central part of the area, and thick accumulation of coarse gravels in the Crazy Mountains basin, all during Lancian and Paleocene time, coincide with the culmination of orogenic activity. Some intense folding and thrusting post-date those events just mentioned, but it is reasonably certain that Laramide compressional deformation had ceased before middle Eocene time in western Montana.

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CORRELATION OF THE CRETACEOUS FORMATIONS OF THE WESTERN INTERIOR OF THE UNITED STATES

BY WILLIAM A. COBBAN AND JOHN B. REESIDE, JR.

CONTENTS

INTRODUCTION

This is Number 10b of a series of correlation charts of North American sedimentary formations prepared by the Committee on Stratigraphy of the National Research Council (Dunbar, 1942).

The compilers of this chart have attempted to show, as nearly completely as is reasonably possible, the present state of classification and nomenclature of the Cretaceous formations in the Western Interior of the United States, chiefly in Arizona, New Mexico, Utah, Colorado, Kansas, Wyoming, Nebraska, Iowa, Montana, the Dakotas, and Minnesota. The generalized map (Fig. 1), after Stose (1946), indicates the major areas of outcrop in the region. The index map (Fig. 2) shows by number the general location of each area represented by a column of the chart (Pl. 1). Columns are given in Plate 1 for 128 areas, arranged by States, and, within each State, from south to north and from west to east. Each column includes the stratigraphic units recognized in the area.

Some 315 stratigraphic names, of various ranks, are noted in the chart, and an index of them referred to column numbers is given at the end of the paper. Some of the names used in earlier publications have long since been displaced and are not considered here. They may be found in Wilmarth's *Lexicon of geologic names* (1938). In some columns variant parallel nomenclatures are shown. Probably some of the later names have been overlooked, but the compilers doubt that many such would be of major importance. In the index and in the chart the source area of the name (typical occurrence) of a stratigraphic unit is indicated by an asterisk (*). Chronologic relations are indicated by horizontal position. Hiatuses are indicated by vertical lining; lack of knowledge, through nonexposure or other cause, is indicated by diagonal lining. Numbers within the columns of the chart refer to annotations given here. The chief sources for the data given are shown by reference numbers at the bottom of each column. (*See* References Cited). Abbreviations used in the chart are as follows:

bent.	bentonite
chk.	chalk
chy.	chalky
cong., congl.	conglomerate
f., fm., form.	formation
forms.	formations

gr.	group
ls.	limestone
m., mem., memb.	member
pt.	part

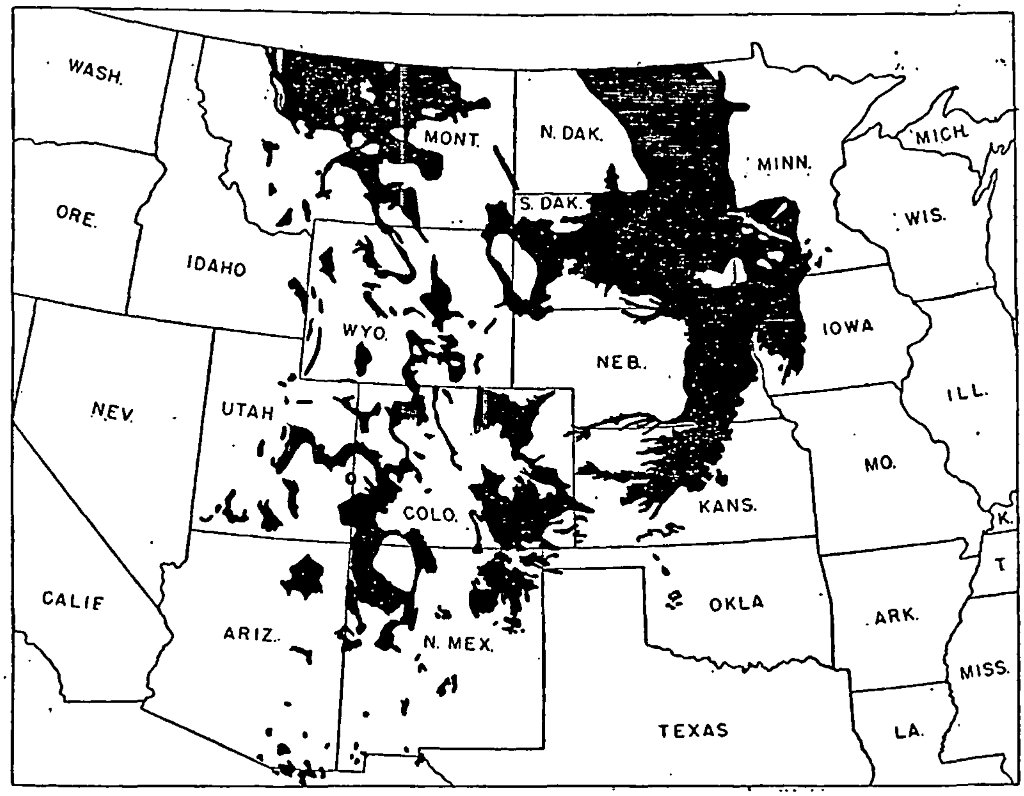

FIGURE 1.—GENERALIZED MAP OF OUTCROP AREAS OF CRETACEOUS SEDIMENTARY ROCKS IN THE WESTERN INTERIOR OF THE UNITED STATES

s., ss., sand.	sandstone
sdy.	sandy
sh.	shale
t., ton., tong.	tongue
up.	upper
z.	zone

The compilers have visited many of the areas considered and have found the first-hand acquaintance with them very useful in examining the voluminous literature of the region. The accumulated fossil collections of the U. S. Geological Survey and the U. S. National Museum have also provided much useful local information. In addition to these data, many associates, by discussions in the field and in the office and by written communications, have supplied unpublished data. It has not been possible to acknowledge individually all such information, and the compilers here express their obligation to their colleagues for this assistance. Special credit is due T. W. Stanton for information used in Column 10, W. W. Rubey for Columns 65 and 66, and R. K. Hose for Column 78.

BOUNDARIES AND MAJOR DIVISIONS OF THE CRETACEOUS

Muller and Schenck in 1943 discussed the Cretaceous system of the World at some length and provided an extensive bibliography of literature pertinent to the history of the term, the subdivisions, and other aspects of the unit. The present notes deal only with more local aspects of some of these matters.

The lower boundary of the Cretaceous system is placed very precisely where marine strata assigned by general agreement to the earliest part of the Berriasian stage rest upon marine strata similarly assigned to the latest part of the Tithonian stage, as in the western Alps. In many regions, however, no such precision is possible, for some of the beds may be nonmarine or unfossiliferous or otherwise places either an arbitrary spearation has to be made or an interval left unassigned.

The upper boundary of the Cretaceous system is much less securely established than

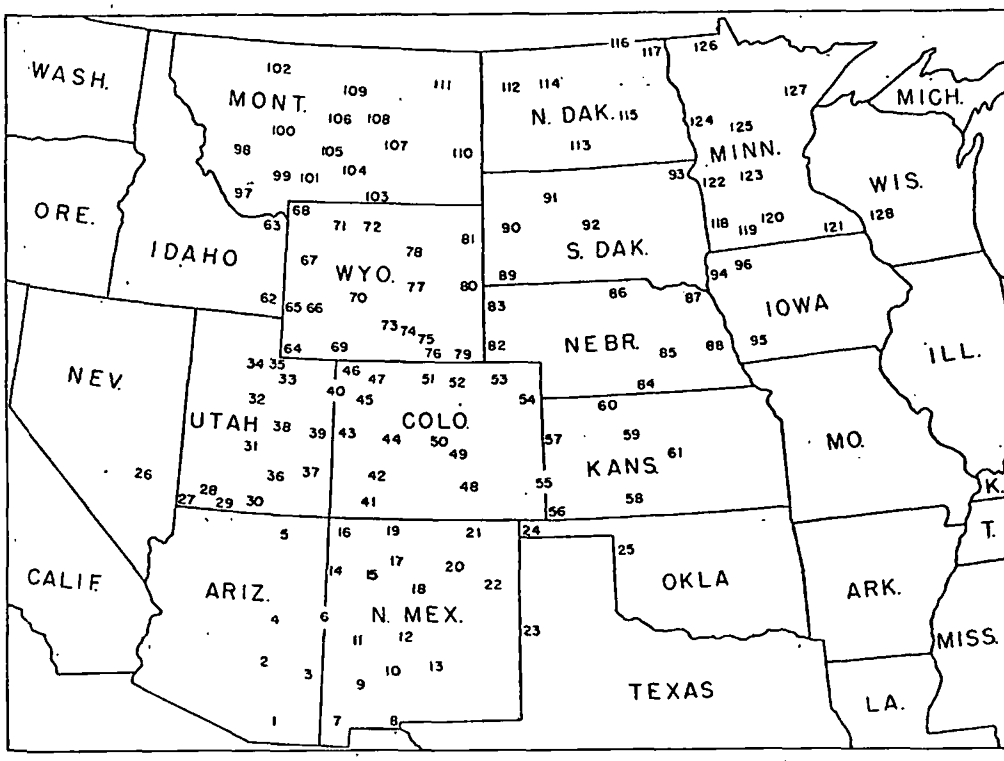

FIGURE 2.—INDEX MAP SHOWING AREAS REPRESENTED BY NUMBERED COLUMNS OF PLATE 1 (CHART 10B)

difficultly assignable, and opinions may differ for each region concerning the position of the boundary. In the Western Interior of the United States the establishment of the boundary between the Jurassic and the Cretaceous systems was long controversial (Baker and others, 1906, p. 58–63), primarily because of a vigorous disagreement as to the age of the Morrison formation. There is now fairly general agreement that the Morrison is Jurassic and that the next overlying beds are Cretaceous. At many places there is little doubt where a boundary is to be drawn. At many other places, however, a fairly uniform sequence of deposits cannot be satisfactorily dated or can be dated only as Jurassic below and Cretaceous above, with no indisputable plane of separation between them; in these

the lower boundary. Customarily the Danian stage is assigned the highest position in the Cretaceous, but opinions differ as to what beds are to be correlated with the typical Danian, and whether the typical Danian is really Cretaceous. For the Western Interior the compilers have arbitrarily included the Danian in the Cretaceous and have placed it at the level of the *Triceratops*-bearing beds. These beds, like the Morrison formation, were the subject of a long controversy. There seems now to be general acceptance of the thesis that the overlying beds, in North Dakota and South Dakota containing the marine Cannonball fauna (Stanton, 1920; Fox, 1942) and elsewhere containing primitive mammals and no dinosaurs, are to be assigned to the Paleocene. In practice the criteria may be locally somewhat difficult to apply, and in some regions there are sedimentary units that, in whole or in part, cannot be assigned with assurance.

Within the Cretaceous, the most widely adopted practice is to divide the system into two series, Lower and Upper (Spath, 1941). In Europe the boundary between the two series is generally placed at the boundary between the Albian and Cenomanian stages. The most common departures from this custom are the usage of many British geologists who put the British Gault (middle and upper Albian) in the Upper Cretaceous (as, for example, Arkell, 1947, p. 2) and the usage of some French geologists who divide the Cretaceous into three parts and recognize Lower, Middle, and Upper series (as, for example, in Émile Haug's *Traité de Géologie*, in which work the Eocretaceous group includes the Valanginian, Hauterivian, Barremian, and Aptian; the Mesocretaceous includes the Albian, Cenomanian, and Turonian; and the Neocretaceous includes the Coniacian, Santonian, Campanian, and Maestrichtian). The compilers believe that, for the Western Interior of the United States, the more usual practice of recognizing two series should be adopted and we should attempt to identify the boundary between the equivalents of the Albian and Cenomanian stages.

Historical Background of Classification Used

C. A. White (1891) has sketched the history of the earlier exploration and interpretation of the Cretaceous rocks of the Western Interior as part of his general account of the Cretaceous system in North America. Much detail concerning the nomenclature up to the end of 1936 is given by Wilmarth (1938). No inclusive discussion of the American Cretaceous has been published since that work.

The earliest published records of the Cretaceous in the Western Interior, dating back to the first decade of the nineteenth century, are primarily paleontologic and are little concerned with stratigraphic nomenclature. It was not until 1856 that F. B. Meek and F. V. Hayden, as a result of their expedition to the Missouri Valley for James Hall, proposed a general classification as follows:

"Tertiary.
Cretaceous system.
5. Gray and yellowish arenaceous clays containing great numbers of marine mollusca with a few land plants. 100 to 150 feet.
4. Plastic clays with numerous marine mollusca. About 350 feet.
3. Grayish and yellowish calcareous marl, containing *Ostrea congesta*, fish scales, etc. 100 to 150 feet...
2. Grayish and lead colored clays having few fossils. 80 feet.
1. Sandstones and clays not positively known to belong to the Cretaceous system. 90 feet.
Limestones of upper coal measures at Council Bluffs.

The numbers for the stratigraphic divisions were used until 1861, when Meek and Hayden substituted for them a series of geographic terms and gave an extended discussion and a table that may be quoted in abbreviated form as follows:

"Upper series
Fox Hills beds. Formation No. 5 — 500 feet
Gray, ferruginous and yellowish sandstone and arenaceous clays, . . .
Fort Pierre group. Formation No. 4. — 700 feet
Dark gray and bluish plastic clays, . . .
Dark bed of very fine unctuous clay, . . . Local; filling depressions in the bed below.
Lower series
Niobrara division. Formation No. 3. — 200 feet
Lead-gray calcareous marl, weathering to a yellowish or whitish chalky appearance above. . . . Passing down into light, yellowish and whitish limestone. . . .
Fort Benton group. Formation No. 2. — 800 feet
Dark gray laminated clays, sometimes alternating near the upper part with seams and layers of soft gray and light-colored limestone. . . .
Dakota group. Formation No. 1. — 400 feet
Yellowish, reddish, and occasionally white sandstone, with, at places, alternations of various colored clays and beds and seams of impure lignite. . . .

Meek and Hayden considered their "Lower series" equivalent to the "Lower or Gray Chalk (and Upper Greensand) of British geologists (*Turonien* and *Cenomanien?* of D'Orbigny)," and their "Upper series" equivalent to the "Upper or White Chalk and Maestricht beds (*Senonien* of D'Orbigny)." With little modification the Meek and Hayden section is still the basic framework of a standard reference section for the Western Interior.

The nonmarine rocks immediately overlying the Fox Hills sandstone, considered Tertiary by Meek and Hayden, were the subject of a long controversy that only in recent years seems to have reached a generally acceptable solution. The nonmarine beds are considered now to be in part Tertiary and in part Cretaceous, the boundary between them and the names applied being chosen on the basis of local features.

As information accumulated over the years, many names, dictated by local development of lithologic facies, have been applied to subordinate divisions of the Cretaceous. Meek and Hayden's "Lower series," modified by the exclusion of the "Dakota group," became in 1878 the Colorado group (White, 1878, p. 21, 22, 30), and their "Upper series" became in 1888 the Montana group (Eldridge, 1888, p. 3). Both these names have had wide application and are still very useful inclusive terms. In the first studies of some areas, local names were applied that proved to be less serviceable than names originally applied elsewhere, and the local names have passed out of use in favor of the other names. The net results, for nomenclature and correlation, of nearly a century of geologic study since the beginning of the Meek and Hayden work constitute the classification shown in Plate 1.

Standard Reference Sequence

A standard reference sequence for the Western Interior is shown near the left margin of Plate 1.

As indicated in Historical Background of Classification Used, the first sequence of lithologic units described and named was that for the Missouri Valley. As it is an entirely marine sequence, it has become the basis of a convenient standard of reference. Continued study of the Cretaceous deposits has naturally added much detail and has dictated the subdivision of Meek and Hayden's units and the addition of certain units to the standard.

In their section Meek and Hayden described their "Fort Pierre group" as filling depressions in the top of their "Niobrara division," implying a discontinuity between their "Nos. 3 and 4." It has become evident that the hiatus represented by the discontinuity was filled farther west by the Telegraph Creek and Eagle formations, and these units have been added to the standard sequence.

Meek and Hayden's original "Fort Benton group" was named for exposures in Montana supposed to be equivalent to "No. 2" of the lower Missouri Valley. Actually these exposures include both "No. 2" and "No. 3" of the lower valley. Usage has, however, effectively restricted the name Benton, as Meek and Hayden intended, to "No. 2." Gilbert in 1896 (p. 564) found it convenient in eastern Colorado to divide the Benton group into three formations—the Graneros shale below, the Greenhorn limestone in the middle, and the Carlile shale above. These names have been widely used over the Great Plains region, but it seems desirable now to modify the scope of the Greenhorn from that of Gilbert's definition and to replace the Graneros in the standard reference sequence by the less equivocal Belle Fourche shale.

In the western Black Hills the Belle Fourche shale is underlain by the Mowry shale, the Newcastle sandstone, the Skull Creek shale, and the Fall River sandstone. The recent recognition by the compilers (1951) of the ammonite genera *Gastroplites* and *Neogastroplites* in the Mowry shale shows that this formation is very late Early Cretaceous. The Skull Creek shale contains a marine fauna and appears to be equivalent to the Purgatoire formation of Colorado and the Kiowa shale of Kansas. As these or equivalent units are widespread, it has seemed appropriate to include them in the standard sequence.

For the still earlier part of the sequence, no unit except the Gannett group of southeastern Idaho and the adjacent part of Wyoming seems to cover the interval. The two limestones, the Peterson and Draney, in the middle part of the group contain a fresh-water fauna like the faunas of the Cloverly and Kootenai formations, with the Ephraim conglomerate below and an unnamed red shale above. With some hesitation the compilers suggest this group as part of the reference sequence, in spite of its relative remoteness from the remainder of the reference sequence.

Suggested Zonal Indices and Other Fossils

The compilers present, near the left margin of Plate 1, a column of some 30 faunal names, which are suggested as zonal indices, and also a diagram indicating the ranges of certain important species of invertebrates, chiefly mollusks. The ammonoids, as in other regions, are the most useful forms, particularly the scaphites and the baculites, both of which are found in abundance and variety, as well as in many kinds of sediment. Among the pelecypods the species of *Inoceramus* are abundant and varied. As parts of the Cretaceous sequence are nonmarine, especially toward the west, some of the nonmarine species are useful markers.

For reasons not well understood, the corals, the echinoderms, the brachiopods, the bryozoans, and the crustaceans are relatively rare and of little value for correlation. Some of the molluscan groups are likewise relatively rare, such as the rudistids and the belemnoids.

The compilers believe that certain groups of fossil organisms have not yet been worked out in the region to the point where they are widely useful as close indices, and no attempt has been made to include them in the palentologic part of the chart. Among these are the marine ostracodes, the foraminifers, the plants, and the vertebrates. These organisms, when adequately studied, will undoubtedly be as useful as any others.

The following discussion considers the suggested zones in order from bottom to top and offers notes on some of the associated fossils and on the geographic distribution of the zones.

UNDETERMINED ZONE: The lowest part of the Cretaceous sequence in the Western Interior is apparently represented in the Ephraim conglomerate of the Gannett group of eastern Idaho and adjacent parts of Wyoming. Whether the lower part of the Ephraim includes Jurassic deposits is not determined. No satisfactory fossils have been found in this interval, and no zonal indicators are suggested. Over large areas, especially in the Great Plains, this interval is probably not represented by sediments.

ZONE OF *Protelliptio douglassi* (STANTON): The interval of the Peterson and Draney limestones and their equivalents, such as parts of the Cloverly formation and of the Kootenai formation (of Montana), is marked by *Protelliptio douglassi* (Stanton) (1903, p. 195). It is associated with *Unio farri* Stanton (1903, p. 194), *Stantonogyra silberlingi* (Stanton) (1903, p. 198), *Campeloma harlowtonensis* Stanton (1903, p. 196), and *Quadrula natosini* (McLearn) (1929, p. 73). Peck (1941, 1951) reports nonmarine ostracodes from this zone: *Pseudocypridina inornata* (Peck), *Cypridea anomala* Peck, *C. compta* Peck, and *C. wyomingensis* Jones; and charophyte oogonia: *Atopochara trivolvis* Peck and *Clavator harrisi* Peck. This nonmarine fauna is known in western Colorado, across Wyoming and Montana, and at an isolated locality in Nevada.

UNDETERMINED ZONE: A time interval in the later Early Cretaceous, immediately before deposition of the Skull Creek shale and its equivalents, is probably only in part represented by sediments in the Western Interior. These sediments have not furnished fossils that would seem useful as zonal indicators, and none is suggested.

ZONES OF *Oxytropidoceras* STIELER AND OF *Inoceramus comancheanus* CRAGIN: The Skull Creek shale and its equivalents are marked by *Inoceramus comancheanus* Cragin (Reeside, 1923a, p. 202). It is associated with *Inoceramus bellvuensis* Reeside (1923a, p. 203). In the Kiowa formation of Kansas a large fauna, including the ammonite genus *Oxytropidoceras* Stieler, is present in this zone (Twenhofel, 1924). The nonmarine Bear River fauna is represented in the western marginal deposits of this interval, including such species as *Unio bellaplicatus* Meek (White, 1895, p. 34), *Ursirivus pyriformis* (Meek) [= *Corbula pyriformis* Meek (White, 1895, p. 38)], *Pyrgulifera humerosa* Meek (White, 1895, p. 55), and *Campeloma macrospira* Meek (White, 1895, p. 60). Peck (1951) reports in this zone the nonmarine ostracodes *Pseudocypridina laevicula* Peck and *Cypridea skeeteri* Peck. The marine facies is especially well shown in Kansas, but the fauna can be followed with progressive restriction into the Purgatoire formation of eastern Colorado, the Skull Creek shale of the Black Hills, and the basal part of the Colorado shale of Montana.

ZONE OF *Gastroplites* MCLEARN: The lower part of the Mowry shale and its equivalents are marked by the ammonite genus *Gastroplites* McLearn (1933, p. 14). The zone may also include the equivalents of the Newcastle sandstone, but the diagnostic fossils have not been found in them. The zone contains the lower part of the ranges of *Metengonoceras* Hyatt (1903, p. 179), *Ostrea anomioides* Meek (Stanton, 1893, p. 55), *Nemocardium* aff. *N. kansasense* (Meek) (1876, p. 170), and *Bicorbula dubiosa* (White) (1879b, p. 249). The nonmarine Bear River formation occupies the interval immediately below the *Gastroplites* zone, but its fauna in part reappears in the marginal facies of the Aspen formation, and the upper part of the ranges of some of the nonmarine species is shown on this chart as extending into the lower part of the *Gastroplites* zone.

ZONE OF *Neogastroplites* MCLEARN: The upper part of the Mowry shale and its equivalents contain ammonites of the genus *Neogastroplites* McLearn (1933, p. 21). It is associated with *Inoceramus nahwisi* McLearn (1931, p. 7). The zone contains the upper part of the ranges of *Ostrea anomioides* Meek, *Nemocardium* aff. *N. kansasense* (Meek), *Bicorbula dubiosa* (White), and *Metengonoceras* Hyatt. This zone is recorded particularly from Wyoming and Montana.

ZONE OF *Calycoceras* HYATT: In eastern Colorado the lower part of the Graneros shale, in northwestern Colorado the upper part of the Dakota sandstone, and in central Wyoming part of the Frontier formation have yielded the characteristic Cenomanian genus *Calycoceras* Hyatt [= *Metacalycoceras* Adkins, 1928, p. 241)]. These beds are equivalent to the lower part of Belle Fourche shale; and it is believed that this interval, though commonly barren, will elsewhere furnish diagnostic species. It is not known whether *Brachydontes multilinigera* (Meek) Stanton, (1893, p. 86) ranges below this zone, although similar forms are known at lower levels.

ZONE OF *Acanthoceras? amphibolum* MORROW: The middle zone in the Belle Fourche shale and its equivalents is marked by *Acanthoceras? amphibolum* Morrow (1935, p. 470). The zone includes the lowest part of the range of *Turritella whitei* Stanton (1893, p. 130) and is well developed in Kansas, eastern Colorado, Wyoming, and Montana.

ZONE OF *Acanthoceras?* SP. A: The uppermost part of the Belle Fourche shale and its equivalents are marked by a readily recognizable ammonite that at present has no formal name, but for convenience of reference is here called *Acanthoceras?* sp. A. This zone includes the lowest part of the ranges of *Ostrea soleniscus* Meek (Stanton, 1893, p. 56) and *Cardium pauperculum* Meek (Stanton, 1893, p. 99). This zone is well developed in Wyoming and Montana.

ZONE OF *Dunveganoceras pondi* HAAS: In central Wyoming rocks equivalent to the lowest member of the Greenhorn formation, the Lincoln limestone member, are marked by *Dunveganoceras pondi* Haas (1949, p. 22). It is associated with *Mantelliceras canitaurinum* Haas (1949, p. 9), *Metoicoceras praecox* Haas (1949, p. 15), and *Inoceramus prefragilis* Stephenson (1952, p. 64). The zone includes the lower part of the ranges of *Exogyra columbella* Meek (Stanton, 1893, p. 63) and *Pseudomelania hendricksoni* Henderson (1934, p. 262), and, farther south, of *Exogyra olisiponensis* Sharpe (Reeside, 1929b, p. 268), *Ostrea prudentia* White (Stanton, 1893, p. 54), and *Gryphaea newberryi* Stanton (1893, p. 60).

ZONE OF *Dunveganoceras* aff. *D. albertense* (WARREN): In central Montana and northern Wyoming rocks equivalent to the second member of the Greenhorn formation, the Hartland shale member, are marked by an unnamed species of *Dunveganoceras* closely related to *D. albertense* (Warren) (1940, p. 149). The zone includes the higher part of the ranges of *Exogyra columbella* Meek and *Pseudomelania hendricksoni* Henderson and, farther south, of *Exogyra olisiponensis* Sharpe, *Ostrea prudentia* White, and *Gryphaea newberryi* Stanton.

ZONE OF *Sciponoceras gracile* (SHUMARD): The third member of the Greenhorn formation, the Jetmore chalk, and its equivalents are marked by *Sciponoceras gracile* (Shumard) [= *Baculites gracilis* Shumard (Stanton, 1893, p. 166)]. It is associated with *Scaphites delicatulus* Warren (1930, p. 66), "*Worthoceras*" Adkins (1928, p. 218), and *Metoicoceras whitei* Hyatt (1903, p. 122). The zone includes the highest part of the range of *Inoceramus prefragilis* Stephenson and the lowest part of the ranges of *Tragodesmoceras* Spath (Morrow, 1935, p. 468), *Watinoceras* Warren (1930, p. 66) [see also *Acanthoceras? coloradoense* Henderson (1908, p. 259)], and *Neocardioceras* Spath [Adkins, 1931, p. 72. See also *Acanthoceras? kanabense* Stanton (1893, p. 181)]. *Sciponoceras* is the oldest baculitid recorded from the Western Interior. The zone is widely distributed in the Great Plains and the Colorado Plateaus.

ZONE OF *Inoceramus labiatus* SCHLOTHEIM: The uppermost member of the Greenhorn formation, the Pfeifer limestone, and its equivalents are marked by *Inoceramus labiatus* Schlotheim (Stanton, 1893, p. 77). It is associated with *Thomasites* Pervinquière (1907) and *Vascoceras* Choffat (Reeside, 1923b, p. 28). This zone includes the highest part of the ranges of *Watinoceras* Warren and *Neocardioceras* Spath and the lowest part of the range of *Inoceramus fragilis* Hall and Meek (1856, p. 388); it is very widely distributed.

ZONE OF *Collignoniceras woollgari* (MANTELL): The lowest member of the Carlile shale, the Fairport chalky shale, and its equivalents are marked by *Collignoniceras woollgari* (Mantell) [= *Prionotropis woollgari* of Meek (1876, p. 455)]. It is associated with *Scaphites larvaeformis* Meek and Hayden (Meek, 1876, p. 418). The zone includes the highest part of the range of *Tragodesmoceras* Spath and the lowest part of the ranges of *Baculites* cf. *B. besairiei* Collignon (1931, p. 37) and *Gyrodes conradi* Meek (Stanton, 1893, p. 136). This zone is widely distributed.

ZONE OF *Collignoniceras hyatti* (STANTON): The second member of the Carlile shale, the Blue Hill shale, and its equivalents are marked by *Collignoniceras hyatti* (Stanton) [= *Prionotropis hyatti* Stanton (1893, p. 176)]. It is associated with *Scaphites carlilensis* Morrow (1935, p. 466) and it includes the higher part of the range of *Inoceramus fragilis* Hall and Meek. The "*Pugnellus* sandstone" of the older literature (Stanton, 1893, p. 28) is part of this zone. This zone is widely distributed in the Great Plains and in eastern Utah.

ZONE OF *Scaphites warreni* MEEK AND HAYDEN: The lower part of the third member of the Carlile shale, the Turner sandy member, and its equivalents are marked by *Scaphites warreni* Meek and Hayden (Cobban, 1951c, p. 21). It is associated with *Prionocyclus macombi* Meek (Stanton, 1893, p. 172) and *Inoceramus dimidius* White (Stanton, 1893, p. 78). The zone includes the lower part of the ranges of *Ostrea lugubris* Conrad (Stanton, 1893, p. 58), *O. malachitensis* Stanton (1893, p. 57), and *Pholadomya coloradoensis* Stanton (1893, p. 116). This zone is known around the Black Hills, eastern Wyoming, western Colorado, eastern Utah, and northern New Mexico.

ZONE OF *Prionocyclus wyomingensis* MEEK: The middle part of the Turner member of the Carlile shale and its equivalents are marked by *Prionocyclus wyomingensis* Meek (Stanton, 1893, p. 171). It is associated with *Scaphites ferronensis* Cobban (1951c, p. 23) and *S. whitfieldi* Cobban (1951c, p. 24). The zone includes the higher part of the ranges of *Ostrea lugubris* Conrad, *O. malachitensis* Stanton, and *Pholadomya coloradoensis* Stanton, and the lower part of the range of *Inoceramus perplexus* Whitfield (1880, p. 392). This zone is widely but irregularly distributed. In New Mexico, Utah, and Colorado it is possible to divide this zone into a lower part with *Scaphites ferronensis* and an upper part with *Scaphites whitfieldi.*

ZONE OF *Scaphites nigricollensis* COBBAN: The upper part of the Turner member of the Carlile shale and its equivalents are marked by *Scaphites nigricollensis* Cobban (1951c, p. 25). It is associated with *Prionocyclus reesidei* Sidwell (1932, p. 318). The zone includes the upper part of the range of *Inoceramus perplexus* Whitfield and is widely distributed in the northern Great Plains.

ZONE OF *Scaphites corvensis* COBBAN: The uppermost member of the Carlile shale, the Sage Breaks member, and its equivalents are marked by *Scaphites corvensis* Cobban (1951c, p. 26). The zone includes the highest part of the range of *Baculites* cf. *B. besaireii* Collignon and the lowest part of the range of *Ostrea congesta* Conrad (Meek, 1876, p. 13) Near the western margin of deposition nonmarine deposits of this age contain "*Cyrena*" *carletoni* (Meek) (White, 1883b, p. 436), *Neritina bellatula* Meek (White, 1883b, p. 458), and *Physa carletoni* Meek (White, 1883b, p 43). This zone is known only in the northern Great Plains.

ZONE OF *Inoceramus deformis* MEEK: The lower member of the Niobrara formation, the Fort Hayes limestone, and its equivalents are marked by *Inoceramus deformis* Meek (Stanton, 1893, p. 85). It is associated with *Scaphites Inoceramus deformis* Meek (Stanton, 1893, p. 85). It is associated with *Scaphites impendicostatus* Cobban (1951c, p. 28), *S. preventricosus* Cobban (1951c, p. 26), *Baculites mariasensis* Cobban (1951b, p. 818), *Barroisiceras* Grossouvre (Reeside, 1932), *Inoceramus erectus*

Meek (1877, p. 145), *Veniella goniophora* Meek (1876, p. 152), *Ostrea sannionis* White (1884, p. 300), and *Cardium curtum* Meek and Hayden (Meek, 1877, p. 151). It includes the lowest part of the range of *Binneyites* Reeside (1927b, p. 4). This zone is very widely distributed. In Montana, where the rocks equivalent to the Fort Hays limestone are characterized, by *Schaphites preventricosus*, a zone of *Inoceramus deformis*, s.s., can be recognized above a zone marked by small variants of *I. deformis* and *I. erectus*.

ZONE OF *Scaphites ventricosus* MEEK AND HAYDEN: The lowest part of the equivalents of the Smoky Hill chalk member of the Niobrara formation is marked by *Scaphites ventricosus* Meek and Hayden (Meek, 1876, p. 425). It is associated with *Inoceramus umbonatus* Meek and Hayden (Meek, 1876, p. 44). This zone includes the lowest part of the ranges of *Baculites asper* Morton (Reeside, 1927a, p. 13) and *Inoceramus grandis* (Conrad) [= *Haploscapha grandis* (Conrad, 1875, p. 23)]. This zone is widespread.

ZONE OF *Scaphites depressus* REESIDE: The second zone in the equivalents of the Smoky Hill member of the Niobrara formation is marked by *Scaphites depressus* Reeside (1927b, p. 7). It is associated with *Phlycticrioceras* Spath (Reeside, 1927b, p. 2), *Texanites shoshonensis* (Meek) [= *Mortoniceras shoshonense* Meek (Reeside, 1927b, p. 9)], and *Inoceramus stantoni* Sokolow [= *I. acuteplicatus* Stanton (1899, p. 634)]. It includes the lowest part of the range of *Baculites codyensis* Reeside (1927b, p. 4). This zone is widespread.

ZONE OF *Clioscaphites vermiformis* (MEEK AND HAYDEN): The third zone in the equivalents of the Smoky Hill member of the Niobrara formation is marked by *Clioscaphites vermiformis* (Meek and Hayden) [= *Scaphites vermiformis* Meek and Hayden (Meek, 1876, p. 423)]. This zone includes the highest part of the ranges of *Binneyites* Reeside, *Inoceramus grandis* (Conrad), and *Ostrea soleniscus* Meek and the lowest part of the range of *Uintacrinus* Grinnell (1876). In the south it includes the lowest part of the ranges of *Texanites omeraensis* (Reeside) [= *Mortoniceras omeraense* Reeside (1927a, p. 38)], *Placenticeras guadalupe* (Roemer) (Reeside, 1927a, p. 36), and *Inoceramus undulatoplicatus* Roemer (1852, p. 59). This zone is widespread.

ZONE OF *Clioscaphites choteauensis* COBBAN: The fourth zone in the equivalents of the Smoky Hill member of the Niobrara formation is marked by *Clioscaphites choteauensis* Cobban (1951c, p. 38). This zone is widespread.

ZONE OF *Desmoscaphites erdmanni* COBBAN: The uppermost zone in the equivalents of the Smoky Hill member of the Niobrara formation is marked by *Desmoscaphites erdmanni* Cobban (1951c, p. 38). It is the highest zone in the Colorado group and includes the highest part of the ranges of *Baculites codyensis* Reeside, *Ostrea congesta* Conrad, *Cardium pauperculum* Meek, *Turritella whitei* Stanton, and *Gyrodes conradi* Meek. It includes the lowest part of the ranges of *Baculites thomi* Reeside (1927b, p. 13) and *Inoceramus lundbreckensis* McLearn (1929, p. 77). In the south it includes the highest part of the ranges of *Texanites omeraensis* (Reeside), *Placenticeras guadalupe* (Roemer), and *Inoceramus undulatoplicatus* Roemer. This zone is best known in Montana but it is probably widespread.

ZONE OF *Desmoscaphites bassleri* REESIDE: The Telegraph Creek formation and its equivalents are marked by *Desmoscaphites bassleri* Reeside (1927a, p. 16). The zone contains the only recorded occurrences of the crinoid *Marsupites* (Thom, 1935, p. 55) in the Western Interior; it includes the highest part of the ranges of *Baculites thomi* Reeside and *Uintacrinus* Grinnell, and the lowest part of the ranges of *Baculites aquilaensis* Reeside (1927a, p. 12), *B. haresi* Reeside (1927a, p. 10), *Placenticeras planum* Hyatt (Reeside, 1927a, p. 31), *P. meeki* Boehm [= *P. whitfieldi* Hyatt (1903, p. 221)], *Ethmocardium* White (1880), and *Cymella montanensis* (Henderson) [= *Liopistha undata* (Meek and Hayden) (Meek, 1876, p. 236)]. Very rarely *Scaphites hippocrepis* (DeKay) (Reeside, 1927a, p. 22) is found in this zone, mostly in the upper part. No trace of this zone has been found east of the Black Hills, but it is widespread to the west.

ZONE OF *Scaphites hippocrepis* (DEKAY): The Eagle sandstone and its equivalents are marked by *Scaphites hippocrepis* (DeKay) and its varieties. Associated with it are *Scaphites aquilaensis* Reeside (1927a, p. 25) and *Haresiceras* Reeside (1927a, p. 17). The zone includes the highest ranges of *Baculites asper* Morton, *Placenticeras planum* Hyatt, and *Inoceramus lundbreckensis* McLearn and the lowest ranges of *Ostrea russelli* Landes (1940, p. 139) and *Inoceramus* "*barabini* Morton" of Meek (1876, p. 49). No trace of this zone has been found east of the Black Hills, but it is widespread to the west.

ZONE OF *Baculites asperiformis* MEEK: The equivalents of the Sharon Springs member of the Pierre shale are marked by *Baculites asperiformis* Meek (1876, p. 405). Associated with it is *Inoceramus pertenuis* Meek and Hayden (Meek, 1876, p. 47). This zone includes the highest ranges of *Baculites aquilaensis* Reeside, *B. haresi* Reeside, and *Ostrea russelli* Landes and the lowest ranges of *Placenticeras intercalare* (Meek) (Hyatt, 1903, p. 207) and of *Acanthoscaphites* Nowak, s. l. This zone is widespread.

ZONE OF *Baculites gregoryensis* COBBAN: The Gregory and Crow Creek members of the Pierre shale and their equivalents are marked by *Baculites gregoryensis* Cobban (1951b, p. 820). Associated with it are *Pachydiscus complexus* (Hall and Meek) (Meek, 1876, p. 447), *Inoceramus oblongus* Meek (White, 1879a, p. 285), and *I. sublaevis* Hall and Meek, (1856, p. 386). The zone includes the lower part of the ranges of *Solenoceras* Conrad [= *Ptychoceras* of Meek (1876, p. 410)], *Didymoceras* Hyatt (1894, p. 573), *Emperoceras* Hyatt (1894, p. 575), and *Ostrea glabra* Meek and Hayden (Meek, 1876, p. 509), and, among the nonmarine species, *Goniobasis? subtortuosa* Meek and Hayden (Meek, 1876, p. 569), *G. judithensis* Stanton (Stanton *et al.*, 1905, p. 117), and *Brachydontes laticostata* White (1883b, p. 423). This zone is widespread; it passes westward into nonmarine units such as the Judith River formation.

ZONE OF *Baculites compressus* SAY: The DeGrey, Verendrye, and Virgin Creek members of the Pierre shale and their equivalents are marked by *Baculites compressus* Say, s. l. (Meek, 1876, p. 400). Associated with it are *Acanthoscaphites nodosus* (Owen), s. l. (1852, p. 581), *Rhaeboceras* Meek (1876, p. 462), and *Exiteloceras* Hyatt [= *Ancyloceras* of Whitfield (1880, p. 452)]. In the upper part of this zone are found *Acanthoscaphites brevis* (Meek) (1876, p. 426) and *A. quadrangularis* (Meek and Hayden) (Meek, 1876, p 428). In the lower part is found *Pholadomya hodgei* (Meek) (Meek, 1876, p. 219) and *Baculites pseudovatus* Elias (1933, p. 304). The zone includes the higher part of the ranges of *Placenticeras meeki* Boehm, *P. intercalare* (Meek), *Solenoceras* Conrad, *Emperoceras* Hyatt, *Didymoceras* Hyatt, *Inoceramus* "*barabini* Morton" of Meek, *Cymella montanensis* (Henderson), and the nonmarine *Goniobasis judithensis* Stanton. The zone includes the lowest part of the ranges of *Inoceramus sagensis* Owen (1852, p. 582) and, near the top, of *Veniella humilis* (Meek and Hayden) (Meek, 1876, p. 155); it also contains the only recorded occurrence in Western Interior of *Exogyra costata* Say (Reeside, 1929b, p. 271). This zone is widespread.

ZONE OF *Baculites baculus* MEEK AND HAYDEN: The lowest part of the Mobridge member of the Pierre shale is marked by *Baculites baculus* Meek and Hayden (Meek, 1876, p. 397). It may also contain *Acanthoscaphites plenus* (Meek and Hayden) (Meek, 1876, p. 429). This zone includes the highest part of the known range of the genus *Ethmocardium* White and the lowest part of the ranges of *Inoceramus fibrosus* (Meek and Hayden) [= *Pteria fibrosa* (Meek, 1876, p. 36)] and "*Belemnitella bulbosa* Meek and Hayden" (Meek, 1876, p. 504). This zone is widespread in the Great Plains.

ZONE OF *Baculites grandis* HALL AND MEEK: Most of the Mobridge member of the Pierre shale is marked by *Baculites grandis* Hall and Meek (1856, p. 402). The zone includes the higher part of the ranges of *Inoceramus fibrosus* (Meek and Hayden) and *Inoceramus sagensis* Owen and to the west, where sandstones appear, the lowest occurrences of *Sphenodiscus* Meek (Hyatt, 1903, p. 58). This zone is widespread.

UNDETERMINED ZONE: The Elk Butte member of the Pierre shale in the lower Missouri Valley is nearly barren, and its equivalents westward have not been determined, except that they must be part of the nonmarine sequence over a large area. No zonal fossil is now suggested.

ZONE OF *Discoscaphites nicolletii* (MORTON): The lower part of the Trail City member of the Fox Hills sandstone is marked by *Discoscaphites nicolletii* (Morton) (1842). It is associated with *D. abyssinus* (Morton) (1842). This zone passes westward into nonmarine beds that contain the highest occurrence of *Goniobasis? sublortuosa* (Meek and Hayden). This zone is present chiefly in the Great Plains.

ZONE OF *Discoscaphites nebrascensis* (OWEN): The two upper members of the Fox Hills sandstone have not yielded distinctive marine fossils, but the Timber Lake member and the upper part of the Trail City member are marked by *Discoscaphites nebrascensis* (Owen) (1852, p. 577) [= *D. conradi* (Meek, not Morton) (Meek, 1876, p. 430)]. Associated with it are *D. cheyennensis* (Owen) (1852, p. 578), *D. mandanensis* (Morton) (Meek, 1876, p. 443), and a small unnamed *Baculites*, the latest species of the genus in the region. This zone includes the highest part of the ranges of *Sphenodiscus* Meek, "*Belemnitella bulbosa* Meek and Hayden," and *Veniella humilis* (Meek and Hayden). The zone is known only in the Great Plains and passes westward into nonmarine beds.

ZONE OF *Triceratops* MARSH: Dinosaurs of the genus *Triceratops* Marsh (Lull, 1933) are widely reported from the latest Cretaceous deposits, exemplified by the Hell Creek formation, the Lance formation, and the Laramie formation and part of the Denver formation, so much so that it has been common usage to speak of the "*Triceratops* beds" as an inclusive term for the deposits. These nonmarine strata also contain a flora, various reptiles, a few mammals, and such fresh-water mollusks as *Viviparus trochiformis* (Meek and Hayden) (Meek, 1876, p. 580), *Tulotoma thompsoni* White (1883a, p. 100), *Proparreysia holmesiana* (White) (1883a, p. 67), and *P. letsoni* (Whitfield) (1906), and the brackish-water forms *Ostrea glabra* Meek and Hayden and *Brachydontes laticostata* White. These mollusks are useful guides in the Great Plains but range down into lower levels in the more westerly areas where the nonmarine deposits begin earlier.

OTHER ZONES: There are indications of a number of additional zones or subzones, which are either too poorly known or known from too few localities to be included among the zonal indices. Future work may reveal that many of these are good zones of widespread distribution.

In the Frontier formation in central and south-central Wyoming, a form of *Dunveganoceras* is known that differs from *D. pondi* Haas in its flexuous costae. It is associated with a *Metoicoceras* that is closely related to *M. praecox* Haas. Whether this fauna is younger or older than the zone of *D. pondi* remains to be determined.

Recently Haas (1951) described a new ammonite—*Dunveganoceras conditum*—from the Frontier formation of central Wyoming. This form is more closely related to the undescribed species in the zone of *Dunveganoceras* aff. *D. albertense* Warren than to *D. pondi*. In all probability it marks a zone slightly older than the zone of *D.* aff. *D. albertense*.

In Colorado, Utah, and New Mexico, *Scaphites ferronensis* Cobban (1951c, p. 23), an ammonite intermediate between *S. warreni* Meek and Hayden and *S. whitfieldi* Cobban, seems to be confined to the lower part of the *Prionocyclus wyomingensis* zone.

In south-central Wyoming and northwestern Montana a fauna that seems to be post-Sage Breaks and pre-Fort Hays is characterized by small variants of both *Inoceramus deformis* Meek and *I. erectus* Meek. Associated fossils include *Scaphites preventricosus* Cobban, which is more common in the overlying beds containing *Inoceramus deformis*, s. s. However, certain other associated fossils—*Scaphites mariasensis* Cobban (1951c, p. 28) and *Scaphites preventricosus* var. *artilobus* Cobban (1951c, p. 27)—have not been found in the typical *I. deformis* beds. In general the fauna appears more closely related to that of the early Niobrara than to that of the late Carlile.

In the Wind River Basin of Wyoming an undescribed scaphite fauna has been discovered at the top of the Mesaverde formation. The fauna includes *Baculites haresi* Reeside and several common pelecypods that range through rocks equivalent in age to the Eagle sandstone and Claggett shale of Montana. Inasmuch as the scaphites just below the Mesaverde formation belong to the *Scaphites hippocrepis* zone, the new species may be of Claggett age although scaphite species known to be of Claggett age are absent.

Work in progress (January, 1952) indicates that the zone of *Baculites compressus* Say, s. l., can be divided into five subzones. The lowest is marked by *Baculites pseudovatus* Elias (1933, p.

304), the second has as its guide *B. compressus* var. *corrugatus* Elias (1933, p. 303), the third has *Baculites compressus* Say, s.s., the fourth has *B. compressus* var. *reesidei* Elias (1933, p. 302), and the fifth and highest is marked by an unnamed form with stout cross section and smooth venter. Each subzone seems to have, in addition, a diagnostic scaphite.

Broad Faunal Relations

It was long ago determined that the Cretaceous rocks of the Western Interior of the United States are part of the deposits formed in a long, wide belt stretching from eastern Mexico into the Arctic region. In the United States these deposits extend from eastern Arizona, New Mexico, and western Texas northward across the eastern part of the Plateau area, the Rocky Mountain area, and the Great Plains to Montana, North Dakota, and Minnesota. At times a seaway connected the Cretaceous Arctic Ocean and the Cretaceous Gulf of Mexico. The history of this region, as shown by the successive faunas and the lithologic character of the enclosing rocks, is far from simple.

In the Western Interior no assured sedimentary record is known of that part of Early Cretaceous time that corresponds to the Neocomian stage of the European sequence, though the nonmarine Ephraim conglomerate of eastern Idaho and adjacent parts of Wyoming probably represents at least part of it. No pertinent paleontologic evidence is known to the compilers. To the south, in Mexico, marine Neocomian deposits are recognized (Imlay, 1944), and in Canada, on the basis of the flora, Canadian geologists assign the nonmarine Kootenay formation to the Neocomian (Bell, 1946).

The succeeding interval in the Early Cretaceous, corresponding to the Aptian stage of the European sequence, is represented in the Western Interior only by nonmarine deposits in the Peterson-Draney interval above the Ephraim conglomerate of Idaho, by the Cloverly formation of central Wyoming, by the Inyan Kara group of the Black Hills, and by the Kootenai formation of Montana. Deposits of this age are probably lacking over much of the Great Plains. The nonmarine invertebrate fauna is not known to have a close parallel in other parts of the world, and the assignment of the deposits to the Aptian is based entirely on the relationships of the flora to those of other regions (Bell, 1946; Berry, 1929). To the south, in southern Arizona, southern New Mexico, and west Texas, marine deposits of Aptian age are known in the Bisbee group (Stoyanow, 1949) and in the Trinity group (Scott, 1940). To the north, in Canada, the beds assigned to the Aptian are nonmarine. The Gething and McMurray formations in northern British Columbia and Alberta and the lower part of the Blairmore formation in southern British Columbia and Alberta contain a nonmarine fauna and a flora like those of the Kootenai formation of Montana and equivalent deposits (McLearn 1945). Apparently the interior of North America was still the site of only continental deposition during Aptian time; a southern sea invaded only the marginal fringe.

The next higher unit corresponds to the Albian stage of the European sequence and represents the latest part of the Early Cretaceous.

In the Western Interior of the United States, the early part of this interval, the early Albian, may not be represented by sediments. To the south, in southernmost Arizona (Stoyanow, 1949) and in west Texas (Scott, 1940), however, marine deposits in the Bisbee group and in the Trinity group represent the early Albian. To the north, in Canada, marine deposits of this age are found in the lower part of the Fort St. John group (McLearn, 1945) of northern British Columbia and Alberta and nonmarine deposits in part of the Blairmore formation of southern British Columbia and Alberta. The marine faunas north and south are in general unlike, though the ammonite genus *Beudanticeras* is reported in both areas. Probably at this time the boreal waters and the southern waters were still widely separated by areas of continental deposition and erosion.

In mid-Albian time marine waters widely invaded the Western Interior from the south, leaving a record in such units as the Kiowa shale of Kansas, the Purgatoire formation of eastern Colorado and New Mexico, the Skull Creek shale of the Black Hills, and the lower part of the Blackleaf member of the Colorado shale of Montana. The fauna of these formations is abundant and varied in the south (Twenhofel, 1924) and progressively scarcer and less varied northwestward (Reeside, 1923a). The nonmarine beds of the lower part of the Thermopolis shale of central Wyoming and the nonmarine Bear River formation of southern Wyoming, with its varied fauna (White, 1895), are of this age. To the south, in Texas, the upper part of the marine Fredericksburg group is of this age, and to the north, in Canada, probably part of the marine Fort St. John group (McLearn, 1945) and part of the nonmarine Blairmore formation. Whether the boreal and southern marine waters were connected is not known; if a connection existed, it probably was to the east, in the Swan River formation of Manitoba (Wickenden, 1932) and in some of the beds currently included in the Dakota group of the Great Plains.

Possibly in part contemporaneous with the southern marine invasion, but more likely in later Albian time, volcanic detritus was laid down over a vast area extending from northern Colorado to central Montana and across the entire width of Wyoming (Rubey, 1929). This material, now altered to porcellanite and bentonite, is included in the Mowry and Aspen formations, which are everywhere noted for their content of scales and bones of marine fishes. A few flattened mollusks occur here and there in the volcanic material; however, well-preserved ammonites of the genus *Gastroplites* McLearn have been found at several localities, and of the genus *Neogastroplites* McLearn at other localities (Cobban and Reeside, 1951). These ammonites provide a correlation with the middle and upper parts of the Fort St. John group and indicate strongly that during Albian time a boreal sea extended as far south as northern Colorado and covered Wyoming and Montana. The physical evidence suggests that there was either erosion or nonmarine deposition across central and southern Utah and Colorado and northern Arizona and New Mexico, and the compilers know of no evidence suggesting that this boreal sea reached eastward into much of the Great Plains. To the south, across southern Arizona and New Mexico into Texas, the later deposits of the Comanche series represent an entirely separate southern invasion of this age, with entirely different faunas. In the fauna of this time the only suggestion of a possible connection is the abundant and widespread occurrence of the ammonite genus *Metengonoceras* Hyatt in association with *Gastroplites* and *Neogastroplites*. *Metengonoceras* has been considered to to belong to a group characteristic of the southern faunas. In exposures near the Wyoming-Idaho boundary that may be equivalent to the Aspen formation, nonmarine faunas occur that are in part similar to those of the Bear River formation.

The next higher unit represents the earliest part of the Late Cretaceous and corresponds to the Cenomanian stage. Over much of their area of deposition these beds are marine deposits, though to the west and southwest they become nonmarine or are perhaps absent. The lower part of the Graneros shale in eastern Colorado, the upper part of the Dakota sandstone in western Colorado, and a middle zone of the Frontier formation in east-central Wyoming contain a fauna including the ammonite genus *Calycoceras* Hyatt. This fauna has not been recognized elsewhere in the Western Interior, though the lower part of the Belle Fourche shale is a barren interval that could appropriately contain it. To the south, the Woodbine formation of Texas contains a similar fauna (Stephenson, 1952). In the upper part of the Graneros shale are found a fauna containing *Acanthoceras? amphibolum* Morrow and another with an unnamed species of *Acanthoceras?* These are widely distributed and also have close relatives in the Woodbine formation and in the European Cenomanian. The general trend of evidence is that a wide seaway was open from the south northward possibly across Canada, and in it was deposited the part of the Cenomanian represented by these interior deposits. The succeeding beds with the ammonite genus *Dunveganoceras* seem to have a wide distribution in Canada and southward across Wyoming. The enclosing beds in the Great Plains are the lower members of the Greenhorn formation and their equivalents. The *Dunveganoceras* faunas are not known in the south, but the presence of species of *Metoicoceras* suggests a connection with the Gulf region during this part of the Cenomanian. Possibly the lower part of the Eagle Ford shale (Adkins, 1932, p. 422) would be equivalent to these late Cenomanian deposits, though faunal similarities with the Western Interior are not close. Along the southern and southwestern margins of the Western Interior the first marine deposits seem to be widely of post-Cenomanian age. The immediately preceding nonmarine deposits are mostly sandy and in Arizona, New Mexico, and Utah have commonly been called Dakota sandstone. In western Wyoming they have been included in the lower part of the Frontier formation. A well-characterized nonmarine fauna has not been found in these marginal deposits, unless some of the unnamed beds at the top of the exposures near the Wyoming-Idaho boundary in southwestern Wyoming should prove to be of this age.

The next higher unit, exemplified particularly by the upper members of the Greenhorn formation, corresponds to the lower part of the Turonian stage of the European sequence. It is widespread and is characterized by cosmopolitan faunas that imply nearly free access to the Western Interior from both north and south. In the lower parts *Sciponoceras gracile* (Shumard), *Metoicoceras* Hyatt, and *Inoceramus prefragilis* Stephenson are distinctive. In the upper parts *Inoceramus labiatus* Schlotheim and various other species are distinctive. In Canada a part of the Alberta shale (McLearn, 1937; 1945) is equivalent, and in the Gulf region the middle parts of the Eagle Ford shale contain the lower Turonian faunas (Adkins, 1932, p. 422). This unit is the earliest marine unit over much of the southern and southwestern border of the Western Interior deposits. At some places these beds are missing.

The next unit, exemplified by the Carlile shale, corresponds to the upper part of the Turonian stage of the European sequence. In the Western Interior of the United States it is divisible into a number of faunal units, which, though widely distributed and in part cosmopolitan, have in this region an irregular distribution marked by absence of some units over considerable areas. The middle part of this unit is widely characterized by the presence of sandy deposits, but the lower part is calcareous shale and locally in the Great Plains is a chalk. The ammonites *Collignoniceras* Breistoffer (*Prionotropis* Meek) and *Prionocyclus* Meek and certain of the scaphites identify the divisions of the unit. Their wide distribution in Canada (McLearn, 1937), the Western Interior, and the Gulf region implies free access from both north and south. Parts of the western marginal deposits are nonmarine and locally coal-bearing, but no well-characterized nonmarine fauna has been recorded from them.

The lowest part of the Niobrara formation and equivalents are widely characterized by *Inoceramus deformis* Meek and associated forms, such as the ammonite genus *Barroisiceras* Grossouvre and certain scaphites. The upper part of the Niobrara and equivalents are divisible into faunal units which are recognizable through the central part of the Western Interior into Canada, and which are characterized particularly by a sequence of scaphites. The eastern part of the region shows a chalk facies with a relatively restricted fauna that provides only a general correlation, and in the western marginal part the sequence includes much sandstone and contains nonmarine deposits, particularly toward the south. The upper part of the Niobrara includes the last occurrences of a number of long-ranging species, especially of the pelecypods. In the Gulf region the Austin chalk and its equivalents provide enough identical species to show that these units are undoubtedly the equivalents of the Niobrara formation, but there are striking differences, notably the absence of the abundant scaphites of the Western Interior. These differences strongly suggest a chiefly endemic source for much of the Niobrara fauna, though that fauna could have been in part boreal. There must have been fairly free communication between the Western Interior and the Gulf region, however. Some of the elements of the fauna are cosmopolitan and indicate that the Niobrara formation includes the equivalents of the Coniacian stage of the European sequence and the lower part of the Santonian stage.

The next higher unit, the Telegraph Creek formation and its equivalents, marks the first appearance of a number of species that extend up into much higher levels. This change and the disappearance of older species noted above were observed long ago by Meek and others and were in part the basis for recognizing a major dividing line at the top of the Niobrara formation, between the Colorado and Montana groups. Though the number of species that cross the boundary is larger than was originally thought, a major break is present. The Telegraph Creek formation is characterized by *Desmoscaphites bassleri* Reeside and certain associated species (Reeside, 1927a). It is widespread west of the Black Hills but is missing along the southwestern margin of the Western Interior and in the Great Plains east of the Black Hills. To the north, in Canada, its presence has been recorded. To the south it is probably represented either by the uppermost part of the Austin chalk or by a hiatus, for little suggestion of its presence is afforded by the published record (Stephenson, 1937). This unit corresponds to the upper part of the Santonian stage. Possibly the Telegraph Creek fauna was largely endemic, and communication with boreal and southern waters was restricted, though the deposits contain cosmopolitan forms, such as the free-floating crinoid *Marsupites*.

The next higher unit, the Eagle sandstone and its equivalents, is marked widely by sandy beds containing *Scaphites hippocrepis* (DeKay) and certain associated species (Reeside, 1927a) Like the Telegraph Creek formation, it is not known in the Great Plains east of the Black Hills and on the southwestern margin of the Western Interior, but is widely distributed west of the Great Plains. To the north, in Canada, there is little record of its presence, but it may represented there. To the south, in the Gulf region, species characteristic of the unit are found in the Taylor marl (Stephenson and Reeside, 1938) and on the Atlantic Coast in the Merchantville clay of New Jersey (Weller, 1907). The suggestion is strong that the Eagle fauna came in from the south. Some of the species of the unit are cosmopolitan and are represented in Europe by identical or closely related forms. The unit corresponds to the lower part of the Campanian stage.

Above the Eagle sandstone and its equivalents are deposits containing a number of faunal units that in the Great Plains constitute the typical Pierre shale. In the Great Plains it is useful to recognize eight lithologic subdivisions, all fine-grained and all marine. Westward, sandstones replace more and more parts of this sequence, and eventually nonmarine deposits make up all of it. In some western marginal areas there are no deposits for much of the interval. In central Montana the Judith River formation and farther west the Two Medicine formation are nonmarine. In central Wyoming, western Colorado, eastern Utah, and northwestern New Mexico the Mesaverde formation is chiefly nonmarine. Along the southwestern margin of the Western Interior, only the latest part of the interval seems to be represented, and the sediments are nonmarine. In the Great Plains a series of faunal zones marks the Pierre shale. Most of these can be traced westward in the marine sandy deposits. The zones are particularly marked by a series of species of *Baculites*, though with each are associated other characteristic species. In general, the faunas are similar to those found to the north, in Canada, and are not matched by closely similar assemblages to the south in part of the Taylor marl and the Navarro group of the Gulf region, (Stephenson, 1941; Stephenson and Reeside, 1938), though enough forms are found to provide a rational correlation. Seemingly the Pierre faunas are either boreal or largely endemic. This aspect is emphasized by the few levels where southern species appear, which indicate a temporarily freer access for these species. These occurrences are all in Colorado, Utah, and southern Wyoming and include such forms as *Trigonia*, *Exogyra costata* Say, *Capulus spangleri* Henderson, and *Anchura haydeni* White. The relation of these interior faunas to those of Europe is not clear in detail, though there seems no doubt that they correspond to those of the upper Campanian and lower Maestrichtian stages of the European sequence. The nonmarine faunas are not well characterized.

Above the Pierre shale in the Great Plains area lies a sandy formation, the Fox Hills sandstone, divisible into four members in the type area. The two upper members, though marine, have not yielded a satisfactory fauna. The two lower members, however, have yielded faunas in part cosmopolitan, in part apparently endemic. Westward these marine members of the Fox Hills sandstone pass rapidly into overlying nonmarine units, such as the Hell Creek and Lance formations. Sandy marine deposits appear at progressively lower levels westward and have generally been designated

Fox Hills, though many of them contain faunas older than those of the typical Fox Hills sandstone. Some forms, particularly the ammonite *Sphenodiscus* Meek, seem to be associated with the sandstone deposits and appear at lower levels westward than in the typical Fox Hill area. The similarities of the faunas of the Western Interior to those of the Gulf region (Stephenson, 1941; Stephenson and Reeside, 1938) suggest relatively free access to the Western Interior from the Gulf region. Further similarities to European faunas suggest that much of the Fox Hills fauna is cosmopolitan and that there may have been free access across the Arctic regions. The Fox Hills fauna corresponds to the upper Maestrichtian fauna of the European sequence. The nonmarine fauna of the later Cretaecous deposits is well characterized by a number of species.

At the top of the sequence in the Western Interior are widespread nonmarine deposits particularly characterized by a reptilian fauna, of which the genus *Triceratops* Marsh was one of the earliest described and is perhaps the best known. This zone is exemplified by the Hell Creek formation in Montana and the Dakotas, but equivalents under various names are widespread. No equivalent of the "*Triceratops* beds" is recognized in the Gulf region, and outside of North America it may be represented in the marine deposits of the latest Maestrichtian or in the still later Danian stage, if that is Cretaceous.

Above the Hell Creek formation in a small area in North Dakota and South Dakota lie marine deposits, with a considerable fauna of larger invertebrates (Stanton, 1920) and of Foraminifera (Fox, 1942), constituting the Cannonball formation. When first recognized as a separate assemblage, it was noted that there were no ammonites, that some of the mollusks were close to species of the Fox Hills fauna, but that others were close to species of the Paleocene faunas. The formation was assigned to the Cretaceous, because of the Cretaceous-like species and because this seemingly isolated fauna is more readily explained as a relic of the Cretaceous than as a result of a Paleocene invasion. The Foraminifera, however, show very close relations to those of the Paleocene Midway formation of the Gulf region and even closer to those of the Paleocene of northern Europe, and it is now generally agreed that the Cannonball formation is a marine Paleocene unit. Probably the marine waters entered from the Arctic at the close of Hell Creek time. No trace of a connection to the south with the Midway sea has been found, but subsurface extension of the Cannonball formation toward the northwest has been noted, and it seems not unreasonable to postulate a connection farther north.

ANNOTATIONS

These annotations supplement or explain items in the chart (Pl. 1), and the application of each annotation is indicated by the position of its number *within* one or more columns of the chart.

1. The placement of the boundary between the equivalents of the Campanian and Maestrichtian stages in the Western Interior has long been very uncertain, though most authors have put it at about the base of the zone of *Baculites compressus* Say. The compilers have little basis for judgment in the matter, and the placement shown follows the advice of Dr. J. A. Jeletzky, of the Geological Survey of Canada, who has given special consideration to this problem in western Europe and in Canada. The following statement kindly furnished by Dr. Jeletzky summarizes his hitherto unpublished views on the subject:

> The uncertainty with respect to the Campanian-Maestrichtian boundary in the Western Interior of North America is essentially a reflection of the similar state of affairs in western Europe, where the type-localities of these stages are situated. The writer (1951a, b) has endeavored to settle this uncertainity with regard to western Europe. He feels that it is now possible to recognize at least the approximate position of Campanian-Maestrichtian boundary, as proposed by him for western Europe, in the Western Interior of North America.
>
> Valuable stratigraphical and palaeontological information concerning the younger Upper Cretaceous of the Western Interior of the United States freely given to the writer by Messrs. W. A. Cobban and J. B. Reeside, Jr., has greatly facilitated the conclusions advanced in the following pages.
>
> The Campanian-Maestrichtian boundary in the Western Interior of North America should, in the writer's opinion, be placed provisionally at about the bottom of the zone of *Baculites baculus* Meek and Hayden, subject to the qualification made below. This zone carries in Canada, and apparently in the United States as well, *Scaphites* forms indistinguishable from *Scaphites* (*Hoploscaphites*) *pungens*

Binckhorst, 1861, which in Western Europe (Belgium, Holland) is known only from the rocks of Early Maestrichtian age, where it occurs together with *Scaphites (Hoploscaphites) constrictus* Sowerby, 1817, and *Pachydiscus neubergicus* Hauer [? = *P. egertoni* (Forbes)]. The uppermost part of the underlying zone of *Baculites compressus* Say carries apparently throughout the Western Interior of North America a densely ribbed ally of *Scaphites (Scaphites) quadrangularis* Meek which, in the writer's opinion, is indistinguishable from *Scaphites (Scaphites) elegans* Tate, 1865 (p. 37), from the Antrim Chalk of Northern Ireland. The Antrim Chalk is known to be of latest Campanian age (Jeletzky, 1951b), which agrees well with the assumed earliest Maestrichtian age of the immediately overlying zone of *Baculites baculus* Meek and Hayden, which therefore is here considered as provisionally correlative with the lower part of the Eurasian zone of *Belemnella lanceolata* (Schlotheim), typical form (Jeletzky, 1951a; 1951b).

It should be stressed, however, that there is not nearly enough reliable information about the stratigraphical ranges of the *Scaphites* and *Baculites* forms discussed above to admit of a positive decision on the subject: While it would seem rather unlikely to the present writer that the Campanian-Maestrichtian boundary in the Western Interior of North America could be situated below the zone of *B. baculus*, it appears possible that this latter zone could be of latest Campanian age in part or even totally. Indeed the stratigraphical ranges of *Baculites compressus* Say and of *B. baculus* Meek and Hayden are uncertain for the Canadian part of the Western Interior. At the same time such species of the *B. compressus* zone as *Scaphites (Scaphites) quadrangularis* Meek, *Scaphites (Scaphites) brevis* Meek and apparently *Scaphites (Scaphites) elegans* Tate appear to ascend into the zone of *B. baculus* and to occur there together with *S. (S.) plenus* Meek and *S. (H.) pungens* Binckhorst through an uncertain part of this zone. This appears to be true of the middle part of Bearpaw formation in Canada, including the Belanger member, of the upper part of the Lake Creek member of Pierre shale in Kansas (Elias, 1933, p. 292), and of the upper 50 feet of Pierre shale on Cedar Creek (Baker-Glendive anticline) in southeastern Montana (personal communication of W. A. Cobban). Further conflicting evidence is supplied by the first appearance of forms, in the writer's opinion, indistinguishable from *Scaphites (Hoploscaphites) constrictus* Sowerby somewhat above the beds referable to the zone of *B. baculus* both in Canada and in the United States [e.g. "*Discoscaphites" abyssinus* of Elias (Elias, 1933, pl. 39, figs. 3, 6, not figs. 2, 4); "*Discoscaphites" abyssinus* of Landes (1940, p. 179–180); and unpublished specimens from the upper Bearpaw in collections of the Geological Survey of Canada]. Also the more or less typical forms of *Scaphites (Hoploscaphites) nicolletii* Morton, probably partly synonymous with nodate variants of *Scaphites (Hoploscaphites) tenuistriatus* Kner, seem to make their first appearance in the beds overlying those with *S. (S.) plenus* Meek and correlative either with the upper part of the *B. baculus* zone or with the overlying zone of *Baculites grandis* Hall and Meek (i.e., upper Bearpaw of Canada; upper part of Mobridge member in Montana, Beecher Island shale member of Kansas, etc.). Both *S. (H.) constrictus* and *S. (H.) tenuistriatus* are commonly accepted as index fossils of the Maestrichtian stage, which do not descend even into the uppermost Campanian (zone of *Bostrychoceras polyplocum* Roemer) with the possible exception of a thin transitional bed between these stages. Therefore, one might feet inclined to draw the Campanian-Maestrichtian boundary in the Western Interior of North America at the first appearance of these forms rather than use the other evidence favored by the present writer (occurrence of *S. (H.) pungens* Binckhorst, and of *S. (S.) elegans* Tate). This was done especially because the downward extension of the stratigraphical ranges of *S. (H.) constrictus* and *S. (H.) nicolletii* into the zone of *B. baculus* and *S. (S.) plenus* appears to be quite likely, to judge from some fragmentary material in the writer's possession.

A typical specimen of *S. (H.) nicolletii* Morton, indistinguishable from the one figured by Meek (1876, pl. 34, fig. 2), was collected by the writer in northwestern Germany (Hemmoor), together with *S. (H.) constrictus* Sowerby, in the upper part of Lower Maestrichtian [zone of *Belemnella lanceolata* (Schlotheim) mut. *sumensis* Jeletzky, 1949]. This gives further support to the above conclusions of the writer and agrees well with the well established fact that, whatever its lowermost occurence might be, the typical *S. (H.) nicolletii* Morton, as well as the numerous, so far strictly North American, forms of *Scaphites (Discoscaphites)* of the group of *conradi* Morton and *Scaphites (Discoscaphites)* of the group of *cheyennensis* (Owen) are essentially characteristic of rocks younger than the zone of *B. baculus* and *S. (S.) plenus*. Whether these latter (i.e., so-called Fox Hill fauna) represent only the higher part of Lower Maestrichtian or embrace some part of Upper Maestrichtian [zones of *Belemnitella junior* Nowak, 1913, and *Belemnella casimirovensis* (Skolozdrowna, 1932, in coll.)] as well is still uncertain. Considering that *Sphenodiscus* spp., which are rather characteristic of the Fox Hills fauna and occur much less commonly in the older Maestrichtian zones of the Western Interior, are essentially characteristic of the Upper Maestrichtian in Europe, it seems by no means unlikely that at least the highest zone with the Fox Hills fauna might be of Late Maestrichtian age.

It may be added in passing that *Belemnitella americana* (Morton, 1829, not Arkhangelsky, 1912) and its Western Interior subspecies *B. bulbosa* Meek, 1876, are rather close allies of the Maestrichtian *Belemnitella junior* Nowak, 1913, and seem to be reliable index fossils of the equivalents of the Maestrichtian stage, at least in the Western Interior of North America. The former species may, however, range into Uppermost Campanian rocks on the Atlantic coast of North America (*e.g.*, New Jersey, Delaware, etc.)

The writer rejects the widely accepted opinion that *Scaphites* of the group of *nodosus* Owen, including *S. plenus* Meek, belong to the subgenus *Acanthoscaphites* Nowak, 1913, which he restricts to the group of *Scaphites (Acanthoscaphites) tridens* Kner with a median row of tubercles on the ventral side of the living chamber. In his opinion, the group of *S. nodosus* Owen represents immediate Campanian (essentially Upper Campanian) and (?) Lowermost Maestrichtian ancestors of *Scaphites (Hoploscaphites)* of the group of *constrictus-nicolletii* and of *Scaphites (Discoscaphites)* of the group of *conradi-cheyennensis* as well. There is an uninterrupted series (plexus) of transitional forms between the three groups above mentioned in the Campanian-Maestrichtian succession of the Western Interior of Canada. *Scaphites* of the group of *nodosus* Owen are placed in the typical subgenus of the genus *Scaphites* Parkinson 1813, s.l., as the writer is unable to see any essential morphological differences between this group and *Scaphites* (*Scaphites*) *binodosus* Roemer, *Scaphites* (*Scaphites*) *hippocrepis* Dekay, *Scaphites roemeri* d'Orbigny and other typical representatives of this subgenus.

1a. Regarding the use of the names *Discoscaphites* and *Acanthoscaphites*, the compilers are in essential agreement with the views expressed in Note 1 by Doctor Jeletzky, but feel that in deference to past usage it would be less confusing, for the purposes of the chart, to continue the old usage until a fully documented and illustrated discussion can be presented.

2. Many authors, particularly the French writers, include the Coniacian and the Maestrichtian stages in the Senonian. Others exclude the Maestrichtian, and others, particularly the German writers, exclude the Coniacian (Emscherian).

3. Col. 1. Nonmarine fossils in the Fort Crittenden formation indicate a very late Cretaceous age for the Sonoita group, which is found in the Santa Rita Mountains (Stoyanow, 1949, p. 58–60).

4. Col. 1. Scant marine fossils suggest a Colorado age for the Amole arkose (Brown, 1939, p. 697).

5. Col. 1. In the Patagonia Mountains (Stoyanow, 1938; 1949, p. 30).

6. Col. 1. In the Ninety-One Hills (Stoyanow, 1938, p. 4–27).

7. Col. 2. Assigned to an early Colorado age on comparison with rocks near Silver City, New Mexico.

8. Cols. 3 and 4. Assigned on the basis of fossils the compilers consider early Colorado.

9. Col. 5, etc. The relations of the sandstone designated "Dakota" in this and many other areas to the typical Dakota sandstone on the Missouri River near Sioux City, Iowa, are not well understood. Such usage of the name may cover beds of both Early and Late Cretaceous ages, though it was apparently the intent originally to include in the Dakota beds no older than the European Cenomanian. There is much doubt that any part of the typical exposures are Late Cretaceous.

10. Col. 7. In Luna County.

11. Col. 7. In the Little Hatchet Mountains.

12. Col. 10. Lee (1906a, p. 240; 1906b, p. 57) reports the presence of *Triceratops*, indicating that at least part of this unit is very late Cretaceous.

13. Col. 10. Paleontologic data indicate the presence of beds of Greenhorn, later Carlile, and Niobrara ages.

14. Col. 10, etc. Presence of beds of early Carlile age here and in several other areas is dubious. The *Collignoniceras woollgari* fauna has not been found, and an interruption in sequence is inferred.

15. Col. 15. Includes the Punta de la Mesa sandstone member of Herrick, as recognized by Lee (Lee and Knowlton, 1917, p. 172, 179).

16. Cols. 16 and 17. On the basis of the dinosaurian faunas, some vertebrate paleontologists assign the interval from the Ojo Alamo sandstone to the Fruitland formation to horizons older than here shown (Gilmore, 1916, 1919).

17. Col. 18. W. T. Lee (1906b, p. 57) at first regarded the Galisteo sandstone as equivalent to the Late Cretaceous deposits of the Engel district (*see* Note 12), because of similarity of lithologic constitution and stratigraphic position, but he later (1917, p. 184) regarded it as Tertiary. Stearns (1943) reports late Eocene or early Oligocene mammals in the uppermost part. The age of the lower part is still undetermined.

18. Col. 26. In the Muddy Mountains.

19. Col. 26. In the Eureka district.

20. Cols. 27 and 28. Paleontological evidence is scant for assignment of these deposits, and they are assigned largely by analogy with deposits to the east.

21. Col. 29, etc. The presence of upper Carlile beds here is dubious. The *Prionocyclus wyomingensis* fauna has not been found, and a hiatus is inferred.

22. Cols. 31, 32, and 38. The lower part of the North Horn formation has yielded Cretaceous reptiles, and the middle part has yielded Paleocene mammals. No sharp boundary between these parts has been noted. Some vertebrate paleontologists assign the reptile-bearing part to horizons older than here shown (Gilmore, 1947). (*See also* Note 16.)

23. Col. 31. The age of the lowest part of the Sanpete formation is not well determined. It may contain beds of Early Cretaceous age.

24. Col. 33. In this area the age of the beds long called "Wasatch" and now designated "Currant Creek" formation is dubious; by analogy with regions to the south they seem likely to be equivalents of the North Horn and Price River formations and at the top may include beds as high as lower Eocene. Adequate paleontologic data are not available.

25. Cols. 34 and 35. Stokes (1944, p. 970) correlates the Kelvin conglomerate with the Buckhorn conglomerate and Cedar Mountain shale (Col. 38). Eardley (1944, p. 838) correlates the type Kelvin conglomerate with the lower part of his Kelvin (?) formation of the Coalville district, Utah (Col. 35), which part appears to be equivalent to the Ephraim formation (Early Cretaceous and possibly Late Jurassic). *See also* Note 42. Adequate paleontologic data are not available.

26. Col. 35. The age of the beds long called "Wasatch" is dubious; it seems likely that they may include equivalents of the Price River and North Horn formations and may extend up into the lower Eocene. Adequate paleontologic data are not available.

27. Col. 35. "Unit W-2," etc., refers to a measured section at Coalville published by Wegemann (1915, p. 163), and "Unit R-1," etc., to a measured section at Rockport published by Stanton (1893, p. 44).

28. Cols. 39 and 43. The relations of the Tuscher formation to the North Horn formation and to the "unnamed sandstone" (Col. 43) are not fully determined. Spieker (1946, p. 140) considers the Tuscher a coarse basal unit of the North Horn formation.

29. Col. 40. The relations of the Mesaverde formation of the Rangely region to that of adjacent areas is not well known. The correlations shown are somewhat arbitrary.

30. Col. 40, etc. The Belle Fourche, Greenhorn, and lower Carlile faunas have not been found here and in several other areas, and a hiatus is inferred.

31. Col. 40, etc. The stratigraphic relations of the strata included in the Dakota sandstone in the areas represented by these columns are not well known. The assignments shown are somewhat arbitrary.

32. Col. 44. The age of the Ohio Creek conglomerate is uncertain, and so is its relation to the "unnamed sandstone" of Col. 43, with which Lee (1912, p. 48) correlated it.

32a. Col. 45. The *Collignoniceras hyatti* and *C. woollgari* zones have not been found here, and an interruption is inferred.

33. Col. 48, etc. No evidence of the Eagle and Telegraph Creek faunas has been found in this or in several other areas, and a hiatus is inferred.

34. Col. 48, etc. Evidence for a disconformity at the base of the Timpas limestone is given by Johnson (1930). In addition, the absence of equivalents of part of the Turner member and of the Sage Breaks member of the Carlile shale may be cited.

34a. Col. 48. The "*Pugnellus* sandstone" of the literature (*see* Stanton, 1893, p. 28) locally occupies the interval between the Codell and Fairport members of the Carlile shale.

35. Col. 48. The Greenhorn and Graneros formations of Gilbert were described in this region (Gilbert, 1896), but, as these names were subsequently applied in the Great Plains to the east, the boundary was moved down to include equivalents of the upper, calcareous part of the original Graneros in the Greenhorn. This revision seems more widely useful.

36. Col. 52. Correlation of the five parts of the Dakota of this region is in dispute. Stanton (1922, p. 266–269) considered all of the Dakota equivalent to the typical Dakota—that is, Late Cretaceous; Reeside (1923a) correlated the marine dark shale with the Glencairn shale, of Kiamichi age; Lee (1927) considered the three lowest parts of the Dakota equivalent to the Cloverly formation of Wyoming and to the Lakota sandstone, Fuson shale, and what is now called the Fall River sandstone of the Black Hills. The compilers believe that Lee's correlation is probably correct, but present evidence is not conclusive.

37. Col. 53, etc. All formations below the level indicated in each column are interpreted from well logs.

38. Col. 54. Correlation of the lower members of the Dakota is arbitrary.

39. Col. 61. The Mentor formation is taken to include all the beds between the Dakota sandstone of common usage and the Permian rocks. Twenhofel (1924, p. 31), who in central Kansas applied the name Mentor to a part of

the interval, adopted the term Belvidere for these strata. For southern Kansas Twenhofel (1924, p. 20) applied the name Belvidere to the beds between the Cheyenne sandstone and the "Dakota" sandstone.

40. Cols. 62, 63, and 65. The Bear River formation of this region has in the lower part fossils related to those of the Cloverly and Kootenai formations and in the upper part fossils more peculiar to the formation—the "Bear River fauna" of the literature. The sandstone called "Tygee" by Mansfield and Roundy (1916, p. 83) and placed by inadvertence at the top of the Gannett group is actually a unit in the Bear River formation. The highest unit of the Gannett group is a discontinuous unnamed red shale (W. W. Rubey, oral communication).

41. Cols. 62 and 63. The Peterson and Draney limestones contain faunas like those of the Kootenai and Cloverly formations.

42. Cols. 62, etc. The Ephraim conglomerate has not yielded significant fossils and is placed arbitrarily. In the lower part it may contain beds of Jurassic age.

42a. Col. 64. The lower part of the typical Adaville formation contains marine fossils of Colorado age. The upper part is not well dated.

43. Col. 64. The lower part of the Beckwith formation has yielded Upper Jurassic fossils; the upper part in this region has not yielded significant fossils and is placed by comparison of lithologic features.

44. Col. 65. In parts of the area the Draney and Peterson limestone are absent.

45. Col. 66. No fossils identifying the equivalents of the Greenhorn and Belle Fourche formations have been reported from this region, and the thickness of beds that could contain them is small. A hiatus is inferred.

46. Col. 67. Post-Bacon Ridge strata are dated only as later Cretaceous. The correlations shown are arbitrary.

47. Col. 67, etc. In much of the literature the name Thermopolis has been applied to dark shales that lie above the Cloverly formation and below the Mowry shale and that contain a brown sandstone member (Muddy). Many geologists now prefer to restrict the name to the lower part of the dark shales, to designate the sandstone the "Muddy sandstone" and view it as a formation, and to include the upper part of the dark shale in the Mowry formation. The compilers think this restricted application of Thermopolis much more useful at many places than the older usage (*see also* Note 52), but in deference to the literature the older usage is shown in the chart.

48. Col. 67. In this region the boundary between the lower member of the Cloverly formation and the Jurassic is in debate. It is not determined whether beds of Morrison age are present or whether all the rocks above the marine Jurassic deposits are part of the early Cretaceous Cloverly formation.

48a. Col. 68. Nomenclature and correlation in this column are largely arbitrary. Paleontologic evidence is scant, and some of the names have been carried far from their original areas.

49. Col. 70. The age of the beds designated "Lewis" and "Lance" is not well known. The assignment shown seems probable but is arbitrary.

50. Col. 70. At many places the Cloverly formation of this region does not present the common threefold sequence. The separation of these beds from the underlying Jurassic is difficult, and at places only arbitrary division is possible.

51. Col. 71. Some authors include this shale and the underlying conglomerate in the Jurassic Morrison formation.

52. Col. 72. The Thermopolis shale, as originally described by Lupton (1916a, p. 168), included the "Rusty beds" usually considered part of the Cloverly formation.

53. Col. 72. The Cloverly formation at its type locality (Darton, 1904) consists chiefly of soft beds and does not show the three divisions—basal conglomerate, middle variegated shale, and upper sandy beds—that at other places led Darton to correlate the formation with the Lakota sandstone, Fuson shale, and Fall River sandstone of the Black Hills. Because the divisions are widely present, they are here indicated.

54. Col. 73. Fossils indicate that the equivalents of much of the Greenhorn formation and lowest part of the Carlile are very thin or missing here, and a hiatus is inferred.

55. Col. 78. The relatively thin sandstone here designated the Cloverly formation may be equivalent to only part of the formation, and

equivalents of the lower parts may have been erroneously included in the Jurassic Morrison formation.

56. Col. 81. The fauna of the Sage Breaks shale was formerly thought to indicate a Niobrara age (Rubey, 1931, p. 4). It is now better known and indicates that the unit is of late Carlile age.

57. Col. 82. Only the Greenhorn limestone is sharply characterized in the log of the Harrisbug well, on which this section is largely based.

58. Col. 83. The Pierre, Niobrara, and Carlile formations are not distinguishable in the log of the Agate well, on which this section is based.

59. Col. 86. The age of the lower part of the Dakota here is not determined.

60. Col. 87. The compilers believe that the marine fauna of the type Dakota sandstone—Omadi sandstone of Condra and Reed (1943)—is part of the general assemblage of marine organisms represented in the Kiowa shale, Mentor formation, and the Purgatoire formation and therefore of about Kiamichi (late Early Cretaceous) age. No evidence of the presence in the type Dakota of equivalents of the Lakota sandstone and Fuson shale is known to the compilers. The age of the lower part of the Graneros shale here is not determined.

61. Col. 90. This was previously called "Middle Creek limestone member" by Wing (1940) and "Bull Creek limestone" by Moore (1949). In a diagram for this region, Moore has used, within the the Greenhorn formation the names "Willow Creek," "Stoneville Flats," and "Crow Creek" for limestone members.

62. Col. 94. The Carlile and Greenhorn formations are reported to contain distinctive fossils, but the age of the Graneros shale is not well determined. Possibly the Dakota sandstone contains no Late Cretaceous deposits.

63. Col. 97. The relations of these beds to the coal-bearing rocks called the Frontier formation in central eastern Idaho (Col. 63) is not known, though they may be equivalent.

64. Col. 100. Very little evidence is available as to the age of these volcanic rocks.

65. Col. 100. Sediments representing the time of the Belle Fourche, Greenhorn, and Carlile formations and the lower part of the Niobrara formation are thin or missing in the central part of Jefferson County (M. R. Klepper, unpublished data). Farther north these strata are present.

66. Col. 102. The limits of the typical Blackleaf sandy member of Stebinger (1918, p. 158) are as shown, but petroleum geologists, for convenience in subsurface studies, carry the name up to include the calcareous member.

66a. Col. 102. The names Cosmos and Vanalta are applied to sands that are local equivalents of the Cut Bank sandstone (Erdmann and Schwabraw, 1941). The names Lander and Moulton are applied to local sands in the Kootenai formation (Blixt, 1941).

67. Col. 104 and 105. The relations of the sandstones in the lower part of the Colorado shale and in the upper part of the Kootenai formation are not determined. Probably equivalents of the Muddy sandstone and of the Greybull sandstone of Wyoming are widely present, and the intervening shales are to be correlated with parts of the Thermopolis shale of Wyoming.

68. Col. 128. The age of the Windrow formation is conjectural. Stauffer and Thiel (1941, p. 102) note that the upper part resembles the Ostrander member of the Dakota formation and that the lower part is of residual material that may be much older than Cretaceous.

Index by Columns of Stratigraphic Names

Numbers refer to numbered columns in Plate 1. Where one column only is cited, it contains the type occurrence of the name; where two or more columns are cited, an asterisk (*) indicates the column containing the type occurrence.

The following units have type occurrences in Canada: Ashville, Assiniboine, Boissevain, Boyne, Keld, Kootenai, Morden, Odanah, Pembina, Riding Mountain, St. Mary River, Swan River, and Vermilion River.

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Fluorite solubility equilibria in selected geothermal waters

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Abstract—Calculation of chemical equilibria in 351 hot springs and surface waters from selected geothermal areas in the western United States indicate that the solubility of the mineral fluorite, CaF_2, provides an equilibrium control on dissolved fluoride activity. Waters that are undersaturated have undergone dilution by non-thermal waters as shown by decreased conductivity and temperature values, and only 2% of the samples are supersaturated by more than the expected error. Calculations also demonstrate that simultaneous chemical equilibria between the thermal waters and calcite as well as fluorite minerals exist under a variety of conditions.

Testing for fluorite solubility required a critical review of the thermodynamic data for fluorite. By applying multiple regression of a mathematical model to selected published data we have obtained revised estimates of the pK (10.96), ΔG_f° (−280.08 kcal/mole), ΔH_f° (−292.59 kcal/mole), S° (16.39 cal/deg/mole) and C_P° (16.16 cal/deg/mole) for CaF_2 at 25°C and 1 atm. Association constants and reaction enthalpies for fluoride complexes with boron, calcium and iron are included in this review. The excellent agreement between the computer-based activity products and the revised pK suggests that the chemistry of geothermal waters may also be a guide to evaluating mineral solubility data where major discrepancies are evident.

INTRODUCTION

THE INCREASED development of geothermal resources to help meet energy demands requires a better understanding of the chemistry of geothermal waters. It is necessary to know not only what the composition of a particular water is, but what processes determine that composition. This knowledge is useful in the design and operation of power plants, in the exploration for new fields and in the evaluation of the potential effects of wastewater disposal. In order to adequately model the chemical processes within a geothermal region, field measurements, experimental laboratory investigations and theoretical considerations must be carefully synthesized. If a model is proved successful, it can then be used to assess the environmental impact of geothermal development.

One of the elements which occurs in relatively high concentrations (commonly greater than 1 mg/l) in many geothermal waters is fluorine. The purpose of this paper is to test the hypothesis that fluoride concentrations are governed by the solubility of the mineral fluorite, CaF_2, in several geothermal regions of the western United States. With the use of high-speed computers, it is now possible to make a quantitative analysis of a possible solubility-controlled reaction without laborious and time-consuming manual calculations. The success of this approach is very encouraging and should provide useful information for other geochemical surveys.

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A preliminary assessment of several geothermal waters for fluorite saturation supported our suspicion that there were errors in the published thermodynamic data for fluorite. This finding provided the impetus for a critical review of the literature on the thermodynamic properties of fluorite from which we have calculated a set of revised values.

FLUORIDE IN GEOTHERMAL WATERS

The fluoride content of surface waters rarely surpasses 1.6 mg/l, the maximum recommended concentration for domestic water supplies when maximum daily air temperatures are 22–26°C (ENVIRONMENTAL PROTECTION AGENCY, 1972). Geothermal waters, however, commonly exceed recommended water quality criteria for dissolved fluoride. Although fluoride concentrations are generally below 20 mg/l in thermal springs and in solutions from rock-leaching experiments (ELLIS, 1967), they have been reported as high as hundreds and even thousands of milligrams per litre in acid (pH < 2) hot springs by ELLIS (1973) and OZAWA *et al.* (1973). Under these acid conditions fluorine would be present largely as aqueous HF, HF_2^- and SiF_6^{2-}, which would partially escape into the air as HF and SiF_4 gases at atmospheric pressures. Low and stable levels (0.5–1.7 mg/l) of dissolved fluoride are required to maintain dental health, prevent teeth mottling and prevent fluorosis in livestock (UNDERWOOD, 1971). Thus, geothermal waters constitute a source of potential fluoride contamination to natural water systems.

In this study a total of 351 water analyses from selected springs, wells and streams in Yellowstone

National Park (COX, 1973), hot springs in Yellowstone (ROWE *et al.*, 1973), as well as hot springs in Nevada (MARINER *et al.*, 1974a), Oregon (MARINER *et al.*, 1974b) and California (WILLEY *et al.*, 1974) were used as input data for our computations. Only water analyses reporting: (1) *in situ* temperatures and pH values, (2) pH values greater than 4.0, (3) all major constituents, (4) fluoride and calcium, and (5) specific conductance were tested. Acid hot springs with pH values less than 4.0 were avoided because compilation and evaluation of the appropriate complexes has not yet been completed.

TESTING FOR FLUORITE SATURATION

MAHON (1964) and ELLIS and MAHON (1964, 1967) have argued that the concentration of fluoride in geothermal waters is controlled by the solubility of fluorite. They base their arguments on rock-leaching experiments and fluorite solubility determinations carried out at 100–350°C and a constant pressure of 345 bars. The rock-leaching experiments demonstrated that fluoride concentrations tended toward limiting values which could be related to the solubility of pure fluorite under similar pressure and temperature conditions. Unfortunately, non-equilibrium conditions were present in some of these experiments, as indicated by increasing and decreasing concentrations of fluoride with time. In addition, they did not account for ionic strength and complexing effects. Their conclusions were based on concentration products rather than activity products. Comparison of their solubility data with thermal water analyses can only be considered a qualitative indication that an equilibrium solubility control exists.

The solubility of fluorite as shown by the following reaction:

$$CaF_{2(s)} \rightleftarrows Ca^{2+}_{(aq)} + 2\,F^{-}_{(aq)} \qquad (1)$$

can be affected by temperature, pressure, ionic strength, particle size, polymorphism, complexing capacity of the solution, and kinetic barriers. In order to simplify the problem, we have assumed equilibrium conditions with no particle size effects. The negative log of the equilibrium constant, K, for reaction (1) is:

$$pK = -\log K = -\log (a_{Ca^{2+}})(a_{F^-})^2, \qquad (2)$$

which expresses the equilibrium concentrations in terms of the activities of dissolved calcium ($a_{Ca^{2+}}$) and dissolved fluoride (a_{F^-}). Since activities are used instead of concentrations, ionic strength effects are taken into account.

Polymorphism is not a major difficulty because the crystalline alpha phase (α) of fluorite is stable up to 1424°K (NAYLOR, 1945). Temperature effects are calculated from the van t'Hoff equation:

$$\frac{d \log K}{d\,(1/T)} = -\frac{\Delta H_r}{2.303\,R}, \qquad (3)$$

where ΔH_r is the partial molal reaction enthalpy, R is the gas constant, and T is the Kelvin temperature. Pressure effects are determined from the relationship:

$$\frac{d \log K}{dP} = -\frac{\Delta V_r}{2.303\,RT}, \qquad (4)$$

where ΔV_r is the partial molal volume change for the reaction.

Complexing can often be the single most important factor which determines the total concentration of fluorite which dissolves. Upon dissolution of fluorite, the ions may associate with themselves to form a monofluoride complex:

$$Ca^{2+}_{(aq)} + F^{-}_{(aq)} \rightleftarrows CaF^{+}_{(aq)}. \qquad (5)$$

Fluoride ion, being a strong ligand, will also complex with several cations, such as magnesium, iron and aluminum:

$$Mg^{2+}_{(aq)} + F^{-}_{(aq)} \rightleftarrows MgF^{+}_{(aq)}\,. \qquad (6)$$

$$Fe^{3+}_{(aq)} + nF^{-}_{(aq)} \rightleftarrows FeF^{(3-n)}_{n(aq)};\ n = 1,2,3 \qquad (7)$$

$$Al^{3+}_{(aq)} + nF^{-}_{(aq)} \rightleftarrows AlF^{(3-n)}_{n(aq)};\ n = 1,2,3,4,5,6. \qquad (8)$$

Due to the low concentrations of iron (usually less than 1 mg/l) and aluminum (less than 0.1 mg/l) in neutral thermal waters, fluoride would not be bound to these cations to any significant extent. Magnesium may be an important complexing cation because its concentration ranges up to 62 mg/l in our samples.

Another species which complexes with $F^{-}_{(aq)}$ is boric acid and since the boron content of geothermal waters occasionally reaches concentrations of 150 mg/l (ELLIS, 1967), these complexing reactions need to be considered:

$$B(OH)_{3(aq)} + nF^{-}_{(aq)} \rightleftarrows BF_n(OH)^{-}_{4-n(aq)} + (n-1)\,OH^{-}_{(aq)};\quad n = 1,2,3,4. \qquad (9)$$

Calcium ion also complexes significantly with carbonate and sulfate ions which can increase the solubility of fluorite. Complexing has the effect of reducing free calcium and fluoride activities, thereby increasing the tendency for fluorite to dissolve. The dissociation constants for some of the above reactions as well as enthalpy and heat capacity considerations are given below in the discussion on thermodynamic data.

When complexing is accounted for, the activity product, $AP = (a_{Ca^{2+}})\,(a_{F^-})^2$, can be calculated from a water analysis containing all of the major constituents. The ratio of the AP and the equilibrium constant, K, gives the degree of saturation of a water with respect to fluorite. To express this in terms of a free energy difference, ΔG_r, we have:

$$\Delta G_r = \Delta G_r^0 + 2.303\,RT \log (a_{Ca^{2+}})(a_{F^-})^2 \qquad (10)$$

$$= -2.303\ RT \log K + 2.303\ RT \log AP \qquad (11)$$

$$= 2.303\,RT \log (AP/K). \qquad (12)$$

When a water is undersaturated, $AP < K$ and $\Delta G_r < 0$; when supersaturated, $AP > K$ and $\Delta G_r > 0$; and at equilibrium (saturation), $AP = K$ and $\Delta G_r = 0$.

The computations involving activity corrections, temperature dependence, effect of complexing, and degree of saturation can be easily made with available computer programs. We employed the PL/I programs WATEQ (TRUESDELL and JONES, 1974) for our computations and EQPRINT and EQPLOT (J. W. Ball, U.S. Geological Survey, unpublished programs) to evaluate our results graphically. In brief, WATEQ uses the chemical analysis and on-site measurements of temperature, pH and Eh and distributes the total concentrations of species among all of the known associated and unassociated species according to their equilibrium constants. Distribution of species is accomplished by iteration and correction of the free anion concentration for each successive cycle. The ionic strength and activity coefficients are also corrected on each iteration. Iteration is stopped when the sum of the weak acids, free anions and their complexes is within 0.5% of the analytical values for each major anion.

Calculated log AP values for fluorite were plotted as a function of on-site temperature with EQPLOT using letter symbols to indicate the basin from which the samples came. These results are shown in Fig. 1. All of the letters plot significantly below the fluorite solubility curve of HELGESON (1969), which suggests two possible explanations. These thermal waters may be undersaturated with respect to fluorite because some other mineral phase is controlling the calcium and fluoride activities at undersaturated values or else kinetic or hydrodynamic factors are preventing saturation. Alternatively, the thermodynamic values used by WATEQ or by HELGESON (1969) or by both are in error. The most striking observation that appears

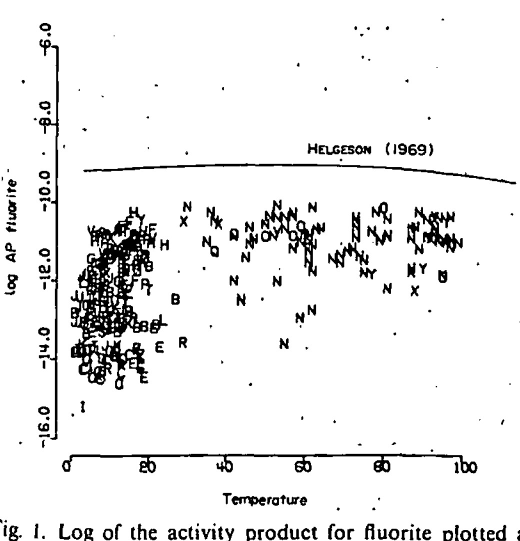


Fig. 1. Log of the activity product for fluorite plotted as a function of on-site temperatures for geothermal waters of the western U.S. Letter symbols (see Appendix 2) represent different basins or regions. The solid line represents the equilibrium solubility of fluorite from HELGESON (1969).

in Fig. 1 is the well-defined upper boundary to the log AP values. This defines a limit proportional to $\log (a_{Ca^{2+}})(a_{F^-})^2$ over a wide temperature and compositional range, thereby making the suggestion of consistent undersatuaration unlikely. Furthermore, 90% of the values for hot springs with temperatures greater than 30°C agree to within 2 log AP units (2.7 kcal of energy). Thus, a critical evaluation of the thermodynamic data was mandated.

THERMODYNAMIC DATA

Proper evaluation of the accuracy of published thermodynamic data needed for chemical equilibria computations of natural waters is a tedious and time-consuming task. We have reviewed the literature for data on: (1) aqueous fluoride complexes, (2) free energies, enthalpies and entropies of fluorite, and (3) the heat capacities of fluorite, $Ca^{2+}_{(aq)}$ and $F^-_{(aq)}$ in order to test the equilibrium control by fluorite solubility. Final revised estimates of these values were obtained by regression of a mathematical model to the data (HAAS, 1974).

Dissolved complexes

Association constants and enthalpy values (or temperature-dependent power functions) are used in WATEQ to calculate species distribution. Included in WATEQ are the values for the association of MgF^+, AlF^{2+}, AlF_2^+, AlF_3^0 and AlF_4^- to which we have added the values for $BF(OH)_3^-$, $BF_2(OH)_2^-$, $BF_3(OH)^-$, BF_4^-, FeF^{2+}, FeF_2^+, FeF_3^0 and CaF^+. The association constants for reactions (9) were determined by GRASSINO and HUME (1971) and their value for $n = 4$ agrees with previous work. Although they measured these constants at two temperatures (25 and 35°C), the lack of precision and the lack of sufficient difference in the association constants makes it impossible to obtain any enthalpy information except for $n = 4$. We have estimated the reaction enthalpies in the following manner, WAGMAN *et al.* (1968) give free energies of formation for $BF_2(OH)_2^-$, $BF_3(OH)^-$ and BF_4^- which give log K values for the association reactions within 10% of the values from GRASSINO and HUME (1971). Unfortunately, standard enthalpies of formation are only listed for $BF_3(OH)^-$ and BF_4^-. A linear free energy relationship holds between the free energies of $BF_2(OH)_2^-$, $BF_3(OH)^-$ and BF_4^- as a function of the number of complexed fluoride ions. Since the entropy difference between BF_4^- and $BF_3(OH)^-$ is quite small, it should be safe to assume that a linear relationship holds for the enthalpies as well. By extrapolation, $\Delta G_f^0\,[BF(OH)_3^-] = -303.05$ kcal/mole, $\Delta H_f^0\,[BF(OH)_3^-] = -342.20$ kcal/mole, and $\Delta H_f^0\,[BF_2(OH)_2^-] = -353.60$ kcal/mole. Reaction enthalpies were then computed using the $\Delta H_f^0\,[F^-]$ from this study and $\Delta H_f^0\,[OH^-]$ from WAGMAN *et al.* (1968). In order to incorporate the distribution of boron species among these fluoride complexes into WATEQ, we found it necessary to modify the program so that iterative calculations for boron were included.

Association constants for the iron fluoride complexes [reaction (7)] were taken from unpublished selected values.* Although enthalpies for reaction (7) calculated from WAGMAN *et al.* (1969) agree with those listed in ASHCROFT and MORTIMER (1970) for $n = 1$ and $n = 2$, a serious discrepancy was found for $n = 3$. The same discrepancy occurs in the free energy calculations for $n = 3$ using WAGMAN *et al.* (1969). Therefore, we have preferred to use the reported enthalpy value from ASHCROFT and MORTIMER (1970) for $n = 3$.

A review of the literature revealed four different investigations of reaction (5) both as a function of temperature (up to 40°C) and ionic strength (TANNER *et al.*, 1968; AZIZ and LYLE, 1969; ELQUIST, 1970; BOND and HEFTER, 1971). All of the pK values at 25°C were plotted as a function of $\sqrt{I}$ and extrapolated to zero ionic strength to obtain a corrected pK. Then the pK values for the same ionic strength were plotted as a function of $1/T$ to obtain the reaction enthalpy. Agreement between investigators was quite good (the variance is less than 0.1 of a pK unit).

These additional values for association constants and reaction enthalpies have been added to WATEQ and are listed here in Table 1. ELLIS (1967) has suggested that fluorosilicate complexing may be important in geothermal waters. CADEK and MALKOVSKY (1966) have shown that silicon fluoride complexes can form in acid solutions, but under the neutral conditions we have selected, fluoride is not affected by silica complexing.

Fluorite, $CaF_2(\alpha)$

Thermodynamic parameters for the heat content, heat capacity, entropy, enthalpy and free energy of fluorite are available from calorimetric, solubility, and electrochemical measurements. Unfortunately, there are major discrepancies between the results from different investigators. It became necessary to make a full compilation of values, to review the methods of measurement, and to select data sets which were expected to be more accurate on the basis of the precision of the results and the reliability of the method used. This task was greatly facilitated by the use of the computer program made available by HAAS (1974). This program, PHAS20, carries out a simultaneous multiple regression of a mathematical model to any group of measurements of thermochemical data for a single species, a reaction or group of chemically related species. The mathematical model is based on an empirically-derived power function of temperature which is a modified version of the Maier–Kelly equation. The heat capacity power function used is:

$$Cp_i = a_i + 2b_iT + c_iT^{-2} + f_iT^2 + g_i\sqrt{T} \quad (13)$$

for a solid species, i, and

$$Cp_i = a_i + 2b_iT + c_iT^{-2} + f_iT^2 - \frac{g_iTf(T)}{\epsilon} \quad (14)$$

for an aqueous species, i, where

$$f(T) = \alpha^2\exp^2(\beta + \alpha T) + \alpha^2\exp(\beta + \alpha T) + \frac{2\alpha}{\theta}\exp(\beta + \alpha T) + \frac{1}{\theta^2}. \quad (15)$$

a_i, b_i, c_i, f_i and g_i are power series coefficients for the heat capacity function, Cp_i, T is the Kelvin temperature, ϵ is the dielectric constant of the solution and α, β and θ are fitted constants. Equation (15) was adopted from HELGESON (1967) by HAAS (1974). PHAS20 provides the user with deviation plots which permit easy evaluation of discordant data.

The thermochemical data inputed to PHAS20 is compiled in Table 2 along with the values obtained from the regression analysis. NAUMOV *et al.* (1974) obtained their values by least squares fit of a mathematical model using a linear heat capacity power function ($Cp_i = bT$) to only one set of data; therefore, we have not used their data. Their methods are outlined in KHODAKOVSKIY *et al.* (1968). The enthalpy value of VECHER and VECHER (1967) was not used because they give no experimental measurements, only a final ΔH_f^0 for $CaF_{2(\alpha)}$ which assumes that the entropy change for their solid-state reaction:

$$CaO + MgF_2 \rightleftarrows CaF_2 + MgO \quad (16)$$

is zero at 1200°K and which utilizes unevaluated enthalpies for the other species. The high free energy value reported by SKELTON and PATTERSON (1973) was not used because of an internal inconsistency as pointed out by CHATTOPADHYAY *et al.* (1975). Furthermore, the latter authors report a ΔG_f^0 for NiF_2 at 298°K of 1.4 kcal/mole more positive than the value reported by SKELTON and PATTERSON (1973).

Table 1. Log K and standard enthalpies of reaction (298°K, 1 atm) for dissolved fluorine complexes†

Reaction	log K	ΔH_r^0 (kcal/mole)
$B(OH)_3^0 + F^- \rightleftarrows BF(OH)_3^-$	−0.30	−6.11
$BF(OH)_3^- + F^- \rightleftarrows BF_2(OH)_2^- + OH^-$	−5.97	13.43
$BF_2(OH)_2^- + F^- \rightleftarrows BF_3(OH)^- + OH^-$	−7.96	13.43
$BF_3(OH)^- + F^- \rightleftarrows BF_4^- + OH^-$	−7.39	13.43
$Fe^{3+} + F^- \rightleftarrows FeF^{2+}$	6.20	2.70
$FeF^{2+} + F^- \rightleftarrows FeF_2^+$	4.60	2.10
$FeF_2^+ + F^- \rightleftarrows FeF_3^0$	3.20	0.60
$Ca^{2+} + F^- \rightleftarrows CaF^+$	0.94	4.12

† See text for sources of data.

* These values were obtained from an unpublished manuscript by E. Hogfeldt and L. G. Sillén (1966) which was made available to us by the courtesy of Dr. J. J. Morgan. The values in the Hogfeldt and Sillén compilation were selected from SILLÉN and MARTELL (1964).

Table 2. Thermodynamic data compilation

Species	G°_f (kcal mole^{-1})	H°_f (kcal mole^{-1})	S° (cal deg^{-1} mole^{-1})	Method	Source
$F_{2(g)}$	0	0	48.44	revised data	Wagman, et al. (1968)
	0	0	48.61	spectroscopy	Moore (1972)
	0	0	48.45	calorimetric	Naumov, et al. (1974)
	0	0	48.438	calorimetric	Hultgren (1973); this study
$Ca_{(\alpha)}$	0	0	9.97	calorimetric	Naumov, et al. (1974)
	0	0	9.902	calorimetric	Hultgren (1973); this study
$Ca^{++}_{(aq)}$	-132.3	--	--	analytic fit	Stull and Prophet (1971)
	-132.1	-129.7	-13.2	calorimetric	Naumov, et al. (1974)
	-132.30	-129.74	-12.7	revised data	Parker, et al. (1971)
	-132.30	-129.72	-12.7	regression anal.	This study
$F^-_{(aq)}$	-66.64	-79.50	-3.3	revised data	Wagman, et al. (1968)
	-66.95	--	--	analytic fit to $HF_{(g)}$	Stull and Prophet (1971)
	-66.92	-79.79	-3.35	calorimetric	Naumov, et al. (1974)
$F^-_{(aq)}$ (cont'd)	--	-80.2	--	calorimetric and estimate	Finch, et al. (1968)
	-66.42	-79.08	-2.7	regression anal.	This study
$CaF_{2(\alpha)}$	--	--	16.46	calorimetric	Todd (1949)
	-280.48	-293	16.389	analytic fit	Stull and Prophet (1971)
	-281.07	-293.58	16.46	analytic fit	Naumov, et al. (1974)
	--	-291.9	--	calorimetric	Finch, et al. (1968)
	-280.35	-292.6(calc.)	17.36(calc.)	emf at high T	Rezukhina, et al. (1974)
	-279.00	-291.50	16.46	revised data	Parker, et al. (1971)
	--	-294.3	--	emf at high T	Vecher and Vecher (1967)
	-278.85	--	--	emf at high T	Skelton and Patterson (1973)
	-280.08	-292.59	16.39	regression anal.	This study

Since NiF_2 is used as a reference electrode, it is clear that its thermodynamic properties need to be more accurately known before free energy calculations can be made from these electrochemical studies. The remainder of the data in Table 2 was weighted in the regression analysis according to the precision reported by the investigator except: (1) TODD (1949), where the reported absolute error of $\pm 0.3\%$ was used, (2) NAYLOR (1945), whose absolute error was estimated at $\pm 1\%$ (reported precision $= \pm 0.3\%$), (3) standard state (298°K, 1 atm) values, which are subject to the greatest variation and are weighted to cover the range of reported values (e.g. ± 1.5 kcal for the free energy and enthalpy of formation of fluorite), and (4) the solubility data of STRÜBEL (1965) which was weighted at ± 0.1 of a pK unit.

Numerous solubility determinations on fluorite have been carried out on both synthetic and natural samples. A literature search revealed pK values for fluorite dissolution at 25°C ranging from 8.27 to 11.19 as shown in Table 3. Many of these values are based on total dissolved solids and do not account for ionic strength or complexing, but with calcium and fluoride concentrations of about 4×10^{-4} M there should be no significant changes in solubility from these effects. Furthermore, it can be shown that the CaF^+ complex is weak and carbonate complexing in these dilute solutions should have little effect on the solubility. The values for pK listed in Table 3 were $\gamma_{Ca^{2+}} = \gamma_{F^-} = 1$ except for the measurements of STRÜBEL (1965) for which activity coefficients were interpolated from the data of KIELLAND (1937) and the values of ROBERSON and SCHOEN (1973) which were obtained from ion-selective electrodes. By assuming stoichiometric dissolution and given the solubility of fluorite as x mg/l of dissolved CaF_2, then $x = x_{Ca^{2+}} + x_{F^-}$. Since 2 moles of fluoride ion are produced for every mole of calcium ion, then

$$x = (40)(M_{Ca^{2+}})(10^{-3}) + (2)(19)(M_{Ca^{2+}})(10^{-3})$$
$$= (78)(M_{Ca^{2+}})(10^{-3})$$

and

$$M_{Ca^{2+}} = x/[(78)(10^{-3})] \quad \text{and}$$
$$M_{F^-} = 2x/[(78)(10^{-3})]. \qquad (17)$$

Table 3. Fluorite solubility data at 0–350°C

T (°C)	-log K (pK)	Method	Reference
0	10.72	conductivity	Kohlrausch (1908)
0	10.01	colorimetric (F^-)	Kazakov and Sokolova (1950)
10	9.78	colorimetric (F^-)	Kazakov and Sokolova (1950)
10	10.40	colorimetric	Ikrami, et.al. (1971)
16	10.36	conductivity	Kohlrausch (1908)
17	10.53	conductivity	Kohlrausch (1908)
17.5	10.44	conductivity	Kohlrausch (1908)
18	10.46	conductivity	Kohlrausch (1904)
18	10.55		Mougnard (1931)
20	9.60	colorimetric (F^-)	Kazakov and Sokolova (1950)
20	10.31	colorimetric	Ikrami, et.al. (1971)
25	10.57		Smyshlyaev and Edeleva (1962)
25	8.27	titration	Lingane (1967)
25	9.77	ion-selective electrodes	Roberson and Schoen (1973)
26	10.37	conductivity	Kohlrausch (1908)
26.6	10.46	conductivity	Kohlrausch (1908)
30	10.31	colorimetric	Ikrami, et.al. (1971)
40	10.41	conductivity	Kohlrausch (1908)
100	8.70	colorimetric (F^-)	Kazakov and Sokolova (1950)
23	11.28	weight loss	Strubel (1965)
25	11.23	weight loss	Strubel (1965)
26.5	11.21	weight loss	Strubel (1965)
39	10.94	weight loss	Strubel (1965)
50	10.70	weight loss	Strubel (1965)
61	10.54	weight loss	Strubel (1965)
76.5	10.44	weight loss	Strubel (1965)
86.5	10.43	weight loss	Strubel (1965)
98.5	10.44	weight loss	Strubel (1965)
150	10.56	weight loss	Strubel (1965)
200	10.75	weight loss	Strubel (1965)
250	10.95	weight loss	Strubel (1965)
300	11.43	weight loss	Strubel (1965)
350	11.67	weight loss	Strubel (1965)

Thus

$$K = (M_{Ca^{2+}})(M_{F^-})^2(\gamma_{Ca^{2+}})(\gamma_{F^-})^2$$

$$= \frac{(4)(x)^3(10^{-3})^3(0.905)(0.975)^2}{(78)^3}$$

$$= (x)^3(0.72)(10^{-14}),$$

where M = molal concentration, and pK values were calculated from:

$$\text{p}K = 14.14 - 3\log(x). \quad (18)$$

The ionic strength has been assumed to be 0.0005.

These calculations are in agreement with the pK values which KHODAKOVSKIY *et al.* (1968) calculated from Strübel's data without explanation of their mode of calculation.

The only determination of fluorite solubility as a function of temperature and pressure has been the work of STRÜBEL (1965) who approached equilibria from undersaturation. These data were used in the regression analysis and found to be consistent with the other experimental measurements mentioned above for the vapor-saturated curve for water. When an attempt was made to include the temperature-dependent data of KOHLRAUSCH (1904, 1908) and the value from SMYSHLYAEV and EDELEVA (1962), a poorer fit was obtained and the added pK values were all significantly discordant with the new fit. The other published solubility determinations were approached from undersaturation and are not very reliable for various reasons. KAZAKOV and SOKOLOVA (1950) analyzed colorimetrically only for fluorine and did not properly characterize their solid phase, and IKRAMI *et al.* (1971) titrated for calcium complexometrically and titrated for HF in the CaF_2–HF mixtures, but it is not clear how they analyzed for fluorine when HF was absent, and there is no indication that more than one measurement might have been taken at each temperature. Furthermore, unpublished data on fluorite solubility (from undersaturation) by the senior author are in closer agreement with those of STRÜBEL (1965).

The only available determination of fluorite solubility determined by titration or by supersaturation are those of LINGANE (1967) and ROBERSON and SCHOEN (1973), respectively. These values are among the highest recorded and are not in agreement. Particle size effects or metastable equilibrium may have been a problem in these determinations. LINGANE (1967) states that his potentiometric measurements of the equilibrium constants for Th, La and Ca fluorides were most difficult for Ca and that true equilibrium had not been reached. Lingane's solutions probably became supersaturated during the titration. This same problem was encountered by EVERSON and RAMIREZ (1967) during their thermometric titrations of calcium and fluoride solutions. ROBERSON and SCHOEN (1973) found precipitates of fluorite (by X-ray diffraction) when they supersaturated four natural thermal waters with excess fluoride, but the precipitation rate was slow. Although only small differences in the log AP for fluorite were noticeable between 10 and 30 days after supersaturation, 3 of the 4 solutions showed a decreasing trend in fluoride activity with time which may indicate that final equilibrium had not yet been reached. The discrepancies in pK determinations by approaching equilibrium from supersaturation have not been adequately explained and it may require some long-term rate studies to clarify this problem.

Heat capacities

Accurate heat capacity data on crystalline, homogenous, pure solids are usually available over a wide temperature range. Ionic heat capacities are not well known, if at all. Values for the heat capacity of $Ca^{2+}_{(aq)}$, $F^-_{(aq)}$, and $CaF_{2(s)}$ at 25°C are compiled in Table 4 based on the following conventions (see CRISS and COBBLE, 1964):

$$\overline{C}^0_{p,H^+} = 0 \quad (19)$$

$$\overline{C}^0_{p,i}(\text{conv}) = \overline{C}^0_{p,i}(\text{abs}) - z_i\overline{C}^0_{p,H^+}(\text{abs}) \quad (20)$$

$$\overline{C}^0_{p,m_jx_k} = j\overline{C}^0_{p,m}v^+ + k\overline{C}^0_{p,x}v^- \text{ at infinite dilution,} \quad (21)$$

where $\overline{C}^0_{p,i}$ is the standard partial molal heat capacity for species i, (conv) and (abs) denote conventional and absolute values, H^+ denotes the aqueous hydrogen

Table 4. Heat capacity data (298°K, 1 atm)

Species	$\bar{C}_{p,i}$(conv) (cal deg^{-1} mole^{-1})	Source
$Ca^{++}_{(aq)}$	-9	Lewis and Randall (1961)
	-6	Gregory, et. al. (1970)
	-2	Criss and Cobble (1964)
	(+9.1)[1]	Mishchenko and Ponomarev (1952)
	(+0.2)	Khodakovskiy, et.al. (1968); Naumov, et. al. (1974)
$F^{-}_{(aq)}$	-29.5	Lewis and Randall (1961)
	-25.5	Parker (1965); Wagman, et al.(1968)
	-29	Criss and Cobble (1964)
	(+4.8)	Mishchenko and Ponomarev (1952)
	(-25.1)	Khodakovskiy, et. al. (1968); Naumov, et. al. (1974)
$CaF_{2(c)}$	16.02	Todd (1949)
	16.393	Stull and Prophet (1971)
	17.0	Naylor (1945)
	16.16	This Study

[1] Values in parentheses are discounted for reasons given in the text.

ion, $m_j x_k$ is an electrolyte with v^+ and v^- denoting the valence states of the dissociated ions, z_i is the absolute value of the charge on i, and j as well as k are stoichiometric coefficients.

Certain published heat capacity values may be discounted. Mischenko and Ponomarev (1952) based all of their values on the erroneous assumption that $\bar{C}^0_{p,NH_4^+} = \bar{C}^0_{p,Cl^-} = \frac{1}{2}\bar{C}^0_{p,NH_4Cl}$. Heat capacities for anions and cations are usually of opposite sign (Lewis and Randall, 1961) and more recent information on ionic heat capacities show better agreement with the early values listed in Lewis and Randall (1961) than with those of Mischenko and Ponomarev (1952). Khodakovskiy *et al.* (1968) have used Mischenko and Ponamarev's values for their reference state. At present, we prefer to use the values of Gregory *et al.* (1970) for calcium and Parker (1965) for fluoride.

The heat capacity values for fluorite are used in the regression analyses by PHAS20. The heat capacity values for the ions as a function of temperature have not been measured so that this information was not available for the regression. Regression analysis may be performed with enthalpy of dilution measurements and the temperature-dependent $HF_{(aq)}$ ionization measurements as well as consideration of the theoretical values obtained by Criss and Cobble (1964). This study will be published elsewhere. We feel that further revision will not make any significant differences in the conclusions stated in this paper, but we acknowledge that further refinement of the data will improve its reliability and needs to be done.

* It should be noted, however, that from the data of Ellis and Mahon (1964) fluorite solubility is only valid to 230°C. Above this temperature non-stoichiometric dissolution takes place.

EVIDENCE FOR EQUILIBRIUM SOLUBILITY

Comparison of log AP values for fluorite from selected geothermal waters with available calorimetric data (Fig. 1) has suggested a re-evaluation of the thermodynamic properties of fluorite. A compilation of calorimetric solubility and electrochemical measurements for fluorite has been examined and a revised set of free energy, enthalpy, entropy, and heat capacity values has been obtained by regression with the computer program PHAS20. An equation for log K as a function of temperature may be derived from equations (13) and (14) (Haas and Fisher, 1976) and substituting coefficients from PHAS20 output, we have:

$$\log K = 109.25 + 0.0024\,T - 3120.98\,T^{-1} - 37.63 \log T - 2088.47\,T^{-2} - 4.9 \times 10^{-7}\,T^2 - 298.4\,T^{-1/2}$$

for fluorite dissolution over the temperature range 0–350°C. This equation is internally consistent with the other thermodynamic functions listed in Table 2. For temperatures above 100°C, the mathematical model assumes the pressure conditions along the vapor-saturated curve for water.* Other thermodynamic values calculated from the regression analysis have been included in Table 2 for comparison.

The revised pK calculated from equation (22) has been used to compute log (AP/K) for the thermal waters. The log (AP/K) values or the 'disequilibrium indices' (Pačes, 1972) are plotted in Fig. 2 as a function of temperature to show the variation from saturation. *If we make an allowance of* ± 0.5 *of a log* (AP/K) unit to account for inaccuracies due to sampling technique, analytical procedures, complexes not considered, and errors in the thermodynamic data,

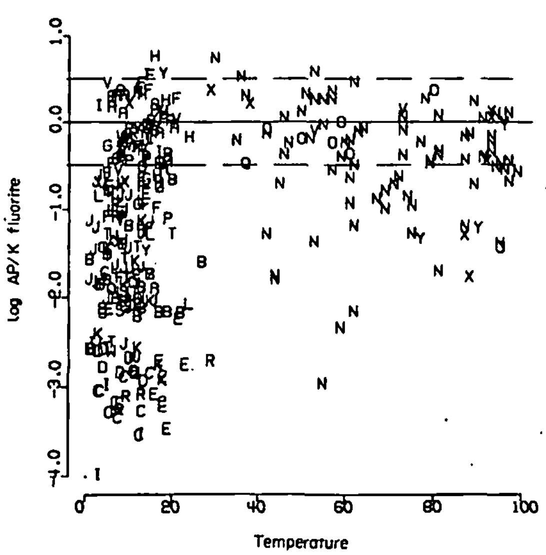


Fig. 2. Variance in the disequilibrium indices as a function of on-site temperature. The equilibrium state is shown by the solid horizontal line at log (AP/K) = 0 calculated from equation (22) with a total error of ± 0.5 as designated by the dashed horizontal lines.

then we can represent the equilibrium state by 0.00 ± 0.5 as suggested by PAČES (1972). The dashed lines in Fig. 2 show these boundaries for equilibrium. It should be noted that the suggested limits on the equilibrium state must vary for different mineral reactions according to their stoichiometry, with much larger limits placed on those reactions containing larger numbers for the stoichiometric coefficients since they become exponents in the activity product expression.

In Fig. 2, only 2% of the values exceed +0.5, demonstrating good agreement between the upper limit of the calculated activity products from geothermal waters and our revised estimate of fluorite solubility. Most of the values which fall below saturation are from creeks, rivers and other surface waters in geothermal areas. It appears that although hot springs are close to saturation with respect to fluorite, when these waters are diluted by surface or near-surface waters, they become undersaturated. Using conductivity as an indication of dilution by non-thermal ground and surface waters, we have plotted the disequilibrium index as a function of log conductivity in Fig. 3. This plot shows a distinct convergence toward equilibrium (accentuated by the arrow) as the conductance increases, and illustrates a regular departure from mineral equilibria by dilution.

Several water analyses from the same drainage area reflect the dilution pattern and one of the best examples is provided by the Firehole River in Yellowstone National Park (Fig. 4). The log (AP/K) values for the Firehole show a linearly decreasing trend with decreasing conductance. The low conductivity values are representative of that part of the river just upstream from the Upper Geyser Basin before any significant influence from hot spring activity. As hot springs enter the river, log conductivity and the disequilibrium index increase until the maximum values are reached which represent water taken from the Firehole downstream from all major hot spring inputs.

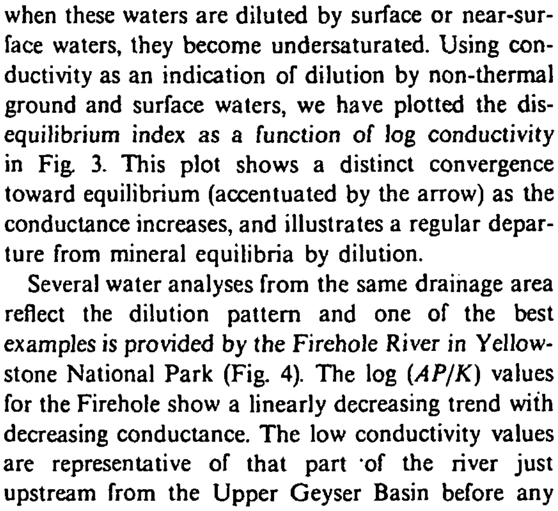


Fig. 3. Variation in the disequilibrium index with the log of the conductivity. The arrow emphasizes the tendency of the disequilibrium indices to approach saturation with increased conductance.

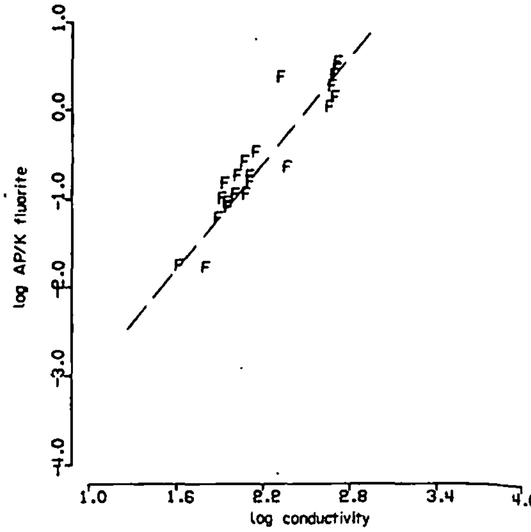


Fig. 4. Variation in the disequilibrium index for the Firehole River in Yellowstone National Park as a function of the log conductivity. The dashed line emphasizes the dilution pattern. The dilution results from a change in discharge or from proceeding upstream away from the thermal basins.

Figure 4 shows a vertical cluster of maximum log (AP/K) values (from Madison Junction where the Firehole joins the Gibbon River) separated from a sloping cluster of lower values (above diversion near Old Faithful). Since the cluster of lower values symbolize waters that are at the edge of Upper Geyser Basin, one would expect changes in the disequilibrium index and log conductivity to change proportionally with the discharge of the Firehole River. As the Firehole decreases in flow seasonally, there should be more contribution from hot springs and consequently higher log (AP/K) and conductance readings. In fact, the lowest two 'F' symbols have the highest discharge of that group and the discharge decreases fairly consistently as one moves up the dashed line. The dilution pattern is remarkably clear from this type of plot and the approach should be applicable in many other types of water chemistry investigations.

We would like to emphasize the agreement between the log AP for hot springs with high conductivity values and the revised log K for fluorite solubility. Using conductivity as a guide to separate dilute surface waters from hot springs we examined a plot of log (AP/K) vs conductivity and found that at 800 $\mu℧$/cm a break occurs which conveniently divides the waters into two major groups. We then replotted all of the log AP-values with conductivities greater than 800 $\mu℧$ vs temperature in Fig. 5a along with the revised log K which is shown by a solid line. By plotting these same values in terms of the disequilibrium index (Fig. 5b) we find that 70% of the geothermal water samples analyzed fall within the equilibrium boundaries (dashed lines). Most of the remaining 30% lie in the undersaturated region and may indicate hot springs which have mixed with dilute ground waters while still maintaining their high temperatures due to heating by rising steam. They may also indicate a low availability of fluorine or of calcium. If saturation with respect to calcite is

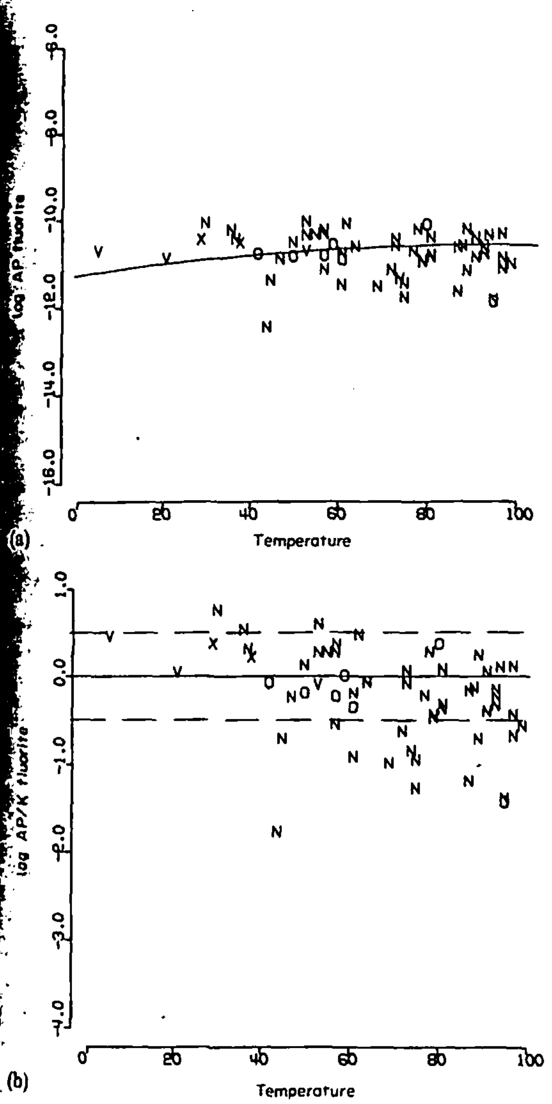


Fig. 5. (a) Log *AP* values for waters with conductivities greater than 800 μ℧ plotted as a function of on-site temperature. The solid line represents the revised log *K* calculated from equation (22). (b) Disequilibrium indices plotted as a function of on-site temperature. The chemical analyses for these samples are given in Appendix 1.

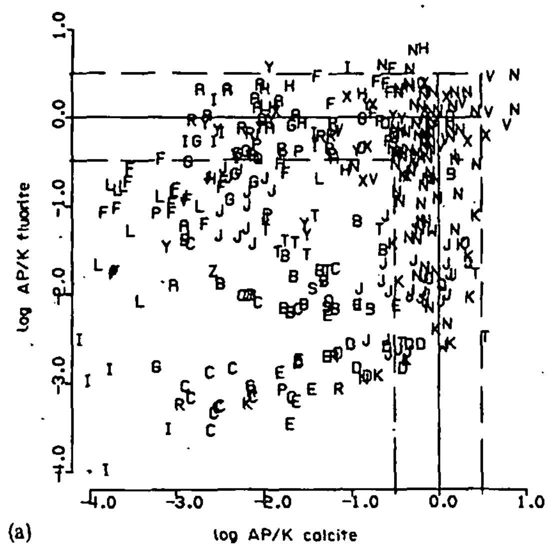
reached as a result of high dissolved carbonate concentrations then calcium concentrations would be suppressed and fluorite undersaturation could result. Unfortunately, the temperature effect on the fluorite solubility curve is less than the variation among log *AP* values and therefore, it is not possible at the present time to distinguish between values which may represent near-surface equilibrium and those which may represent deep, subsurface equilibrium. Direct mineralogic analysis of core samples is perhaps the best available method of determining the spatial distribution of fluorite which will affect its saturation in associated water.

One of the implications from the log *AP* data presented here is that fluorite must be present in the subsurface in these geothermal regions. Unfortunately, only very limited drill core information is available. Bargar *et al.* (1973) have described several hydrothermal minerals including fluorite from a drill core located near Ojo Caliente hot spring in the Lower Geyser Basin, Yellowstone National Park. A water analysis of Ojo Caliente was given from which a disequilibrium index was calculated to be about +0.05, well within the saturation boundaries of ±0.5. Further drill core mineralogy should show fluorite to be a widespread hydrothermal mineral in many geothermal regions of the western United States.

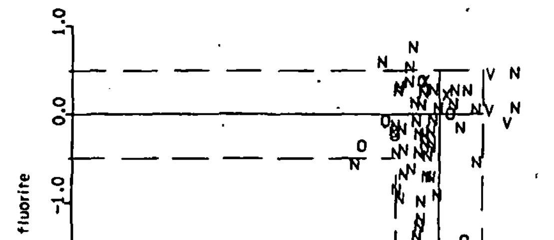
Ellis (1967) points out the common occurrence of calcite at depth in hydrothermal regions and the importance of this mineral in controlling calcium concentrations. By plotting log (AP/K) for fluorite vs log (AP/K) for calcite as shown in Fig. 6a we are able to simultaneously test the effect of solubility by both of these minerals on the chemical composition of these thermal waters. This shows that the solubility limits for fluorite and calcite provide a natural control on water composition, such that calcium, fluoride and carbonate activities are interdependent. In Fig. 6b we removed all of the low conductivity values (<800 μmhos/cm) from Fig. 6a and the remaining waters plot in a group which clusters close to the intersection of fluorite and calcite solubility. The importance of the chemical control of water composition stands out very clearly in this diagram. In addition, it can be seen that all but one of the waters which plotted in the fluorite undersaturated region in Fig. 5b plot within the calcite saturation zone of Fig. 6b. This lends credence to the suggestion that either some of the locations may have low availability of fluorine, or that calcite saturation is preventing fluorite saturation by reducing the calcium activity. Low availability could mean that fluorine occurs in less abundance in the source reservoir at some geothermal areas, or it may indicate other mineral reactions are selectively removing fluorine from the water during its movement to the surface to give an undersaturated *AP* for fluorite.

SUMMARY AND CONCLUSIONS

The concentration of fluorine and calcium of geothermal waters in the western United States is influenced by the equilibrium solubility of calcite and fluorite. Fluorite solubility control on fluoride concentrations is indicated by the near absence of log (AP/K) values greater than 0.5. Convergence of the fluorite activity product to the equilibrium value occurs more systematically with increasing conductivity than with increasing temperatures. This trend suggests that geothermal waters are at equilibrium with fluorite at depth but are diluted to varying degrees upon mixing with low-fluoride surface waters and non-thermal ground waters. Since some of the mixed waters are reheated with rising steam, temperature is a poor indicator of the relative portion of the spring water which is of deep origin. The significant number of samples (70%) which are in equilibrium [for example, log $(AP/K)_{fluorite} = 0.00 \pm 0.5$] suggests that either: (1) some of the waters rise to the surface without dilution by near surface water; or (2) steam loss is balanced by dilution (which seems unlikely);



(a)



(b)

Fig. 6. (a) The disequilibrium indices of fluorite vs calcite show definite bounding conditions for the geothermal waters of the western U.S. These two minerals provide a strong control on the chemistry of hot springs discharging at the surface. (b) The high conductivity waters (see Appendix I) tend to congregate about the intersection of fluorite with calcite saturation which suggests that both of these minerals are equally important in hydrothermally active regions.

or (3) fluorite precipitation with steam loss and dissolution with dilution from ground waters are equilibrium processes as long as the temperature remains sufficiently high for the reaction to proceed rapidly enough.

These tests for equilibrium required revision of the thermodynamic data on fluorite. Critical evaluation of the available data followed by computer refinement gave a pK for fluorite dissolution of 10.96 at 25°C and 1 atm. The agreement of the log AP from higher conductivity waters with this pK provides the major evidence for solubility control by fluorite. It also indicates that careful studies of the chemistry of geothermal waters may provide an indication of the reliability of existing thermodynamic data.

In this study techniques are presented for (1) evaluating thermodynamic data, (2) determining solubility controls on the composition of geothermal waters, and (3) determining the effects of mixing geothermal water with cool dilute waters. The results of this study imply that fluorite should be widely distributed in geothermal areas of the western United States.

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APPENDIX I. PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SA

DATA SET#	PLOT CHAR	DATE	DISCHG CU M/S	TEMP DEG C	PH	SPEC COND	TOT DISS SOLIDS	CA	MG	K
1124	O	5/18/72	0.0	79.0	6.5	1950	1260.0	50.00	0.60	30.0
854	N	5/1/74	0.0	88.0	7.4	2430	0.0	44.00	0.60	26.0
855	N	5/1/74	0.0	72.0	8.6	914	0.0	3.60	0.02	6.5
856	N	5/1/74	0.0	96.0	7.6	6910	0.0	108.00	1.70	42.0
858	N	5/1/74	0.0	56.0	7.2	908	0.0	60.00	15.50	39.0
864	N	5/1/74	0.0	61.0	7.3	1650	0.0	75.00	37.00	31.0
865	N	5/1/74	0.0	54.0	7.2	818	0.0	48.00	12.00	22.0
867	N	5/1/74	0.0	90.0	7.0	1760	0.0	49.00	13.00	41.0
869	N	5/1/74	0.0	56.0	6.3	1730	0.0	53.00	35.00	58.0
870	N	5/1/74	0.0	98.0	9.0	1020	0.0	1.00		16.0
1125	O	5/19/72	0.0	94.0	9.2	1920	1420.0	0.90	0.10	45.0
1126	O	5/24/72	0.0	60.0	7.2	1800	1300.0	3.30	0.10	25.0
1128	O	5/22/72	0.0	56.0	6.5	1790	1260.0	25.00	0.60	37.0
1129	O	5/22/72	0.0	49.0	6.6	1900	1340.0	22.00	0.60	43.00
1163	N	5/1/74	0.0	52.0	6.8	1168	0.0	18.00	0.80	10.80
1164	N	5/1/74	0.0	36.0	7.3	2410	0.0	16.00	0.30	31.00
1165	N	5/1/74	0.0	96.0	7.3	2020	0.0	14.00	0.30	28.00
1166	N	5/1/74	0.0	76.0	6.7	4590	0.0	13.00	2.20	69.00
1167	N	5/1/74	0.0	73.0	8.0	2490	0.0	0.90	0.10	35.00
1168	N	5/1/74	0.0	68.0	7.3	2970	0.0	12.00	1.80	13.00
1169	N	5/1/74	0.0	78.0	8.1	810	0.0	3.70	0.10	3.90
1206	V	5/23/68	0.0	20.0	7.8	1430	985.0	139.00	48.00	34.00
1207	V	5/11/67	0.5	52.0	7.7	1740	1240.0	156.00	59.00	51.00
1233	X	9/13/68	0.0	28.0	7.3	988	699.0	21.00	2.80	22.00
1132	N	5/1/74	0.0	74.0	6.5	810	0.0	33.00	6.80	22.00
1133	N	5/1/74	0.0	80.0	7.9	902	0.0	4.80	0.10	4.50
1135	N	5/1/74	0.0	92.0	7.6	1520	0.0	4.60	0.10	25.00
1136	N	5/1/74	0.0	93.0	7.1	1560	0.0	14.00	0.40	23.00
1138	N	5/1/74	0.0	90.0	7.5	934	0.0	10.00	0.10	8.20
1139	N	5/1/74	0.0	80.0	8.0	947	0.0	8.40		8.70
1141	N	5/1/74	0.0	72.0	6.5	1180	0.0	43.00	9.40	36.00
1143	N	5/1/74	0.0	49.0	6.5	1530	0.0	45.00	4.90	34.00
1145	N	5/1/74	0.0	35.0	7.6	1640	0.0	40.00	3.30	16.00
1151	N	5/1/74	0.0	29.0	7.1	1040	0.0	36.00	4.40	20.00
1152	N	5/1/74	0.0	77.0	6.5	3220	0.0	95.00	25.50	80.00
1153	N	5/1/74	0.0	92.0	7.4	811	0.0	8.80	0.50	13.00
1154	N	5/1/74	0.0	56.0	8.4	6200	0.0	260.00	0.10	160.00
1155	N	5/1/74	0.0	86.0	7.1	7610	0.0	68.00	1.20	130.00
1156	N	5/1/74	0.0	80.0	7.9	1800	0.0	31.00	4.20	17.00
1157	N	5/1/74	0.0	94.0	7.2	3340	0.0	16.00	0.70	66.00
1159	N	5/1/74	0.0	86.0	7.6	1720	0.0	35.00	0.10	7.10
1160	N	5/1/74	0.0	46.0	6.5	2570	0.0	38.00	7.80	36.00
1170	N	5/1/74	0.0	74.0	7.7	1140	0.0	40.00	0.20	7.20
1172	N	5/1/74	0.0	78.0	7.3	1490	0.0	16.00	0.20	11.00
1173	N	5/1/74	0.0	88.0	7.8	1370	0.0	8.80	0.10	9.00
1174	N	5/1/74	0.0	96.0	7.8	1120	0.0	13.00		8.50
1175	N	5/1/74	0.0	43.0	8.4	1790	0.0	2.10	0.10	4.60
1176	N	5/1/74	0.0	71.0	7.6	4300	0.0	210.00	0.20	15.00
1177	N	5/1/74	0.0	44.0	7.8	2890	0.0	225.00	0.10	6.30
1180	N	5/1/74	0.0	63.0	7.4	1330	0.0	34.00	0.50	9.70
1181	N	5/1/74	0.0	60.0	7.6	1090	0.0	24.00	0.20	6.00
1182	N	5/1/74	0.0	87.0	7.3	1010	0.0	8.80	0.20	16.00
1185	N	5/1/74	0.0	92.0	7.3	4030	0.0	100.00	1.30	31.00
1187	N	5/1/74	0.0	60.0	8.2	1173	0.0	72.00	0.20	7.00
1189	N	5/1/74	0.0	52.0	8.3	1370	0.0	3.20		3.40
850	X	9/17/68	0.0	37.0	7.4	1330	949.0	18.00	1.90	31.00
851	V	5/26/67	0.0	4.0	8.0	1320	933.0	133.00	62.00	29.00
1130	O	5/20/72	0.0	58.0	7.5	1500	1000.0	15.00	0.40	22.00
1131	O	5/23/72	0.0	41.0	6.6	1630	1130.0	23.00	1.20	28.00

THE SAMPLES PLOTTED IN FIGS. 5 AND 6b

MG/L							
K	NA	HCO3	CL	SO4	SIO2	F	B
30.00	410.00	735.00	200.00	96.00	110.00	8.40	10.60
26.00	450.00	114.00	380.00	470.00	180.00	7.90	2.40
6.50	190.00	111.00	126.00	111.00	115.00	16.30	0.89
42.00	1480.00	90.00	2200.00	190.00	170.00	5.00	15.00
39.00	120.00	488.00	16.00	72.00	65.00	1.90	0.70
31.00	300.00	1135.00	27.00	32.00	105.00	7.20	0.89
22.00	130.00	482.00	14.00	40.00	40.00	5.20	0.67
41.00	390.00	1180.00	40.00	18.00	84.00	7.20	0.77
58.00	230.00	913.00	1.00	7.00	67.00	6.60	2.10
16.00	230.00	321.00	69.00	130.00	320.00	17.00	2.10
45.00	390.00	450.00	280.00	130.00	340.00	12.00	15.00
25.00	380.00	466.00	250.00	120.00	300.00	11.00	13.00
37.00	310.00	828.00	150.00	68.00	250.00	4.60	7.70
43.00	400.00	845.00	170.00	69.00	240.00	4.80	8.80
10.80	270.00	439.00	24.00	204.00	105.00	12.80	0.89
31.00	500.00	420.00	300.00	350.00	190.00	9.00	16.60
28.00	450.00	374.00	250.00	434.00	160.00	7.20	15.00
69.00	960.00	1196.00	780.00	220.00	120.00	10.20	30.00
35.00	550.00	774.00	240.00	230.00	200.00	16.00	10.50
13.00	630.00	566.00	590.00	140.00	92.00	3.30	11.30
3.90	170.00	202.00	79.00	86.00	83.00	9.00	7.90
34.00	82.00	243.00	107.00	411.00	40.00	1.80	2.10
51.00	117.00	208.00	149.00	547.00	48.00	2.40	3.20
22.00	201.00	528.00	57.00	15.00	113.00	6.20	0.90
22.00	130.00	429.00	18.00	56.00	66.00	1.80	1.10
4.50	180.00	261.00	59.00	120.00	105.00	10.00	1.80
25.00	320.00	436.00	160.00	130.00	160.00	14.00	6.90
23.00	330.00	495.00	160.00	120.00	150.00	12.00	7.50
8.20	180.00	156.00	47.00	230.00	150.00	6.80	2.10
8.70	180.00	139.00	48.00	220.00	160.00	7.10	2.90
36.00	200.00	672.00	22.00	51.00	77.00	4.70	2.60
34.00	250.00	813.00	29.00	110.00	80.00	4.80	2.30
16.00	305.00	112.00	87.00	597.00	46.00	7.40	2.30
20.00	180.00	374.00	40.00	150.00	110.00	7.80	1.90
80.00	540.00	544.00	770.00	51.00	150.00	5.70	3.80
13.00	160.00	366.00	29.00	53.00	135.00	7.80	1.20
160.00	1100.00	24.00	1900.00	340.00	110.00	3.00	6.10
130.00	1400.00	83.00	2200.00	400.00	165.00	4.50	9.90
17.00	340.00	458.00	240.00	46.00	82.00	7.00	1.90
66.00	680.00	364.00	837.00	73.00	270.00	2.10	47.00
7.10	300.00	56.00	430.00	140.00	81.00	1.40	2.60
36.00	610.00	1710.00	50.00	13.00	82.00	3.90	15.00
7.20	190.00	53.00	59.00	400.00	98.00	1.20	1.00
11.00	280.00	153.00	240.00	200.00	180.00	4.90	13.60
9.00	280.00	232.00	170.00	240.00	130.00	5.40	11.20
8.50	210.00	79.00	120.00	260.00	140.00	4.40	6.90
4.60	39.00	406.00	280.00	120.00	94.00	2.20	6.90
15.00	690.00	17.00	1300.00	170.00	96.00	1.20	6.40
6.30	392.00	19.00	788.00	260.00	50.00	0.80	5.10
9.70	240.00	160.00	140.00	290.00	110.00	4.80	6.60
6.00	200.00	161.00	55.00	290.00	170.00	4.70	4.70
16.00	190.00	198.00	120.00	120.00	180.00	9.40	4.10
31.00	720.00	142.00	1300.00	140.00	83.00	3.40	4.10
7.00	190.00	26.00	77.00	400.00	80.00	1.20	2.20
3.40	325.00	493.00	155.00	34.00	104.00	21.00	2.60
31.00	293.00	748.00	67.00	14.00	148.00	6.80	1.00
29.00	58.00	333.00	60.00	393.00	31.00	2.20	0.87
22.00	310.00	516.00	170.00	81.00	150.00	7.50	7.90
28.00	320.00	695.00	150.00	59.00	205.00	4.60	8.10

APPENDIX 2. DESCRIPTION AND SOURCE OF SAMPLES PLOTTED IN FIGS. 5 AND 6b

DATA SET	PLOT CHAR	SAMPLE SOURCE	REFERENCE
1124	O	CA, Long Valley, Hot Spring, Little Hot Creek, 3S/28E-13ES3	Willey, et al., 1974
854	N	NV, Churchill Co., Lee Hot Springs	Mariner, et al.,1974a
855	N	NV, Churchill Co., Dixie Valley Hot Springs	"
856	N	NV, Churchill Co., Flowing well in Stillwater	"
858	N	NV, Elko Co., Hot Hole	"
864	N	NV, Elko Co., Unnamed hot spring near Wells	"
865	N	NV, Elko Co., Unnamed hot spring (Wild Horse Reservoir)	"
867	N	NV, Elko Co., Hot Sulfur Springs	"
869	N	NV, Eureka Co., Hot Springs Point	"
870	N	NV, Eureka Co., Beowawe Hot Spring	"
1125	O	CA, Long Valley, Geothermal Well Magma-Richie 5, 3S/28E-32E95	Willey, et al., 1974
1126	O	CA, Long Valley, Hot Bubbling Pool, 3S/28E-35ES1	"
1128	O	CA, Long Valley, Hot Spring, 3S/29E-21NS1	"
1129	O	CA, Long Valley, Hot Spring, 3S/29E-28HS1	"
1163	N	OR, Harney Co., Unnamed hot spring (Trout Creek)	Mariner, et al.,1974b
1164	N	OR, Harney Co., Hot Lake	"
1165	N	OR, Harney Co., Unnamed hot spring (near Hot Lake)	"
1166	N	OR, Harney Co., Alvord Spring (Indian Spr)	"
1167	N	OR, Harney Co., Mickey Springs	"
1168	N	OR, Harney Co., Unnamed hot spring (near Harney Lake)	"
1169	N	OR, Harney Co., Crane Hot Springs	"
1206	V	WY, Yellowstone Nat'l Park, discharge from Jupiter Terrace, Mammoth Hot Springs	Cox, 1973
1207	V	WY, Yellowstone Nat'l Park, Hot River, near Mammoth	"
1233	X	WY, Yellowstone Nat'l Park, Madison Junction 1	"
1132	N	NV, Humboldt Co., Unnamed hot spring, near Golconda	Mariner, et al.,1974a
1133	N	NV, Humboldt Co., Double Hot Springs	"
1135	N	NV, Humboldt Co., West Pinto Hot Spring (well)	"
1136	N	NV, Humboldt Co., East Pinto Hot Spring	"
1138	N	NV, Humboldt Co., Flowing well near Baltazar Hot Spring	"
1139	N	NV, Humboldt Co., Baltazar Hot Spring	"
1141	N	NV, Lander Co., Spencer Hot Springs	"
1143	N	NV, Lander Co., Buffalo Valley Hot Springs	"
1145	N	NV, Mineral Co., Soda Springs	"
1151	N	NV, Pershing Co., Unnamed hot spring (Jersey Valley)	"
1152	N	NV, Pershing Co., Kyle Hot Springs	"
1153	N	NV, Pershing Co., Leach Hot Springs	"
1154	N	NV, Washoe Co., Steam Geyser (Needle Rocks)	"
1155	N	NV, Washoe Co., Great Boiling Spring	"
1156	N	NV, Washoe Co., Flowing well near Gerlach	"
1157	N	NV, Washoe Co., Steamboat Springs	"
1159	N	OR, Clackamas Co., Austin Hot Springs	Mariner, et al.,1974b
1160	N	OR, Grant Co., Weberg Hot Spring	"
1170	N	OR, Klamath Co., Olene Gap Hot Springs	"
1172	N	OR, Lake Co., Crump (Charles Crump's Spring)	"
1173	N	OR, Lake Co., Berry Ranch Hot Springs	"
1174	N	OR, Lake Co., Hunters Hot Springs	"
1175	N	OR, Lake Co., Summer Lake Hot Spring	"
1176	N	OR, Lane Co., Belkap Hot Springs	"
1177	N	OR, Lane Co., Cougar Reservoir Hot Spring	"
1180	N	OR, Malheur Co., Unnamed hot spring (near Riverside)	Mariner, et al.,1974b
1181	N	OR, Malheur Co., Beulah Hot Springs	"
1182	N	OR, Malheur Co., Neal Hot Springs	"
1185	N	OR, Marion Co., Breitenbush Hot Spring	"
1187	N	OR, Union Co., Medical Hot Springs	"
1189	N	OR, Wasco Co., Kahneeta Hot Springs (Kah-Ne-Tah)	"
850	X	WY, Yellowstone Nat'l Park, Madison Junction 3	Cox, 1973
851	V	WY, Yellowstone Nat'l Park, Mammoth 1	"
1130	O	CA, Long Valley, Hot Spring, 3S/29E-31AS1	Willey, et al., 1974
1131	O	CA, Long Valley, Hot Spring, 3S/29E-34KS1	"

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mineral Resources"
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Geothermal Potential of Western United States—Summary[1]

JOHN E. KILKENNY[2]

Introduction

Most of the commercial geothermal potential of the United States is in Washington, Idaho, Montana, Oregon, Wyoming, California, Utah, Colorado, Arizona, and New Mexico. Figure 1 shows the geologic and geomorphic provinces of the western United States, whose boundaries are influenced by geothermal characteristics. This area is characterized by above-average heat flow, numerous hot springs, recently active volcanoes and calderas, large areas of young volcanic rocks, and numerous active faults.

The distribution of volcanic rocks in the area is shown in Figure 2. The Quaternary volcanic rocks are predominantly basalts but include some andesites and other less basic rocks. Two areas in particular stand out—the Cascade Range and the Snake River downwarp. Smaller areas of Quaternary volcanic rocks are found east of the southern Sierra Nevadas—the Mono Lake and Mammoth areas, California; southwestern Utah; the San Francisco Peaks, Arizona; an area around the southern Arizona–New Mexico border; and the Valles (Baca) Caldera area, north-central New Mexico. Two other important areas of Holocene volcanism are too small to be shown—the Clear Lake area just north of The Geysers steam field in northern California and the southeastern edge of the Salton Sea in the Imperial Valley, southern California. Older volcanics rocks, mostly late and middle Tertiary, are also mainly basic but include some andesites, dacites, and pyroclastic rocks. Some of the early Tertiary volcanic rocks are coarser textured and more silicic. Recently active volcanoes and calderas are considered favorable for geothermal prospecting. The recently discovered geothermal field on the Baca Ranch, Valles Caldera, New Mexico, is a notable example. The late Mesozoic batholiths are drawn to include associated older metamorphic rocks. The Franciscan Complex (Berkland et al, 1972) has a higher than normal heat flow and is the producing formation in The Geysers field.

Figure 3 shows some of the more important hot springs in the western United States. Those springs shown by solid black dots have had at least one exploratory well drilled. None of these wells have been commercially productive because of lack of sufficient temperature, lack of reservoir, or insufficient permeability. Some of the areas, such as Klamath Falls in southern Oregon, are currently producing hot water for space heating. It is possible that some of these areas can be commercially productive with the perfection of heat-exchanger or binary-fluid techniques. Deeper drilling in some areas offers promise of higher temperatures and possibly greater permeability.

The large circles (Fig. 3) represent geothermal fields that are producing or capable of producing geothermal power commercially. In addition to The Geysers and the Valles Caldera, the Cerro Prieto field (in the Salton trough), just south of the California-Mexico border, is shown.

Most of the hot springs in the region are associated with faulting (Fig. 3); normal and lateral faults are most common.

Geothermal Provinces

The presence of significant faults, young volcanic rocks, and hot springs, plus temperature information from wells and gradient holes, permits us to conclude that the Cascades, Snake River downwarp, Basin and Range province, Rio Grande rift, and Salton trough (Fig. 1) all appear to have geothermal potential. The California Coast Ranges, especially the areas of Franciscan outcrops, are warm and interesting. The Coa
Ranges of Oregon and Washington are cool. T
Transverse Ranges and the White-Datil volc
areas are warm.

Unfavorable areas include the young sedi
filled basins of the Rockies and the Grea
of California. The batholithic areas have
heat values. The Sierras are cool, wh
Peninsular Ranges offer some potentia
ly along the Elsinore and San Jacinto
there are many hot springs. The Id
has numerous hot springs, most
along Miocene igneous dikes. All
areas have one unknown factor
All of the important, present
mal fields produce from fra
permeability, and this type o

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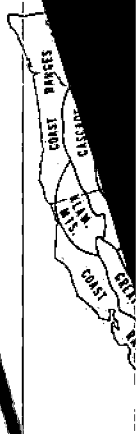

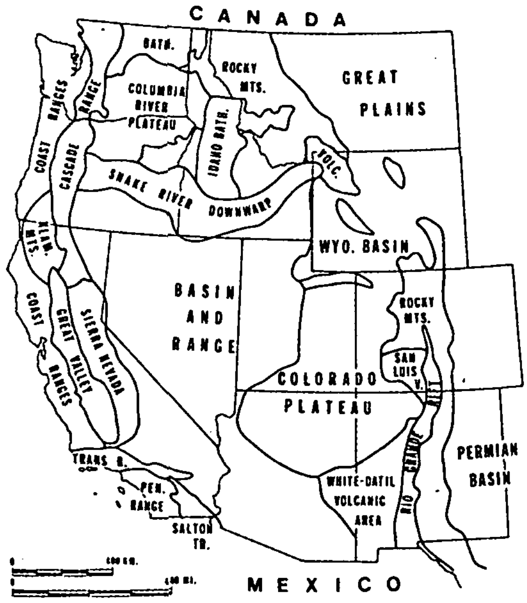

FIG. 1–Geologic and geomorphic provinces of western U.S. High lava plains of eastern Oregon are included with Snake River downwarp.

ficult to predict. Even in sedimentary basins, such as the Salton trough, the porosity of young strata is altered by the high-temperature fluids.

Plate Tectonics

Some of the recently identified oceanic crustal features (Fig. 4) may have a bearing on the source of heat underlying the western United States. The East Pacific Rise extends toward the continent and the Gulf of California. It continues northwesterly up the gulf, offset at intervals by northwest-trending transform fracture zones. Exploratory work on the floor of the gulf indicates that the rise is hot. Elders et al (1972) projected the rise onshore through the Cerro Prieto field and through some boiling mud pots across the border into California, where it is offset by continental "transform" faults such as the San Jacinto. It continues to the Salton Sea and is the source of heat for the Niland geothermal brine field. Just north of this field the rise intersects the San Andreas fault. Menard (1964), Wilson (1970), and Atwater (1970) have made further postulations regarding the northerly continuation of the East Pacific Rise.

A trench is believed to exist along the edge of the continental shelf north of the Mendocino fracture zone parallel with the Oregon and Washington coastline (Silver, 1971). This trench is proposed as an active current subduction zone. The Cascade Range, with its numerous recently active volcanoes, lies about 330 km to the east parallel with the trench. A similar feature—the Middle America Trench—is present off the west coast of Mexico, and an andesitic volcanic chain lies onshore at about the same distance as that between the Cascades and Silver's proposed trench. This volcanic chain is marked by active volcanoes and several geothermal areas including Los Negritos, which is thought to have prospects of developing into a large geothermal field like Cerro Prieto.

Lowell (1974) proposed a subduction zone along the common boundary of the Basin and Range province and the Colorado Plateau. This boundary is also marked by considerable volcanism and the presence of hot springs. Lowell's belief that the Basin and Range crust is underthrusting the Colorado Plateau crust, possibly by as much as 100 km, is substantiated by magnetic data. He proposed another belt of subduction along the Rocky Mountain front where the Rockies meet the Great Plains.

Another interesting theory recently advanced is that of a "fixed-mantle hot spot" (Morgan,

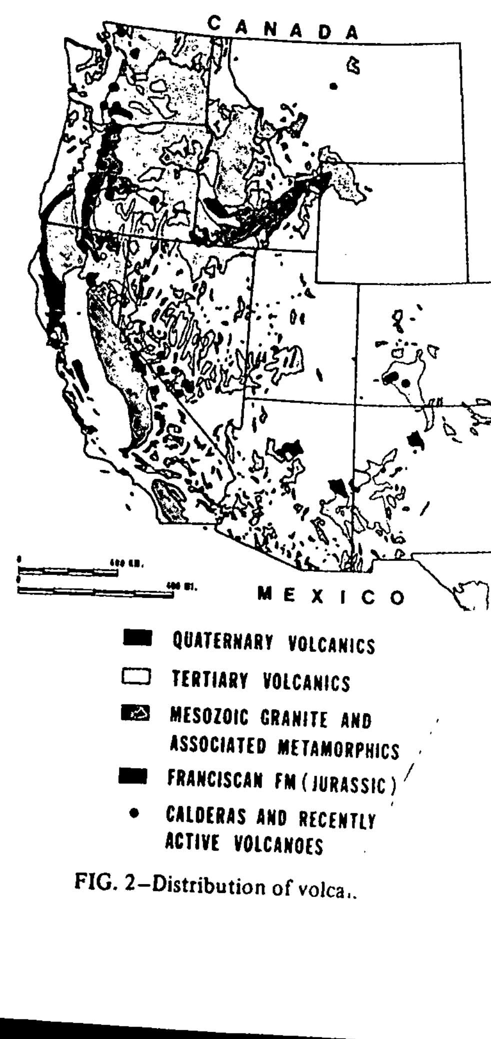

FIG. 2–Distribution of volca..

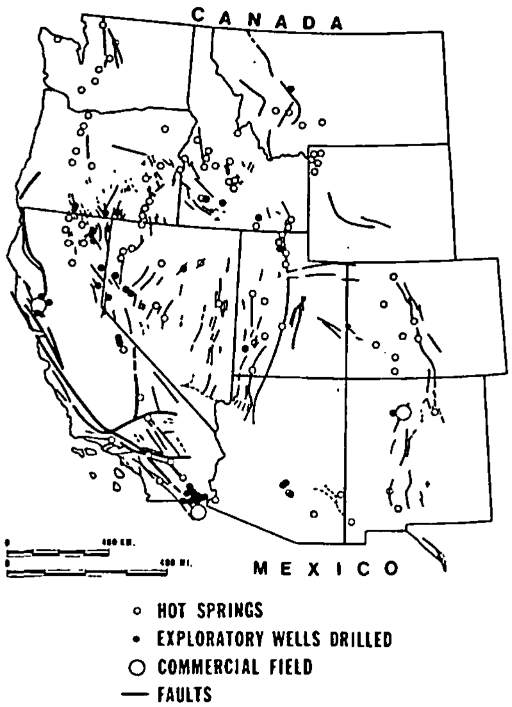

FIG. 3–Hot springs and faults. Most springs with temperatures over 50°C are shown. In places several springs are combined because of map scale.

1971), which explains volcanic trends such as the Hawaiian Island Chain, where volcanism is progressively younger toward the southeast. This is explained as plate motion over a fixed-mantle convection plume. Examples in the western United States might be: (1) the Snake River downwarp, (2) southern Nevada and southern Utah, and (3) the Coast Ranges of California. Several volcanic areas are aligned northwest-southeast. At the southeast end, the volcanic rocks are Miocene. In the vicinity of The Geysers, the volcanic deposits are Pleistocene and Holocene. This progression is explained as the result of southeasterly movement of the American plate with respect to the Pacific plate, and apparent northwesterly movement of the fixed-mantle hot plume.

Promising Areas in Western United States

Figure 5 shows promising areas for geothermal exploration in the United States (Godwin et al, 1971). Known geothermal resource areas (KGRA, category *1*) represent areas where phenomena such as boiling hot springs, shallow test holes, or hydrothermal alteration indicate that the chances for geothermal power production are good. The other areas shown (category *2*) contain lesser hot springs, young volcanic rocks, fumaroles, or hydrothermal alteration of the surface rocks.

In January 1974, the U.S. government opened up lands for geothermal prospecting to individuals and private companies. Lands in category *1* were put up for competitive sealed bids. Lands in category *2* have been made available for simultaneous filing. If two or more companies file on the the same acreage, it is automatically put into category *1* and then put up for competitive bidding.

Explored and/or Producing Areas

The Geysers field—The first recorded drilling for geothermal power at The Geysers, in northern California, was in the 1921–25 period. A group of local businessmen drilled eight shallow wells, the deepest of which went to 200 m. Although steam was encountered, local demand for electricity was insufficient to justify further drilling. Thirty years later, Magma Power Co. began development of the field as a dry-steam reservoir. Deep drilling began in 1966 with Union Oil Co. as operator. The Geysers now is the world's largest geothermal field. Present capacity is over 500 Mw and average well depth is 2,000 m. The reservoir is in fractured graywacke of the Franciscan.

Valles (Baca) Caldera field—Exploration drilling in the Valles Caldera, in Sandoval County, New Mexico, began in 1960 by Westates Petroleum Co. The objective was oil and gas believed to be trapped in the Rio Grande graben in Paleo-

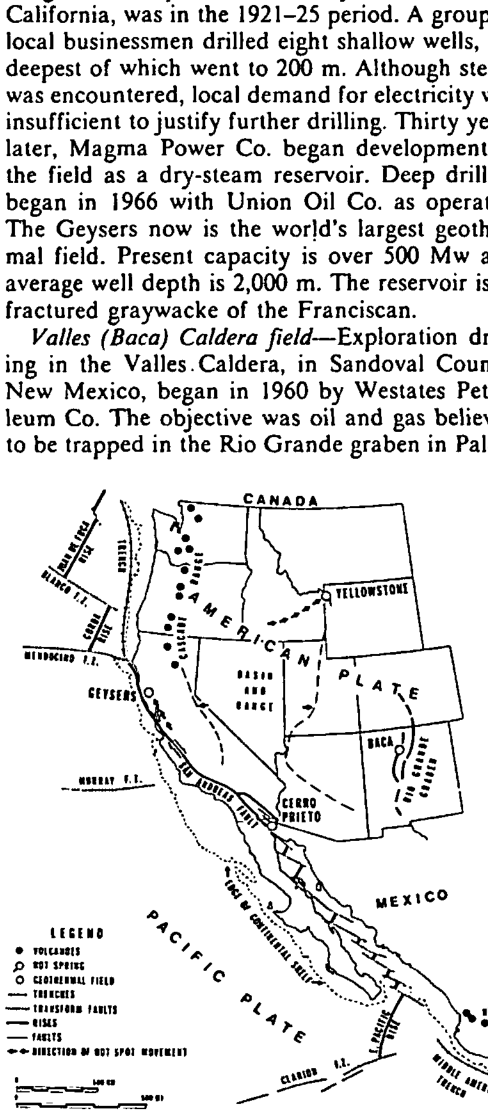

FIG. 4–Plate-tectonic map.

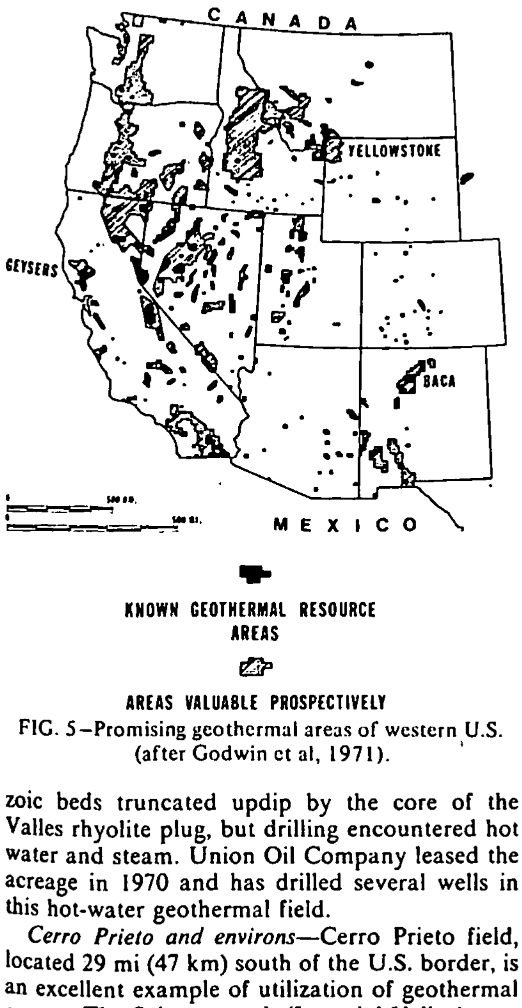

FIG. 5–Promising geothermal areas of western U.S. (after Godwin et al, 1971).

zoic beds truncated updip by the core of the Valles rhyolite plug, but drilling encountered hot water and steam. Union Oil Company leased the acreage in 1970 and has drilled several wells in this hot-water geothermal field.

Cerro Prieto and environs—Cerro Prieto field, located 29 mi (47 km) south of the U.S. border, is an excellent example of utilization of geothermal energy. The Salton trough (Imperial Valley) area has been the site of much exploratory drilling in southern California. More than 20 wells have been drilled in the Niland wet-steam field. Temperatures range as high as 350°C. The high brine content causes a severe corrosion problem and has prevented commercial production to date.

Exploration

Exploratory wells drilled for geothermal prospects, including wells drilled for oil and gas on geothermal anomalies, number 174 in the western United States, in 62 different areas. Of this number, 61 have been drilled below 1,500 m and only 4 have been drilled below 3,000 m. Several deep wells have been drilled for oil and gas in areas of interbedded sedimentary and volcanic rocks with a high heat flow. In addition, hundreds of shallow (less than 100 m deep) water wells, mainly in Idaho, Oregon, and California, have encountered warm or hot water, and some have been used for space heating. Government agencies are conducting geophysical surveys and drilling temperature holes and a few deep tests in selected areas such as Marysville, Montana; Battle Mountain, Nevada; and Los Alamos, New Mexico.

Conclusion

Geothermal exploration has an advantage over early-day oil and gas exploration because of the availability of geophysical methods such as electrical resistivity, gravity, magnetics, seismic noise, magnetotellurics, micro-earthquake recordings, and infrared surveys. Although these tools have been of value in selecting locations, the problems of complexity of the geology, the irregular permeability of igneous and metamorphic rocks, and lack of knowledge of the character of geothermal traps make exploration more risky than searching for oil or gas. So far, the best place to look for geothermal accumulations has been around hot springs.

Any conclusion as to the success ratio and the role that geothermal energy will play in the future must await further drilling. Considerable exploratory drilling should take place in the next few years, because a large amount of exploratory acreage has been leased. Another factor in future exploration will be the perfection of equipment and methods of utilization of lower temperature (150–225°C) fluids with heat-exchanger techniques.

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