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PETROLOGY OF THE MEADE PEAK MEMBER OF THE PHOSPHORIA FORMATION AT COAL CANYON, WYOMING

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by

Robert A. llen Gulbrandsen, 1922–

U. S. Geological Survey
Open File Report

[May, 1958]

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2. Structure and ore deposits of the Darwin quadrangle, Inyo County, California, by Wayne E. Hall. 153 p., 23 figs., 10 pl., 6 tables.

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ABSTRACT

The Coal Canyon, Wyoming, section of the Meade Peak member of the Phosphoria formation is located about 20 miles southeast of the type locality of the Meade Peak member and within the region in which the Meade Peak is characteristically developed. The member is 143 feet thick at Coal Canyon and consists of dark thin-bedded phosphorites, carbonate and quartz-silicate rocks. The rocks of the section have been studied in detail with particular emphasis upon the characteristics of the phosphorites and carbonate rocks and their modes of formation.

The average chemical composition, in percent, of the member is: SiO_2 - 26.5, TiO - 0.2, Al_2O_3 - 4.5, Fe_2O_3 - 1.8, MgO - 4.5, CaO - 27.0, Na_2O - 0.9, K_2O - 1.6, P_2O_5 - 10.6, CO_2 - 13.8, F - 1.1, SO_3 - 2.0, H_2O^- - 0.9, and carbonaceous material - 4.8. This "average rock" contains unusually high amounts of phosphorus and fluorine. The average CaO:MgO ratio for the member is 6, but it ranges from a high of 88 for the average phosphorite to a low of 2.9 for the average carbonate rock.

Important minor constituents that occur in the rocks in significant amounts are vanadium, selenium, and uranium. In four feet of carbonaceous quartz-silicate rock, the vanadiferous zone, vanadium averages 0.7 percent V_2O_5 and selenium contents range from 90 to 150 ppm. Se. The uranium content

of the whole member ranges from 0.0005 to 0.034 percent U and averages 0.004 percent. The higher uranium contents are in phosphorites.

Dolomite makes up 21 percent of the member and calcite 8 percent. Both minerals contain only small amounts of cation substitutes, as indicated by the position of x-ray diffraction peaks. The principal ion diadochic for calcium in calcite is magnesium, and the principal ion diadochic for magnesium in dolomite is calcium. Ratios of calcite to dolomite in the carbonate rocks of the member, determined by an x-ray method, compare favorably with ratios calculated from chemical analyses.

Carbonate-fluorapatite makes up 28 percent of the member. Small amounts of ionic substitutions in the mineral are indicated - sodium, strontium and uranium for calcium; sulfur and silicon for phosphorus; and possibly some fluorine for oxygen.

The quartz-silicate group of minerals makes up 33 percent of the member and is composed of quartz and microcrystalline quartz, orthoclase, microcline, albite, muscovite, biotite, illite, kaolinite, titanite, zircon, and tourmaline. The principal feldspars, orthoclase and albite, were identified by x-ray. Illite-muscovite, determined by x-ray, is more abundant than kaolinite.

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Carbonate-fluorapatite, dolomite, and calcite, chemically related compounds that have calcium and carbonate ions in common, occur in the rocks of the member in three principal associations: carbonate-fluorapatite alone, dolomite--carbonate-fluorapatite mixtures, and dolomite--calcite mixtures. As a basic hypothesis, these occurrences are considered to represent approximately the solid phase or phases in equilibrium with the sea water from which they formed. Where found alone carbonate-fluorapatite represents a first stage differentiation of sea water by evaporation, or a precipitation due to a sustained addition of phosphate to sea water by the dissolution of dead organisms, for example. The dolomite--carbonate-fluorapatite mixtures represent a second stage differentiation, following the precipitation of apatite alone, in which the two minerals form together in proportions high in dolomite. These two closely related kinds of mineral associations are the dominant ones in the section. The dolomite-calcite mixtures cover a wide range of proportions that is not readily explained in terms of simple phase relations. Under conditions in which dolomite is the single solid phase in equilibrium with sea water, however, calcite could precipitate metastably and change with time, while in contact with sea water, to dolomite. In this manner, the amount of dolomite formed is a function of the time during which calcite is in free contact with sea water, and all proportions of dolomite and calcite are possible.

INTRODUCTION

Phosphorites of the Phosphoria formation of Permian age are among the largest and most widely known phosphate deposits in the world and make up a major part of the phosphate resources of this country. The formation contains, in addition, large potentially valuable amounts of minor elements. Because of the present and future economic importance of these deposits, the U. S. Geological Survey has undertaken, partly on behalf of the Division of Raw Materials of the U.S. Atomic Energy Commission, an extensive detailed study of them in the region composed of southwestern Montana, southeastern and southcentral Idaho, western Wyoming, northern Utah, and northeastern Nevada (see figure 1). The present study which is only one of the manifold aspects of the broad program, is concerned with specific knowledge of the Meade Peak member of the Phosphoria formation at Coal Canyon, Wyoming regarding element, mineral, and rock compositions, and the relationships among the constituents. These data bear on many problems of geology, but it has been possible to treat, in some detail, only a few here. Emphasis of the study is on the characteristics of the phosphorites and associated carbonate rocks, and some hypotheses regarding the mode of formation of these rocks are presented.

The stratigraphy of the Phosphoria formation has been

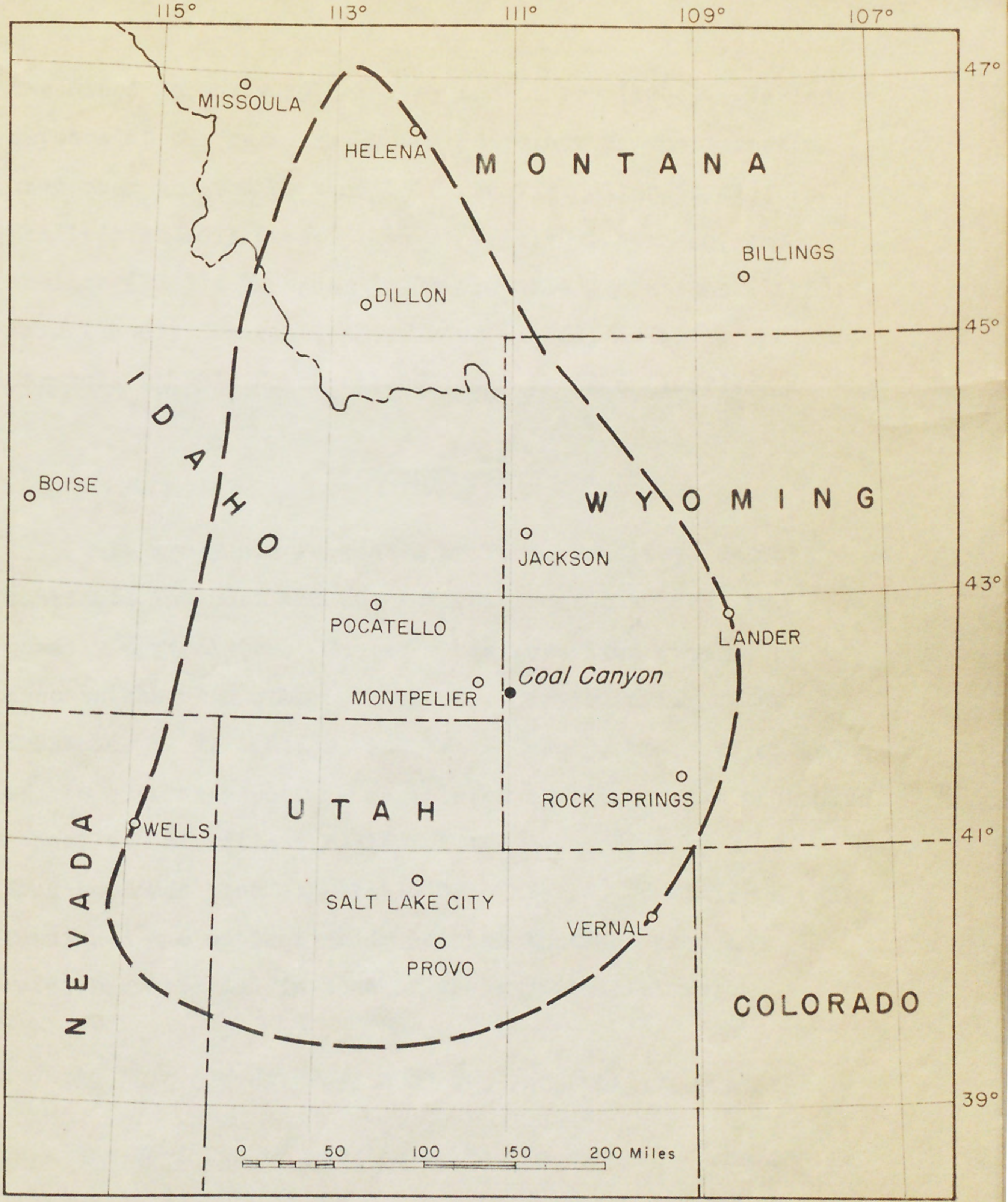

Figure 1.—Index map showing approximate limits of the western phosphate field and location of Coal Canyon stratigraphic section.

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This map or illustration is preliminary and has not been edited or reviewed for conformity with Geological Survey standards or nomenclature.

described recently by McKelvey and others (1956). Various aspects of the petrography and petrology of the formation have been treated by Mansfield (1927); Keller (1941); McKelvey (1946); Lowell (1952); McKelvey, Swanson, and Sheldon (1953); Thompson (1953 and 1954); Cressman (1955); Herr (1955); Weaver (1955); Emigh (1956); McKelvey and Carswell (1956); Rooney (1956); and Sheldon (1957).

ACKNOWLEDGMENTS

This study was suggested by V. E. McKelvey, and his continued interest and suggestions about the work are greatly appreciated. The work has benefited from my discussions with other colleagues, particularily E. R. Cressman, R. P. Sheldon, and T. M. Cheney, who have worked or are currently working on related aspects of the phosphate deposits. A critical review of the manuscript by K. B. Krauskopf has been especially helpful. J. P. Miller kindly furnished the optical grade calcite that was used as reference material in some of the experimental work.

THE COAL CANYON SECTION OF THE PHOSPHORIA FORMATION

The Coal Canyon section of the Phosphoria formation is located in sec. 7, T. 26 N., R. 119 W., Lincoln County, Wyoming (figure 1). A trench exposing the formation, where not naturally exposed, is located on the south side of the canyon on the steeply dipping east limb of the Sublette anticline. The section was measured and described by V. E. McKelvey, L. E. Smith, and D. M. Larrabee, and sampled by R. A. Gulbrandsen. Along with chemical and spectrographic analyses, the section is included in a compilation of stratigraphic sections of the Phosphoria formation by McKelvey, Smith, Hoppin, and Armstrong (1953).

Coal Canyon is about twenty miles southeast of the type section of the Phosphoria at Phosphoria Gulch, Idaho, described by Richards and Mansfield (1912), and lies near the eastern margin of the region in which the Phosphoria is typically developed. McKelvey and others (1956), on the basis of detailed stratigraphic studies, recognize six members of the formation, and reference should be made to their work for descriptions of the units and their regional relationships. The members present at Coal Canyon are, from the base upwards, the Meade Peak phosphatic shale member, the Rex chert member, and the Retort phosphatic shale member. A generalized section taken from McKelvey, Smith, Hoppin, and Armstrong (1953) is presented in figure 2. The Meade Peak member is composed of 144 feet of interbedded soft to hard, fissile to thick-bedded, dark gray phosphorite, carbonate rock and mudstone. The Rex chert member, 67 feet thick, consists of hard gray massive chert and a small amount of gray limestone randomly distributed in the chert as

irregularly-shaped nodules and lenses. The Retort member, 57 feet thick, is composed mostly of thin-bedded hard brownish black mudstone and phosphorite with minor chert, and is similar to the Meake Peak member in general character.

MEADE PEAK PHOSPHATIC SHALE MEMBER

The Meade Peak phosphatic shale member is the economically important member of the Phosphoria formation in the southeastern Idaho-western Wyoming-northern Utah area. The Coal Canyon section lies within this area, and the member has been studied at this locality to obtain detailed information about the nature of the rocks, their associations, and factors relating to their origin.

A detailed columnar section of the member is presented in plate 1. It shows graphically, color, grain size, rock composition, and thickness of bedding, along with a description of mineral composition, structure, and special features of the rocks. Color was determined on crushed rock samples by comparison with a color chart based on the color solid dimensions of the Munsell system; for example, bed P-50 is the color brownish black designated as hue 5 yellow-red of chroma 1 and value 3, or in short-hand notation 5 YR 3/1. The procedure for calculating the mineral norms of the rock composition column is described in a following section.

METHODS OF STUDY

Fine-grained rocks such as those considered here are difficult to study and require complementary types of analysis for the determination of even a minimum of rock characteristics. The analyses utilized here are thin section, x-ray, chemical, and spectrographic. Thin sections were used for the purpose of mineral identification and the study of texture and mineral relationships. X-ray analysis was used for mineral identification, a study of diadochy in the carbonate minerals, the calculation of calcite-dolomite ratios, and differentiation of feldspar types. Chemical and spectrographic analysis was used to determine rock composition and geochemical relationships, for the calculation of mineral norms, and for the study of diadochy in carbonate-fluorapatite and the carbonate minerals.

✓ CHEMICAL COMPOSITION

✓ Major constituents - chemical analyses

constituents

of Sixteen chemical determinations have been made of all but two beds of the section by the Tennessee Valley Authority under the direction of J. H. Walthall (table 1). The analyses were made on splits of channel samples collected from each bed, giving in effect a complete analysis of all the rocks of the section. The chemical analyses serve as the basic data for calculating mineral and mineral

TABLE 1
CHEMICAL ANALYSES

BED NO.	CaO	MgO	CO_2	P_2O_5	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	V_2O_5	F	S AS SO_3	H_2O-	A.I.	L.O.I.	EU	CHEM.U
P-107	29.80	11.1	33.8	0.76	17.58	2.5	0.9	0.54	0.63	0.14	0.04	0.13	0.51	0.26	20.0	35.7	.0005	.001
P-106	39.40	0.47	2.6	25.45	17.80	4.1	1.5	1.50	1.50	0.20	0.05	2.5	2.3	0.67	17.8	6.2	.005	.003
P-105	5.60	0.82	0.9	3.25	61.52	13.3	4.0	0.35	3.90	0.01?	0.07	0.37	0.60	0.79	75.6	5.9	.003	.002
P-104	9.00	0.67	0.8	6.15	57.58	10.9	3.1	0.59	3.30	0.47	0.06	0.59	0.91	1.02	68.8	6.3	.004	.002
P-103	6.60	0.63	0.6	4.35	61.14	12.1	3.4	0.40	3.57	0.45	0.04	0.48	0.76	1.04	73.3	6.3	.003	.001
P-102	9.00	4.2	10.4	0.65	55.26	9.3	3.0	0.84	2.53	0.54	0.02	0.15	0.31	0.43	66.9	13.7	.002	.001
P-101	10.40	0.90	3.2	4.51	57.11	10.2	3.3	1.02	1.67	0.43	0.04	0.52	0.77	0.93	69.3	7.7	.002	.001
P-100	40.80	0.39	3.8	25.9	17.70	3.6	1.1	1.09	0.80	0.17	0.04	2.4	2.0	0.62	19.0	6.5	.005	.003
P- 99	22.20	10.0	26.6	0.81	30.02	4.3	1.5	1.00	1.22	0.31	0.06	0.15	0.48	0.31	35.6	28.3	.001	.001
P- 98 ?	46.2	0.24	4.4	29.8	9.91	1.4	0.8	0.83	0.60	0.09	0.07	3.1	2.3	0.50	8.2	6.2	.009	.008
P- 97 ?	49.1	0.20	2.0	32.9	4.73	0.9	0.6	1.01	0.39	0.07	0.10	3.8	2.9	0.46	3.2	5.4	.022	.021
P- 96 ?	39.8	0.37	1.7	27.2	13.87	2.3	1.1	0.76	1.10	0.16	0.23	2.9	2.9	1.47	12.4	8.6	.034	.034
P- 95 ?	44.1	0.34	2.3	29.8	8.85	1.5	0.7	1.03	0.67	0.07	0.26	3.1	3.2	1.26	7.2	8.0	.026	.028
P- 94	39.7	0.36	1.9	26.9	13.28	2.1	1.0	0.91	0.92	0.12	0.24	2.7	4.0	1.73	11.4	9.6	.018	.019
P- 93 ?	45.7	0.24	2.2	32.7	6.49	1.2	0.5	1.16	0.54	0.05	0.15	3.4	3.5	1.02	5.2	6.9	.019	.019
P- 92	32.40	0.39	1.3	21.6	27.10	4.2	1.7	1.20	1.80	0.26	0.16	2.2	2.8	1.12	22.2	9.0	.017	.008
P- 91	12.80	3.8	8.8	3.80	47.36	7.8	2.6	0.96	2.30	0.42	0.09	0.51	1.1	0.83	58.5	13.5	.004	.002
P- 90	25.60	4.9	24.8	0.20	32.32	3.4	2.0	0.90	1.47	0.01?	0.08	0.12	0.85	0.32	38.6	26.6	.001	.001
P- 89	42.24	0.33	1.6	29.3	12.90	2.0	2.3	1.00	0.77	0.14	0.10	3.0	3.2	0.89	10.6	9.5	.009	.007
P- 88	48.42	0.41	11.8	24.09	6.70	0.8	0.8	1.14	0.45	0.08	0.06	2.6	2.3	0.56	4.7	15.0	.005	.003
P- 87 ?	31.46	0.42	1.8	21.03	27.70	4.4	1.6	1.09	1.24	0.32	0.11	1.9	2.5	0.87	29.2	8.3	.007	.003
P- 86	41.60	0.31	2.1	27.45	15.50	2.1	1.2	1.25	0.70	0.16	0.06	2.9	2.9	0.89	13.9	8.1	.007	.005
P- 85	44.18	0.29	4.7	27.44	14.10	1.4	1.1	1.20	0.40	0.16	0.06	3.0	2.3	0.58	11.3	8.1	.005	.004
P- 84	25.41	0.43	2.0	16.52	34.24	5.3	1.9	1.09	1.60	0.40	0.05	1.6	2.4	1.08	40.4	9.5	.005	.012
P- 83	44.00	0.26	2.3	29.41	13.20	2.3	1.7	0.94	0.62	0.15	0.05	3.2	1.6	0.47	11.80	5.4	.009	.006
P- 82	26.80	2.1	20.8	2.11	35.27	5.8	2.1	0.74	1.45	0.19	0.06	0.24	0.90	0.34	41.2	22.1	.002	.0005
P- 81	13.40	4.2	10.0	4.04	47.21	8.8	2.5	0.84	2.43	0.42	0.05	0.45	0.90	0.62	56.8	14.2	.003	.001
P- 80	26.4	0.90	9.6	9.90	31.21	6.7	2.3	0.45	1.89	0.32	0.09	1.1	2.1	1.35	37.0	16.8	.006	.003
P- 79	15.40	2.21	10.5	2.16	47.41	9.7	3.0	0.62	2.45	0.10	0.05	0.31	1.0	0.86	54.7	16.5	.003	.000
P- 78	42.10	0.43	1.9	28.67	7.70	1.9	2.1	0.90	0.67	0.14	0.11	2.8	3.5	1.55	5.62	13.1	.006	.004

Who made analyses? Should be on Table - acknowledgments rather than

TABLE 1 (CONTINUED)

BED NO.	CaO	MgO	CO_2	P_2O_5	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	V_2O_5	F	S AS SO_3	H_2O-	A.I.	L.O.I.	EU	✓ CHEM.U
P- 77	30.80	1.70	14.0	9.92	✓21.10	6.2	2.6	1.00	1.49	0.26	0.07	1.1	2.2	1.37	25.2	22.0	.003	.003
P- 76	50.22	1.8	40.2	0.36	✓4.82	1.1	0.5	0.60	0.72	0.03	0.06	0.06	0.44	0.13	5.90	41.1	.004	.001
P- 75	8.40	1.9	5.0	2.73	✓47.18	8.6	3.4	1.25	2.12	0.52	0.52	0.44	8.6	0.51	59.30	16.7	.006	.002
P- 74	6.05	2.3	5.9	0.34	41.64	9.8	3.9	0.78	2.55	0.18	1.75	0.15	12.5	0.83	51.2	24.9	.005	.002
P- 73	4.20	2.7	5.1	0.20	✓45.64	9.6	4.0	0.99	2.78	0.23	1.45	0.23	10.6	0.52	56.38	22.6	.003	.001
P- 72	4.20	2.9	5.6	0.05	✓52.58	9.7	4.4	1.30	2.85	0.36	0.37	0.08	8.4	0.32	65.75	16.6	.003	.0005
P- 71	15.60	1.4	6.4	6.30	✓37.36	7.1	3.3	1.27	2.11	0.28	0.14	0.67	9.4	0.37	46.66	17.4	.004	.002
P- 70	36.40	1.8	29.3	0.80	✓22.98	2.6	1.2	1.10	0.70	0.06	0.06	0.10	0.60	0.29	27.6	30.07	.001	.0005
P- 69	13.20	0.53	0.52	8.31	✓48.07	9.2	3.6	1.30	2.38	0.48	0.08	0.80	1.6	1.33	57.9	10.03	.004	.002
P- 68	5.40	2.4	5.1	0.76	✓59.80	9.3	2.8	1.50	2.30	0.42	0.08	0.09	0.90	0.99	73.0	11.4	.002	.0005
P- 67	9.48	0.48	0.59	6.02	✓53.23	10.3	3.4	1.20	2.62	0.61	0.06	0.57	1.6	1.41	65.1	10.3	.003	.001
P- 66	23.20	5.4	23.0	0.66	33.46	5.7	1.9	1.20	1.30	0.24	0.05	0.08	0.62	0.46	41.4	25.9	.001	.0005
P- 65	22.2	1.2	6.1	9.97	✓35.28	8.0	2.6	1.20	2.14	0.38	0.03	1.1	2.0	1.32	42.4	14.3	.004	.002
P- 64?	20.20	8.6	23.3	1.51	✓32.75	5.9	1.9	1.44	1.25	0.27	0.05	0.18	0.55	0.39	39.9	25.7	.001	.001
P- 63	24.40	0.80	5.1	12.38	✓29.90	8.5	2.6	1.02	1.95	0.38	0.08	1.3	2.2	1.62	25.23	15.9	.003	.002
P- 62	28.40	1.0	7.3	13.73	20.82	5.1	2.1	0.94	1.35	0.26	0.17	1.4	3.0	1.85	25.1	18.7	.007	.004
P- 61	32.40	5.3	30.1	0.69	✓19.60	4.3	1.4	0.95	0.95	0.13	0.05	0.09	0.56	0.45	15.0	33.1	.001	.000
P- 60	25.6	12.3	30.3	2.22	✓18.63	3.6	1.3	1.26	0.97	0.10	0.05	0.22	0.80	0.54	23.4	33.7	.001	.002
P- 59	26.40	3.4	7.9	14.29	✓22.60	7.1	2.3	0.89	1.70	0.29	0.08	1.3	2.5	1.76	26.53	18.2	.004	.004
P- 58	29.60	15.1	36.2	2.10	✓8.27	2.2	0.7	0.80	0.50	0.06	0.07	0.22	1.0	0.77	10.47	40.7	.001	.001
P- 57	20.07	0.63	0.86	13.63	✓32.60	10.5	3.1	0.75	2.60	0.38	0.05	1.5	2.5	1.86	38.27	15.2	.004	.002
P- 56	29.72	15.0	36.7	2.24	✓7.82	2.2	0.7	0.60	0.71	0.10	0.05	0.27	0.60	0.43	25.48	40.0	.001	.001
P- 55	32.05	6.1	14.4	14.85	✓13.10	4.3	1.4	0.79	1.22	0.18	0.21	1.5	2.5	1.23	15.28	22.4	.005	.002
P- 54	31.80	10.9	32.3	5.38	✓8.69	1.3	0.9	0.50	0.66	0.11	0.04	0.56	1.1	0.58	10.8	35.9	.002	.001
P- 53	32.82	1.0	2.4	21.00	✓10.60	4.5	1.7	0.75	1.20	0.13	0.09	2.1	3.9	1.00	11.68	18.9	.005	.003
P- 52	36.00	13.0	33.00	8.11	✓5.20	0.1?	0.5	0.60	0.40	0.13	0.07	0.78	1.0	0.41	4.93	35.8	.002	.001
P- 51	36.45	0.77	2.2	24.35	✓15.53	2.8	1.7	1.15	1.12	0.25	0.08	2.6	3.1	1.24	16.55	11.9	.006	.003
P- 50	27.20	8.0	28.6	4.42	✓14.50	3.0	1.1	0.78	1.12	0.04	0.06	0.47	1.7	1.07	18.02	34.8	.002	.001
P- 49	40.37	0.98	3.4	26.01	✓11.50	3.1	1.4	1.56	0.95	0.16	0.06	2.9	3.0	0.53	10.08	11.2	.005	.002
P- 48	26.60	13.2	31.2	4.04	✓11.19	1.7	1.0	0.58	0.82	0.07	0.07	0.44	1.7	1.00	13.63	37.0	.001	.001

TABLE 1 (CONTINUED)

BED NO.	CAO	MGO	CO_2	P_2O_5	SIO_2	AL_2O_3	FE_2O_3	NA_2O	K_2O	TIO_2	V_2O_5	F	S AS SO_3	H_2O–	A.I.	L.O.I.	EU	CHEM.U
P- 47	27.36	13.9	32.8	3.05	10.47	1.7	0.9	0.84	0.69	0.06	0.09	0.35	1.6	1.10	12.92	38.7	.000	.000
P- 46	24.96	9.9	24.4	4.85	19.38	3.7	1.7	0.89	1.59	0.22	0.08	0.56	1.6	1.15	23.8	30.5	.002	.001
P- 45	45.45	0.39	4.3	28.85	5.17	1.3	0.9	1.00	0.49	0.07	0.08	3.3	2.7	1.01	3.46	11.0	.007	.008
P- 44	38.80	0.58	2.0	26.24	12.80	2.3	1.2	1.35	0.79	0.15	0.25	2.9	3.8	1.46	10.0	13.6	.015	.012
P- 43	43.73	0.57	1.8	29.26	9.50	1.2	1.0	0.97	0.54	0.11	0.13	3.2	3.0	0.79	8.9	8.7	.016	.010
P- 42	28.40	12.8	30.6	4.41	14.42	2.0	0.8	0.70	0.85	0.11	0.05	0.44	0.96	0.44	17.8	33.7	.001	.001
P- 41	18.40	1.9	4.3	10.75	36.80	7.9	2.5	1.44	1.62	0.28	0.05	1.1	1.8	1.06	48.2	11.7	.005	.002
P- 40	16.2	8.4	19.5	1.55	38.32	4.6	2.1	1.19	2.17	0.06	0.05	0.19	0.63	0.59	47.4	22.5	.001	.001
P- 39	20.00	1.5	3.5	12.33	36.80	8.5	2.5	0.87	3.27	0.34	0.07	1.1	1.8	0.20	47.2	10.2	.004	.002
P- 38	23.2	12.4	28.6	1.90	25.56	2.2	0.9	0.45	0.85	0.06	0.04	0.21	0.71	0.41	28.7	31.5	<.011	.007
P- 37	24.20	10.3	24.4	4.75	26.12	2.3	0.8	0.80	1.05	0.26	0.05	0.50	1.0	0.54	29.2	27.6	.001	.000
P- 36	24.53	9.1	22.6	7.08	25.76	2.4	0.8	1.00	0.97	0.13	0.05	0.75	1.2	0.60	28.8	24.7	.002	.001
P- 35	34.40	0.41	1.6	23.34	23.70	3.7	1.3	1.00	1.40	0.22	0.06	2.8	2.9	0.77	25.2	8.2	.006	.002
P- 34	43.65	0.19	1.6	30.00	10.75	1.8	0.7	1.08	0.51	0.08	0.09	3.2	3.4	0.72	9.4	7.6	.011	.007
P- 33	12.7	0.64	1.1	8.1	44.45	3.0	2.6	0.30	2.73	0.40	0.35	0.83	4.5	3.88	48.9	19.6	.009	.006
P- 32	--	5.4	13.1	7.2	--	2.2	2.0	--	--	--	--	0.71	2.0	--	41.1	19.1	.004	.004
P- 31	27.2	0.39	1.3	18.1	30.01	2.0	1.8	0.86	1.81	0.33	0.42	1.8	3.7	2.10	33.3	11.6	.014	.014
P- 30	--	3.0	7.2	8.0	--	2.5	2.2	--	--	--	--	0.84	2.1	--	49.5	13.4	.007	.006
P- 29	21.5	4.8	11.6	6.0	36.28	2.4	1.9	1.10	2.03	0.36	0.23	0.88	3.1	1.19	40.2	16.6	.008	.007
P- 28	26.7	9.5	22.9	6.4	22.93	1.3	1.2	1.02	1.30	0.23	0.18	0.71	1.3	0.75	25.5	25.7	.002	.002
P- 27	37.5	0.46	2.0	26.3	15.75	2.1	1.1	0.95	1.35	0.16	0.30	2.4	3.5	1.52	14.6	9.4	.015	.020
P- 26	39.7	1.5	4.9	26.1	14.06	1.6	0.9	0.77	1.36	0.13	0.17	2.4	2.8	1.09	13.6	9.3	.016	.007
P- 25	42.9	0.59	2.5	29.5	12.04	1.1	0.7	0.72	0.99	0.10	0.08	3.0	2.4	0.99	10.9	7.1	.007	.007
P- 24	42.3	0.60	3.3	28.6	11.63	1.4	0.7	0.90	0.88	0.10	0.09	2.6	2.8	0.87	10.5	7.8	.010	.010
P- 23	41.2	0.80	3.6	26.7	13.36	1.9	0.8	0.95	1.07	0.12	0.14	2.7	3.1	1.22	12.3	9.1	.012	.013
P- 22	35.4	2.2	6.4	21.1	18.16	2.0	1.0	0.83	1.51	0.16	0.10	2.1	3.1	1.48	18.5	12.2	.008	.010
P- 21	30.4	3.7	9.8	16.4	22.77	2.2	1.3	0.70	1.88	0.21	0.09	1.8	2.7	1.39	24.4	14.7	.012	.010
P- 20	27.8	5.0	12.5	12.8	25.87	2.8	1.4	0.60	1.53	0.21	0.08	1.4	2.1	1.30	28.0	17.1	.005	.004
P- 19	29.4	3.3	8.6	15.5	25.91	2.7	1.3	0.63	2.26	0.21	0.06	1.7	2.3	1.38	27.3	14.0	.007	.006
P- 18	26.[illegible]	9.0	23.5	6.9	21.20	2.0	1.2	0.30	2.29	0.11	0.06	0.82	1.1	0.70	23.8	26.5	.002	.002

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This map or illustration is preliminary and has not been edited or reviewed for conformity with Geological Survey standards or nomenclature.

TABLE 1 (CONTINUED)

BED NO.	CAO	MGO	CO_2	P_2O_5	SIO_2	AL_2O_3	FE_2O_3	NA_2O	K_2O	TIO_2	V_2O_5	F	S AS SO_3	H_2O-	A.I.	L.O.I.	EU	CHEM.U
P- 17	30.9	5.9	16.0	13.3	✓ 21.25	1.7	1.1	0.42	1.65	0.31	0.05	1.6	1.5	0.71	22.7	19.0	.004	.004
P- 16	28.2	12.2	33.2	5.2	✓ 16.21	1.2	0.5	0.33	0.79	0.09	0.05	0.55	1.0	0.59	16.1	32.6	.008	.002
P- 15	36.40	2.4	7.1	21.55	✓ 16.64	3.1	1.3	0.83	1.52	0.15	0.05	2.5	2.6	0.71	18.5	11.9	.004	.003
P- 14	30.60	12.3	29.8	6.4	✓ 15.20	0.5	0.8	0.40	0.78	0.08	0.05	0.74	1.1	0.57	16.5	31.7	.001	.001
P- 13	35.00	6.7	17.7	15.69	✓ 16.02	1.2	1.5	0.77	0.83	0.17	0.05	1.6	1.2	0.55	16.2	20.2	.003	.002
P- 12	32.15	10.1	25.3	11.5	✓ 13.00	0.9	0.7	0.62	0.69	0.12	0.05	1.3	2.3	1.46	12.2	27.3	.004	.003
P- 11	43.82	0.6	3.7	28.9	✓ 10.09	1.1	0.7	1.09	0.45	0.16	0.11	3.4	3.5	0.70	7.9	9.1	.015	.013
P- 10	16.32	3.7	8.0	7.5	✓ 39.08	5.6	2.7	0.45	2.25	0.24	0.09	0.91	2.8	1.53	44.0	18.3	.008	.005
P- 9	26.8	9.5	21.9	9.7	✓ 17.98	2.4	1.4	0.42	1.31	0.14	0.09	0.93	2.1	1.35	20.0	25.6	.002	.001
P- 8	31.1	0.57	1.9	20.6	✓ 26.27	3.2	1.6	0.79	1.58	0.19	0.17	2.2	3.7	1.82	26.4	9.0	.008	.007
P- 7	9.1	0.80	0.8	5.0	✓ 55.29	4.2	3.4	0.59	3.96	0.45	0.36	0.77	3.1	2.36	62.7	11.5	.005	.003
P- 6	10.00	5.8	13.3	0.26	✓ 53.36	7.5	2.5	0.40	4.10	0.18	0.09	0.12	0.392	0.33	64.7	14.9	.002	.002
P- 5	4.96	3.0	6.1	0.3	✓ 61.56	9.7	3.1	0.17	4.63	0.16	0.04	0.19	1.5	0.78	73.5	10.7	.003	.001
P- 4	0.64	0.87	0.3	0.44	✓ 61.56	9.8	4.6	0.24	5.03	0.11	0.19	0.29	3.7	1.58	74.7	12.8	.004	.001
P- 3	7.28	0.72	0.3	0.16	✓ 71.04	8.8	3.7	0.30	5.07	0.10	0.11	0.23	1.6	0.95	81.5	6.6	.002	.001
P- 2	2.60	1.4	2.3	0.67	✓ 69.28	10.1	3.1	0.35	4.50	0.18	0.08	0.25	1.1	0.75	80.3	6.5	.003	.001
P- 1	42.24	1.9	5.1	29.05	✓ 10.20	2.5	0.7	0.95	0.40	0.07	0.10	2.9	2.2	0.42	8.3	7.4	.009	.005

group norms, and for determining the geochemical relationships of the elements.

Quantitative chemical analysis of rocks of the Phosphoria is complex and difficult. The accuracy of the analyses is not known, but some measure of precision is obtained from a number of duplicate analyses. For these the mean deviation ranges from about 0.5 percent to 1.5 percent for a number of constituents. Percentage error (mean deviation divided by average amount of constituent) is greatest for those constituents in small amount and is as much as 50 percent. In general the precision is sufficient for most purposes for those constituents in large amount. The overall precision is not sufficient for the calculation of silicate mineral norms, yet the mineral norm calculations for carbonate-fluorapatite, calcite, and dolomite are the best quantitative estimates that can be made for these minerals. Comparisons of the constituents among individual beds are hazardous, but the comparisons of averages of groups of beds are very useful.

Averages and comparisons

The average chemical composition of the Meade Peak member (table 2) is unique among stratigraphic units for which chemical data are known because of its high phosphorus (about 11 percent P_2O_5) and fluorine (about one percent)

Table 2

Average chemical composition of end-member rock types (15 samples of each type) and of total Meade Peak member

	Weight percent			
	Carbonate rock	Phosphorite	Quartz-silicate rock	Meade Peak member
CaO	28.9	43.9	7.0	27.0
MgO	9.9	0.5	1.7	4.5
CO_2	30.3	3.0	3.4	13.8
P_2O_5	2.6	29.5	2.6	10.6
SiO_2	17.7	10.0	58.1	26.5
Al_2O_3	2.5	1.5	9.6	4.5
Fe_2O_3	1.1	1.0	3.4	1.8
Na_2O	0.8	1.0	0.7	0.9
K_2O	0.9	0.6	3.4	1.6
TiO_2	0.1	0.1	0.4	0.2
V_2O_5	0.1	0.1	0.1	0.1
F	0.3	3.1	0.4	1.1
SO_3	1.0	2.9	2.3	2.0
H_2O-	0.6	0.8	1.0	0.9
L.O.I. (loss on ignition)	33.8	8.3	10.4	19.5
Carbonaceous material (L.O.I. $-CO_2 - H_2O-$)	2.9	4.4	6.1	4.8

contents. Calcium and silica are present in about equal amount. The silica content (about 26.5 percent) is low, however, relative to its amount in many sedimentary rocks, and this indicates the subordinate role of detrital components in the rock section. Some measure of the range in concentration of the constituents is shown in table 2 which compares the average values of the member as a whole with the averages of the three major end-member rock types that occur in the section.

These end-member rocks, fifteen of each type, are those that contain the greatest amounts of their characterizing constituents--carbonate minerals, carbonate-fluorapatite, and quartz and silicate minerals, respectively. The number of samples was largely arbitrarily determined, but an equal number of each type was selected in order to simplify statistical calculations, which are used in other kinds of comparisons, that are described farther on.

The average end-member carbonate rock is magnesium-rich and contains more dolomite than calcite. The average quartz-silicate rock is fairly similar to average shale, although phosphorus is still more than ten times greater than Clarke's (1924, p. 30) value.

Ratios of constituents, which are often better than absolute amounts for comparison purposes, are presented in table 3. Some of the larger differences suggest that titanium of all the Meade Peak rocks is low, relative to

Table 3

Comparison of ratios of constituents in end-member rock types and entire Meade Peak member with other shale and limestone averages.

	$\frac{SiO_2}{TiO_2}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3^*}$	$\frac{CaO}{MgO}$	$\frac{K_2O}{Na_2O}$
Meade Peak member (total)	130.	5.9	2.4	6.0	1.8
Carbonate rock (15 samples)	150.	7.1	2.3	2.9	1.1
Phosphorite (15 samples)	100.	6.7	1.5	88.0	0.6
Quartz-silicate rock (15 samples)	170.	6.0	2.8	4.1	4.8
Average shale (Clarke, 1924, p.30)	90.	3.8	1.6	1.3	2.5
Average limestone (Clarke, 1924, p.30)	86.	6.4	1.5	5.4	6.6
Average carbonate rock of Mississippian, Pennsylvanian and Permian ages (Chilingar, 1956, p. 2257)				13.5	

*Total Fe calculated as Fe_2O_3

silica, in comparison with average shale and limestone; aluminum is low, possibly iron is too, in the quartz-silicate rocks as compared to shale; magnesium is relatively very low in phosphorite and high in carbonate rock in comparison with average limestone, and low in quartz-silicate rock versus average shale; and sodium is high in phosphorite and carbonate rock as compared to average limestone, but low in the quartz-silicate rock as compared with shale.

It is not known to what extent these variations are significant, but they may reflect particular conditions of origin of the rocks. The high sodium relative to potassium in the carbonate rock as compared with the average limestone, for example, may indicate greater salinity, with respect to sodium, of the solution in which the carbonate minerals formed, particularly if much of the sodium occurs in occluded liquid, or in substitution in the carbonate minerals.

Minor constituents

Spectrographic analyses

Spectrographic analyses for 29 minor elements, including vanadium and titanium which were also analyzed chemically, have been made on samples of all the beds of the section by the U. S. Bureau of Mines Laboratory in Albany, Oregon--included in an earlier report by McKelvey, Smith, Hoppin, and Armstrong (1953). The results of these analyses are shown graphically in plate 2 in which the heavy vertical lines represent the modal class (i.e., the most frequently occurring class) for each element, and the blocks represent those samples whose values are above or below the modal class. Patterns within the blocks indicate the principal end-member rock type--phosphorite, carbonate rock or quartz-silicate rock--occurring in the section. For example, bed 34 is a phosphorite; its copper content falls in class F, one class above the modal class; the silver value falls in the modal class and so is not represented by a block; and so on.

Table 4 summarizes the spectrographic data with respect to the end-member rock types. On the basis of the frequency of occurrence of the classes of values with the rock types, phosphorite contains relative concentrations, with respect to one or both of the other rock types, of Ag, Sr, Zn, V, and Ni (?); quartz-silicate rock contains relative concentrations of B, Ti, Zr, V, Nb, Mo, Mn, and Ni; and carbonate rock contains Mn (?). Some of these relationships can be explained readily. Strontium undoubtedly occurs in apatite of the phosphorite; titanium in titanite (sphene), zirconium cca in zircon, and boron in tourmaline are associated with the quartz-silicate components; and manganese is an expectable constituent of calcite and dolomite. The others cannot be explained so simply as constituents of specific minerals although McConnell (1953) believes vanadium can occur as

Table 4

Occurrence of minor elements in end-member rock types. The number of samples of each rock type falling within each concentration class are listed below.

Element	Rock Types	Concentration Class* D	E	F	G	ND
Copper (Cu)	Phosphorite			3	12	
	Carbonate rock			1	14	
	Quartz-silicate rock			1	14	
Silver (Ag)	Phosphorite		1		14	
	Carbonate rock				9	6
	Quartz-silicate rock				8	7
Beryllium (Be)	Phosphorite				3	12
	Carbonate rock				1	14
	Quartz-silicate rock				1	14
Strontium (Sr)	Phosphorite	1	10			4
	Carbonate rock		6			9
	Quartz-silicate rock		4	2		9
Barium (Ba)	Phosphorite		7			8
	Carbonate rock		9			6
	Quartz-silicate rock		10			5
Zinc (Zn)	Phosphorite		7	2		6
	Carbonate rock		2			13
	Quartz-silicate rock		3			12
Boron (B)	Phosphorite		1	14		
	Carbonate rock		1	14		
	Quartz-silicate rock		13	2		
Titanium (Ti)	Phosphorite		15			
	Carbonate rock		15			
	Quartz-silicate rock	10	5			

Table 4 (Continued)

Occurrence of minor elements in end-member rock types.

Element	Rock Types	Concentration Classes* D	E	F	G	ND
Zirconium	Phosphorite		5	10		
(Zr)	Carbonate rock		4	11		
	Quartz-silicate rock		15			
Lead	Phosphorite		3			12
(Pb)	Carbonate rock		2			13
	Quartz-silicate rock		2			13
Vanadium	Phosphorite	4	10	1		
(V)	Carbonate rock		13	2		
	Quartz-silicate rock	4	10	1		
Niobium	Phosphorite	1	2	2		10
(Nb)	Carbonate rock		2			13
	Quartz-silicate rock		10			5
Chromium	Phosphorite	1	14			
(Cr)	Carbonate rock		13	2		
	Quartz-silicate rock		13	2		
Molybdenum	Phosphorite			13		2
(Mo)	Carbonate rock			11		4
	Quartz-silicate rock		5	9		1
Manganese	Phosphorite		2	11		2
(Mn)	Carbonate rock		5	10		
	Quartz-silicate rock		9	6		
Nickel	Phosphorite		10	5		
(Ni)	Carbonate rock	1	6	7		1
	Quartz-silicate rock		13	2		

* Concentration classes:

D = 0.1-1.0%
E = 0.01-0.1%
F = 0.001-0.01%
G = 0.001%
ND = not detected

an ion substitute in apatite, and W. W. Rubey (in McKelvey, 1946, p. 30) suggests that vanadium occurs in part in a clay mineral or mica; J. Owen (written communication) and A. D. Weeks (written communication) have identified sphalerite in Meade Peak rocks at other localities, which could account for the mode of occurrence of some zinc, at least. Manganese tends to favor quartz-silicate rock but the reason for this is not known. The other elements, Ag, Ni, Mo, and Nb, are likely associated with the carbonaceous component of the rocks.

Krauskopf (1955, p. 422) found that the group of elements, Ag?, As, Mo, Ni, Pb, V, Zn, and Cr, is enriched in both black shales and phosphorites, and he attributes this to the carbonaceous material common to both. In addition to these elements he found Co, R. E. (rare earths), Sr, Be?, and Nb? enriched in the phosphorites. In the Coal Canyon samples, Co was not detected at the sensitivity level, .01 percent, of the method at the time the analyses were made; R. E. were not looked for; Sr is enriched as noted above; Be would be of questionable enrichment, again because of its sensitivity level; Nb, in contrast is distinctly enriched in the quartz-silicate rocks, but all the determinations here are probably in error, on the basis of later and better analyses of other Phosphoria rocks.

In a study of the factors controlling concentrations of rare metals in sea water, Krauskopf (1956, p. 30) found that adsorption and biologic processes are the most general controls, that sulfide formation may be of local importance for a few elements, and that one element, chromium, forms an hydroxide in a reducing environment. He determined from his experiments that adsorption of the rare metals by a variety of kinds of materials was significant in nearly all cases, but that only copper, zinc, and lead were strongly adsorbed by all constituents and that iron and manganese oxides were the best overall adsorbents. Prediction of the amount and kind of adsorption with respect to specific solid phases under various conditions does not appear possible, at least with much confidence; but it is apparent that the process of adsorption is important in the concentration of minor elements. All of the above factors, in addition to diadochy of minor elements in major mineral phases, have apparently played roles of varying importance in the concentration of minor elements in the rocks of this section, and this is illustrated in part by the relationships of the constituents in the vanadiferous zone.

Vanadiferous zone

Beds P-71 through P-75, totalling 3.7 feet, compose an extraordinary rock unit that contains an average of 0.7 percent V_2O_5 and greater than modal concentrations (plate 2), for a majority of beds in the zone, of Cu, Zn, Pb, Cr, and Mo--elements included in Krauskopf's (1956) investigations. In addition the unit is rich in carbonaceous material and contains about 10 percent total sulfur, expressed as SO_3, which occurs in part as sulfide and probably in part as an organic complex.

Although sphalerite was not identified in this section, its occurrence in the correlative vanadiferous zone of the Paris, Idaho, locality (A. D. Weeks, written communication) is an example of minor element sulfide formation. On the basis of Krauskopf's work, Cu and Pb could occur, in part at least, in this manner also. Cu, Zn, and Pb, however, are elements that are strongly adsorbed by many kinds of materials, and it seems possible that they might have been concentrated first by adsorption on the carbonaceous material or mineral phases and could have formed sulfides secondarily. Chromium probably occurs as an hydroxide as mentioned above. Molybdenum can be considered as a product of organic action, following Krauskopf (1956, p. 31), although no direct evidence is available here. The unusual concentration of vanadium is difficult to explain. Its mode of occurrence is not known, although, as mentioned previously, its occurrence in a mica or clay mineral has been suggested. Krauskopf (1955, p 421) cites references to two principal kinds of occurrence--in micas and in organic compounds. Sulfide formation should not be a major control of V on the basis of solubilities (Krauskopf, 1956, p. 14), and in some black shales S and V are not associated

(Krauskopf, 1955, p. 421). In this vanadium zone, however, sulfur is abundant and the possibility of some vanadium occurring as a sulfide cannot be excluded at this time. Krauskopf (1956, p. 31) suggests that biological processes may play a large role in concentrating vanadium, an explanation compatible with the rock characteristics but also one that cannot be proved or disproved with the data at hand. In summary, the concentration of minor elements in the rocks of the vanadiferous zone is not due to any single factor, but all the possible factors involved are closely related to the general conditions of an environment in which organic materials play a principal role.

Selenium

Nine samples of this section, four of them phosphorites and five quartz-silicate rocks, have been chemically analyzed for selenium (table 5) by J. A. McCarthy, J. L. Siverly, and H. Levine.

The samples of quartz-silicate rocks show about a ten-fold concentration of selenium as contrasted with the phosphorites. This is not, however, a relationship that is general for Phosphoria rocks. Unpublished analyses of samples from other localities show that some phosphorites and oil-rich shales contain selenium in amounts of the same magnitude as those of the quartz-silicate rocks of this section. Selenium is not, however, consistently associated with the organic component of the rocks either as

Table 5

Selenium analyses

Bed no.	Rock type	Percent Se
P-98	Phosphorite	< .001
P-97	Phosphorite	< .001
P-96	Phosphorite	.002
P-95	Phosphorite	.001
P-75	Quartz-silicate rock	.015
P-74	Quartz-silicate rock	.015
P-73	Quartz-silicate rock	.015
P-72	Quartz-silicate rock	.010
P-71	Quartz-silicate rock	.009

some carbonaceous-rich rock contains very little. The quartz-silicate rocks of this section that were analyzed for selenium are from the vanadiferous zone, discussed above, which is rich not only in carbonaceous material but also in sulfur. The association of sulfur and selenium is predictable on the basis of their chemical properties and is found in natural occurrences; for example, Coleman (1956, p. 112), among others, has found selenium in significant amounts (0.65 to 18 percent) in some sulfides from sedimentary rocks, and A. D. Weeks (written communication) identified selensulfur in samples of the vanadiferous zone of the Meade Peak member at the Paris, Idaho, section. The correlation of sulfur and selenium, however, for Phosphoria rocks in general is poor. Thus the principal factor, or factors, controlling the concentration of selenium is not known, but the controls are probably the kind investigated by Krauskopf (1956) and discussed above with respect to the concentrations of other minor elements.

Uranium

Chemical and radiometric determinations of uranium have been made on samples of all beds of the section (table 1). The average content of the member is 0.004 percent and the range in content is 0.0005 to 0.034. A sub-sample from bed P-96 contains 0.060 percent U (Thompson, 1953, p. 56), the greatest amount yet found in any rocks of the Phosphoria formation. From a glance at the analyses in table 1 a general correlation of percent U and percent P_2O_5 is obvious, but Thompson (1953) has found that the correlation of equivalent U-P_2O_5 in phosphorites is consistently good only among samples in which the average percent equivalent uranium is high. Thompson found also that equivalent U and organic matter generally are negatively correlated, but one group of samples that has an average low content of equivalent uranium did show a positive correlation. This may indicate, as suggested by McKelvey and Carswell (1956, p. 485), that small amounts of uranium occur in some organic matter but that large amounts only occur in the phosphate mineral, carbonate-fluorapatite. Despite complications of this kind, the overall correlation of uranium and P_2O_5 is good, and the work of Altschuler and others (1954, p. 1125) shows that uranium occurs in apatite as a quadrivalent ion in substitution for calcium.

No attempt has been made to study the detailed relationships of uranium in this section, but such studies by others on a larger scale are in progress. Much about the occurrence of uranium in Phosphoria rocks, however, is already known and reference should be made for a more complete treatment to McKelvey and Nelson (1950), McKelvey, Everhart, and Garrels (1955), and Thompson (1954), in addition to the references mentioned above.

MINERAL COMPOSITION

The suite of minerals found in the Meade Peak member is unusual only with respect to the occurrence of carbonate-fluorapatite and fluorite; the others are common sedimentary rock constituents. Carbonate-fluorapatite makes up about 28 percent of the member and is the most abundant single mineral, though quartz and the silicate minerals together compose about 33 percent. Other major constituents in order of abundance are dolomite, 21 percent; calcite 8 percent; and carbonaceous material about 5 percent. The silicate minerals are orthoclase, microcline, albite, muscovite, biotite, illite, kaolinite, tourmaline, titanite, leucoxene, sphene can and zircon. Iron oxides are represented by limonite and hematite, iron sulfides by pyrite and possibly a simple iron sulfide (FeS). Fluorite is a minor constituent of many phosphorites. The character of the mineral suite is essentially constant throughout the member, and the many different rock compositions are due principally to different mineral proportions rather than different mineral suites.

Mineral norm calculations

Mineral norms are calculated from the chemical analyses for apatite, dolomite, calcite, a mineral group estimate of quartz plus the silicate minerals, and a rough estimate of carbonaceous material. These calculations are shown graphically in the rock composition column of plate 1, and the values for carbonate fluorapatite, dolomite, and calcite are listed in table 6.

Carbonate-fluorapatite is the only phosphate mineral present and all phosphorus is assigned to that mineral. Its composition, however, is not precisely known because it is not possible to obtain pure separations for analysis; and it is apparently complex, as discussed further on. For the purpose here, as an approximation and somewhat arbitrarily, carbonate-fluorapatite is assumed to contain 38 percent P_2O_5; and a factor of 2.6 times the percent P_2O_5 in the rocks provides an estimate of their contents of carbonate-fluorapatite.

Normative dolomite is calculated by multiplying the percent MgO by the factor 4.58. Here the assumption is made that magnesium occurs only in dolomite. It is known that Mg substitutes for Ca in calcite in small amount, though this is largely counterbalanced by some substitution of Ca for Mg in the $MgCO_3$ phase of dolomite. Possibly some Mg occurs in carbonate-fluorapatite or illite; the amount of such occurrences cannot be large, however, and does not seriously affect the usefulness of the normative calculation of dolomite. Nevertheless, the calculation gives maximum values for dolomite, and that they do tend to run high is suggested by the comparison of calcite-dolomite ratios as determined from chemical analyses with the ratios determined from x-ray analyses, discussed in the following section.

Table 6

Mineral norms for carbonate-fluorapatite, dolomite, and calcite

Bed no.	Percent by weight Carbonate-fluorapatite	Dolomite	Calcite
P-107	2.0	50.8	21.6
P-106	66.2	2.2	--
P-105	8.4	3.8	--
P-104	16.0	3.1	--
P-103	11.3	2.9	--
P-102	1.7	19.2	2.7
P-101	11.7	4.1	2.3
P-100	67.3	1.8	3.8
P- 99	2.1	45.8	10.7
P- 98	77.5	1.1	5.4
P- 97	85.5	0.9	--
P- 96	70.7	1.7	--
P- 95	77.5	1.6	--
P- 94	69.9	1.6	--
P- 93	85.0	1.1	--
P- 92	56.2	1.8	--
P- 91	9.9	17.4	0.7
P- 90	0.5	22.4	32.0
P- 89	76.2	1.5	--
P- 88	62.6	1.9	22.0
P- 87	54.7	1.9	--
P- 86	71.4	1.4	--
P- 85	71.3	1.3	6.1
P- 84	42.9	2.0	0.7
P- 83	76.4	1.2	0.7
P- 82	5.5	9.6	36.5
P- 81	10.5	19.2	1.4
P- 80	25.7	4.1	16.1
P- 79	5.6	10.1	12.7
P- 78	74.5	2.0	--

Table 6 (Continued)

Bed no.	Percent by weight Carbonate-fluorapatite	Dolomite	Calcite
P-77	25.8	7.8	22.2
P-76	0.9	8.2	82.4
P-75	7.1	8.7	1.6
P-74	0.9	10.5	2.0
P-73	0.5	12.4	--
P-72	0.1	13.3	--
P-71	16.4	6.4	6.8
P-70	2.1	8.2	57.6
P-69	21.6	2.4	--
P-68	2.0	11.0	--
P-67	15.6	2.2	--
P-66	1.7	24.7	25.4
P-65	25.9	5.5	6.8
P-64	3.9	39.4	10.0
P-63	32.2	3.7	6.1
P-62	35.6	4.6	10.0
P-61	1.8	24.3	42.0
P-60	5.8	56.3	7.5
P-59	37.2	15.6	--
P-58	5.5	69.2	6.8
P-57	35.4	2.9	--
P-56	5.8	68.7	8.6
P-55	38.6	27.9	0.4
P-54	14.0	49.9	18.4
P-53	54.6	4.6	--
P-52	21.1	59.5	9.3
P-51	63.3	3.5	--
P-50	11.5	36.6	24.7
P-49	67.6	4.5	--
P-48	10.5	60.5	4.8
P-47	7.9	63.7	5.2
P-46	12.6	45.3	6.1
P-45	75.0	1.8	4.5
P-44	68.2	2.6	--
P-43	76.1	2.6	--

Table 6 (Continued)

Bed No.	Percent by weight		
	Carbonate-fluorapatite	Dolomite	Calcite
P-42	11.5	58.6	5.4
P-41	28.0	8.7	--
P-40	4.0	38.5	2.3
P-39	32.0	6.9	--
P-38	4.9	56.8	3.0
P-37	12.4	47.2	3.6
P-36	18.4	41.7	5.2
P-35	60.7	1.9	--
P-34	78.0	0.9	--
P-33	21.1	2.9	--
P-32	18.7	24.7	2.0
P-31	47.1	1.8	--
P-30	20.8	13.7	0.4
P-29	15.6	22.0	1.8
P-28	16.6	43.5	4.1
P-27	68.4	2.1	--
P-26	67.9	6.9	0.7
P-25	76.7	2.7	--
P-24	74.4	2.7	1.1
P-23	69.4	3.7	0.9
P-22	54.9	10.1	1.1
P-21	42.6	16.9	2.0
P-20	33.3	22.9	1.8
P-19	40.3	15.1	1.4
P-18	17.9	41.2	7.9
P-17	34.6	27.0	5.4
P-16	13.5	55.9	14.1
P-15	56.0	11.0	1.8
P-14	16.6	56.3	5.9
P-13	40.8	30.7	5.0
P-12	29.9	46.2	5.9
P-11	75.1	2.7	2.0
P-10	19.5	16.9	--
P- 9	25.2	43.5	1.4
P- 8	53.6	2.6	--

Table 6 (Continued)

Bed no.	Percent by weight		
	Carbonate-fluorapatite	Dolomite	Calcite
P-7	13.0	3.7	--
P-6	0.7	26.6	1.4
P-5	0.8	13.7	--
P-4	1.1	4.0	--
P-3	0.4	3.3	--
P-2	1.7	6.4	--
P-1	75.5	8.7	--

Calcite is calculated by multiplying the percent CO_2 not assigned to dolomite and carbonate-fluorapatite by the factor 2.27. The calculation is made from CO_2 rather than CaO because the assignment of CaO is complicated by its occurrence in many other minerals, such as carbonate-fluorapatite, dolomite, albite, titanite, and fluorite. In using CO_2 as the base, the calcite calculation is low if dolomite is estimated too high; it also depends upon the amount of CO_2 assigned to carbonate-fluorapatite. The amount of CO_2 in carbonate-fluorapatite is taken as 2 percent, a value more likely too low than high.

The acid insoluble (A.I.) determinations, table 1, are good estimates of the amounts of the quartz-silicate group of minerals, although the values are consistently low due to the partial solution of some minerals. It has not been found possible to approximate even roughly the amounts of the principal individual silicate minerals because of the complexity of the assemblage and the lack of precision of the analyses. A rough estimate of quartz content can be made, however, by utilizing the silica to alumina ratios of the principal silicate minerals. The theoretical ratio for orthoclase and albite is about 3.5, and the ratio for muscovite, illite, and kaolinite generally falls in the range of 1.2 to about 2.0. If an intermediate value between these two groups is taken, an estimate of the amount of silica combined in silicate minerals can be made; and the estimate of quartz is made by subtracting the combined silica from total silica. For example, using a ratio of 2.5, bed P-3 contains 49 percent quartz, the greatest amount of all the beds, and 22 percent combined silica; and the bed containing the least amount is P-45 with 2 percent quartz and 3 percent combined silica.

The amounts of carbonaceous material in the rocks are calculated as the difference between the L.O.I. (loss on ignition) determination and the sum of the CO_2 and H_2O^- determinations of table 1. Besides carbonaceous material, these values include structural water from clay minerals, sulfur from iron sulfides, and possibly as Jacob and others (1933) found, some fluorine and silica that volatilizes at high temperature. The calculated amount of carbonaceous material is therefore consistently high. More accurate values probably can be obtained by a partial combustion method described by Grimaldi (in Thompson, 1953, p. 64) that does not go to a temperature high enough to drive off structural water. Using this method, determinations by Bond Taber average approximately one percent less than the others, and give some idea of the magnitude of the inexactness of the carbonaceous material determination.

Comparison of percentage ratios of calcite to dolomite calculated from chemical analyses with ratios calculated from x-ray analyses

Chemical and x-ray analyses permit independent calculations of the percentage ratio of calcite to dolomite in carbonate rocks. The amounts of calcite and dolomite in fifteen end-member rocks have been calculated from the chemical analyses as previously described, and are the values used throughout this study. These values have been checked, however, by x-ray analyses using a method described in the appendix, which is based on the observation that the ratio of x-ray peak heights of calcite to dolomite give a good estimate of the percentage ratios of the two minerals.

The two sets of estimates of the percentage ratios of calcite to dolomite in the fifteen end-member carbonate rocks are listed in table 7 along with the calculation of t, a test of the hypothesis that the two sets of paired data are not significantly different. The calculated t value of 0.55 is far below the t value of 2.14 at the 5 percent probability level, indicating with a good deal of confidence that the hypothesis may be accepted. However, an examination of the data shows that the amount of variation between the ratio measurements is large, indicating poor precision of measurement of one or both methods; and that twelve of the fifteen ratios determined from x-ray analyses are larger than those determined by the other

Table 7

Comparison of ratios of calcite to dolomite as determined by two independent methods.

Sample no.	1 X-ray $\log 100 \frac{\%\text{ calcite}}{\%\text{ dolomite}}$	2 Chemical $\log 100 \frac{\%\text{ calcite}}{\%\text{ dolomite}}$	3 Difference (1-2)
P-107	1.741	1.629	0.112
P- 99	1.386	1.369	0.017
P- 90	2.337	2.155	0.182
P- 76	3.277	3.002	0.275
P- 70	3.120	2.846	0.274
P- 60	1.142	1.124	0.018
P- 58	1.014	0.993	0.021
P- 54	1.135	1.567	-0.432
P- 50	1.046	1.829	-0.783
P- 48	0.865	0.899	-0.034
P- 47	0.973	0.912	0.061
P- 46	1.565	1.129	0.436
P- 42	1.048	0.965	0.083
P- 38	0.938	0.723	0.215
P- 37	1.084	0.882	0.202

$\bar{X} = 0.043$

$s^2 = 0.0899$

$t = 0.55$

$P_{.05} = 2.14$

method, indicating a systematic difference between the two sets of values that is counterbalanced in the total summation of differences by two exceptionally large negative differences in which the ratios calculated from chemical analyses are larger.

In summary, the test in which the two sets of values are compared indicates that within the precision of measurement of the ratios, the two methods yield the same results. However, the lack of precision makes the comparison unsatisfactory; and extremely large variation of a few measurements may have occurred by chance in such a way as to obscure a significant difference between the two methods of measurement.

MINERALOGY

Carbonate minerals

Dolomite and calcite are the carbonate minerals of the section and one or both occur in all beds. Dolomite is more abundant than calcite and is found in all parts of the section, although it is concentrated more in the lower half as shown in the columnar section, plate 1. These minerals contain only small amounts of ion substitutes. They occur mostly as fine-size particles, usually mixed with one another in a large range of proportions. Fossil fragments are not common.

Dolomite and calcite are the common rock carbonate minerals and have been studied intensively by many workers, yet much about their natural occurrences is imprecisely or poorly known. An extensive summary of most of the present day knowledge of the properties of calcium and magnesium carbonates has been made by Graf and Lamar (1955). The application of x-ray techniques, one of which is described here, in conjunction with other types of analysis, to the study of dolomite and calcite is providing valuable new information on the composition of the minerals and on proportions of the two in carbonate rocks. These kinds of data, though limited in amount at the present time, are contributing to a better understanding of the conditions under which these minerals have formed.

Diadochy in dolomite and calcite

Diadochy (ionic substitution) for calcium or magnesium in calcite and dolomite is well known for a number of elements, such as Mn and Sr for Ca, and Fe and Mn for Mg. The kind of diadochy is determined principally by the radius and valence of the ions, though the size range is unusually large in some cases. Ions larger than Ca (0.99)*, such as Sr (1.12) and Ba (1.34), substitute for Ca in calcite in small amount because of the size limitation imposed by the calcite structure. They are diadochic in greater amount in the aragonite structure and tend to stabilize it (Faivre, 1944; and Faivre and Chaudron, 1948).

* Ionic radii in angstroms from Ahrens (1952, p. 168)

Mn (0.80), intermediate in size between Ca (0.99) and Mg (0.66), is diadochic in all proportions with Ca between the calcite and rhodochrosite end-members on the basis of the range of proportions found in natural samples by Wayland (1942) and Krieger (1930), but the experimental work of Goldsmith and Graf (1957) indicates that the complete range of diadochy is only possible at temperatures greater than 550° C. and with CO_2 pressure sufficient to prevent decomposition. Mn and Mg diadochy in all proportions between dolomite and mangandolomite appears possible (Winchell, 1951, p.73). Mg (0.66) and Fe (0.74) are diadochic in all proportions between dolomite and ankerite (Palache, Berman, and Frondel, 1951, p. 212; and Winchell, 1951, p. 73), though compositions near the ankerite end member are apparently rare. Ferrari and Colla (1936) have found that Co (0.72), Zn (0.74), and Cd (0.97) are diadochic with Ca and Mg to various degrees, and many other elements probably occur naturally in such relationships. Although substitutions for Ca and Mg of calcite and dolomite are common, substitutions for C or O in the carbonate radicle are not known.

Diadochy of Ca and Mg for one another in dolomite and calcite is theoretically prohibited because of their large difference in size, 0.99 for Ca as compared to 0.66 for Mg, a difference much larger than the empirical limit of 15 percent for those ions that readily substitute for one another in nearly all proportions. Mg, however, substitutes for Ca in the calcite of the tests of modern organisms in amounts frequently more than 10 percent by weight equivalent $MgCO_3$, and up to as much as 29 percent (Chave, 1952 and 1954a; Goldsmith and others, 1955; and Clarke and Wheeler, 1922). Most natural calcitic fossils contain less than 10 percent $MgCO_3$ (Chave, 1954b, p. 595), as do many natural calcites (Goldsmith and others, p. 222 and 223) and most modern calcareous sediments (Chave, 1954b, p. 598). Most of the Mg in calcites formed at low temperatures is unstable (Graf and Goldsmith, 1955, p. 109), but at high temperatures highly magnesian calcites are stable, although the relationships near the dolomite composition end are not known (Harker and Tuttle, 1955; and Graf and Goldsmith, 1955).

Considerable information is now available, as noted above, about the diadochy of Mg for Ca in calcite, whereas essentially nothing is known of the diadochy of these ions for one another in their ordered positions in natural dolomite. Small variations of the Ca:Mg atomic proportions in high temperature synthetic dolomite were noted by Harker and Tuttle (1955, p. 278) but were not considered significant. In other high temperature synthetic work, Graf and Goldsmith (1955, p. 124) measured amounts of excess $CaCO_3$ in dolomite of as much as 5 mole percent. It should be pointed out in considering diadochy in calcite and dolomite that the two minerals are not strictly isomorphic. Dolomite has an ordered arrangement of Ca and Mg atoms that occur in alternating planes normal to the trigonal axis. All the Mg substitutions in calcite are of a random or disordered nature, and Harker and Tuttle (1955, p. 274) suggest that a disordered dolomite may be stable at high temperatures. Graf and Goldsmith (1955, p. 124) found 1-1$\frac{1}{2}$ mole percent $CaCO_3$ in some synthetic high temperature ordered dolomites. It is clear that more information is needed on these relationships.

A measure of the approximate amount of diadochy in the calcite and dolomite of fourteen end-member carbonate rocks of this section was made by x-ray powder analysis using the old Norelco "spectrometer" and chart recorder. The method consists of the measurement of the amount of shift ($^{\circ}2\theta$) of the most intense peak (104) of calcite and dolomite with respect to standard calcite and dolomite, and the correlation of the shift with the element or elements in diadochy that produced it. The measurements were made with reference to quartz as shown in figure 3. The dolomite-quartz interval was measured in the fourteen samples of carbonate rocks, and the calcite-quartz interval was measured in all but one of the same samples. Since the precision of measurement with this equipment was not high, the values were averaged to give mean dolomite-quartz and calcite-quartz intervals. These averages were then compared with average values of the same kind obtained on fourteen samples of prepared mineral mixtures, described in the

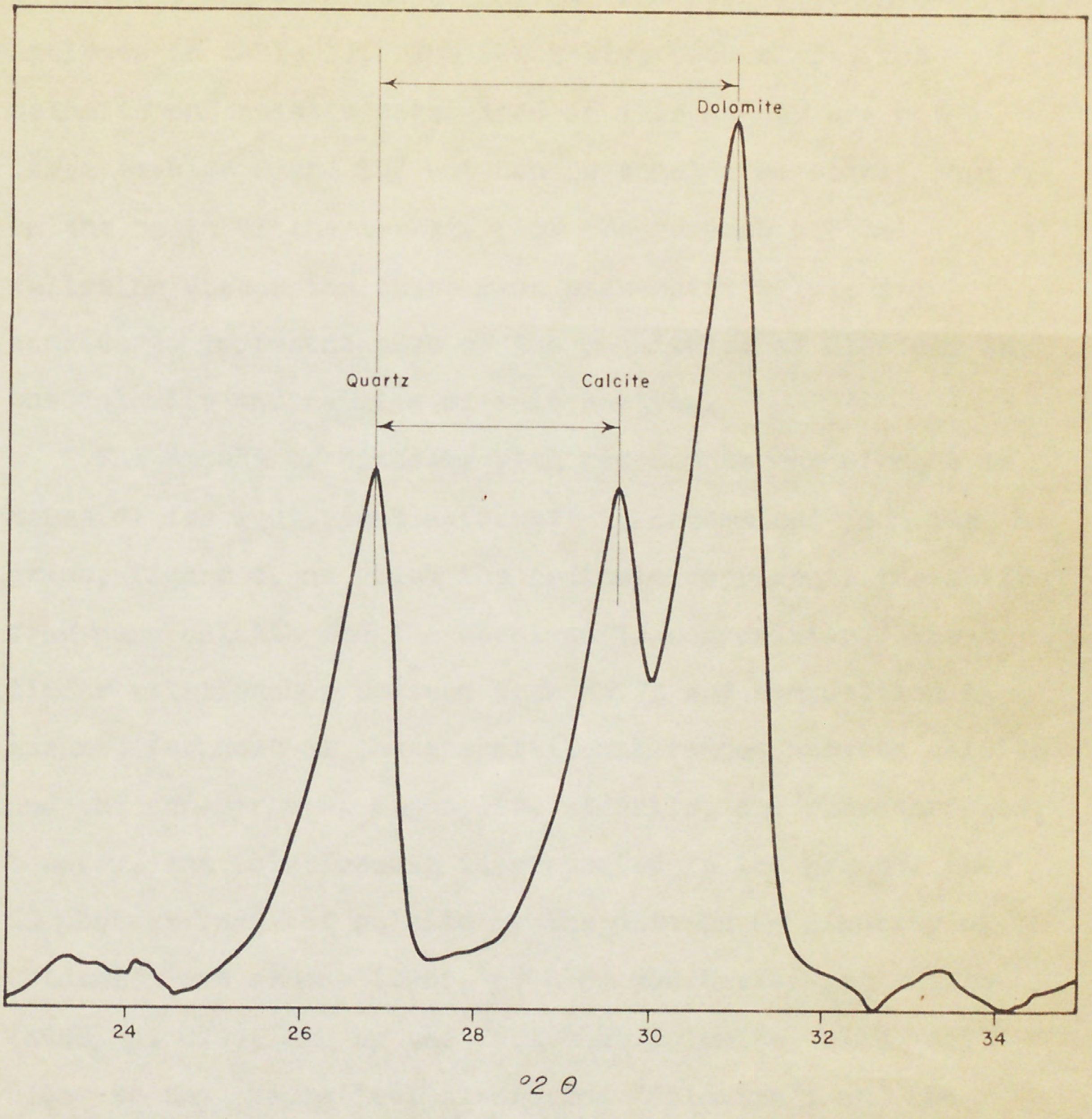

Figure 3.—Method of measurement of diadochy in calcite and dolomite using quartz as reference by x-ray spectrometer analysis.

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appendix, that all contained quartz and varying proportions of calcite and dolomite standards (see spectrographic analyses in table 8). The respective peak shifts for dolomite and calcite determined in this manner are not large (tables 9 and 10) but can be considered significant on the basis of the t-test. For the purpose of the following discussion these mean peak-shift values are considered representative of the magnitudes of diadochy in the dolomite and calcite of this section.

The amount of diadochy with respect to one element in terms of its equivalent carbonate is determined from the graph, figure 4, on which the ordinate represents the shift from pure calcite and the abscissa is composition. The linear relationship between peak shift and composition is assumed for most of the compositional ranges between calcite and the end-members, magnesite, siderite, and rhodochrosite; however, the relationship is supported in the greater than 50 percent range of calcite by the data on Mg diadochy of Goldsmith and others (1955, p. 215) and Harker and Tuttle (1955, p. 279), and by the fact that dolomite falls very close to the theoretical disordered "dolomite"; and the linear relationship holds for Mn diadochy in this same range, as shown by Andrews (1950, p. 92), using Krieger's data; but no data of this kind dealing with Fe are available, though it is reasonable to expect the relationship to apply equally well for Fe diadochy. In figure 4 the mean value of the

Table 8

Spectrographic analyses of dolomite and calcite standards

Calcite*

Al - 0.001-0.01
Ba - 0.001-0.01
Mg - 0.001-0.01
Sr - 0.01-0.1
Ti - 0.001-0.01
V - 0.001-0.01
As - none detected
Ag - none detected
B - none detected
Bi - none detected
Co - none detected
Cr - none detected
Cu - none detected
Fe - none detected
K - none detected
Li - none detected
Mn - none detected
Mo - none detected
Na - none detected
Ni - none detected
Pb - none detected
Sb - none detected
Sn - none detected
W - none detected
Zn - none detected
Zr - none detected

Dolomite**

Ba - 0.01-0.1
Co - 0.01-0.1
Cu - 0.01
Fe - 0.1-1.0
Mn - 0.01-0.1
Na - 0.01
Sr - 0.10-1.0
Zn - 0.01-0.1
Al - none detected
Ni - none detected

* Calcite from near Manuel Benevides, Chihuahua, Mexico. Analyzed by R. Allen for Miller (1952).

** Dolomite locality unknown. Analyzed by H. L. Lovell, Pennsylvania State University.

Table 9

Comparison of the mean differences (degrees 2θ, λ= Cu) between x-ray peaks of calcite (104 peak) and quartz (101 peak) in carbonate rocks and in prepared mineral mixtures.

Carbonate rocks calcite-quartz interval		Prepared mineral mixtures calcite-quartz interval	
Sample no.	Degrees 2θ	Sample no.	Degrees 2θ
P-37	2.82	1R	2.79
P-42	2.83	2R	2.68
P-46	2.82	3R	2.75
P-47	2.80	4R	2.70
P-48	2.95	5R	2.82
P-50	2.78	6R	2.73
P-54	2.70	7R	2.74
P-58	2.87	8R	2.77
P-70	2.70	9R	2.78
P-76	2.81	10R	2.69
P-90	2.80	11R	2.67
P-99	2.78	12R	2.77
P-107	2.72	13R	2.80
		15R	2.79

$\overline{X}_1 = 2.7985$ $\qquad$ $\overline{X}_2 = 2.7486$

$SS_1 = 0.0564$ $\qquad$ $SS_2 = 0.0302$

$\overline{X}_1 - \overline{X}_2 = 0.0499$

pooled $s^2 = 0.003464$

$t = 2.20$*

* significant at $P_{.05}$ probability level

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Table 10

Comparison of the mean differences (degrees 2 θ, λ= Cu) between x-ray peaks of dolomite (104 peak) and quartz (101 peak) in carbonate rocks and in prepared mineral mixtures

Carbonate rocks dolomite-quartz interval		Prepared mineral mixtures dolomite-quartz interval	
Sample no.	Degrees 2 θ	Sample no.	Degrees 2 θ
P-37	4.25	1R	4.36
P-38	4.26	2R	4.28
P-42	4.20	3R	4.34
P-46	4.18	4R	4.39
P-47	4.28	5R	4.29
P-48	4.40	6R	4.26
P-50	4.26	7R	4.35
P-54	4.22	8R	4.34
P-58	4.24	9R	4.35
P-70	4.21	10R	4.21
P-76	4.32	11R	4.28
P-90	4.26	12R	4.33
P-99	4.17	13R	4.30
P-107	4.12	15R	4.35

$\bar{X}_1 = 4.2407$ $\bar{X}_2 = 4.3164$

$SS_1 = 0.0607$ $SS_2 = 0.0301$

$\bar{X}_2 - \bar{X}_1 = 0.0757$

pooled $s^2 = 0.003492$

$t = 3.39^{**}$

** significant at $P_{.01}$ probability level

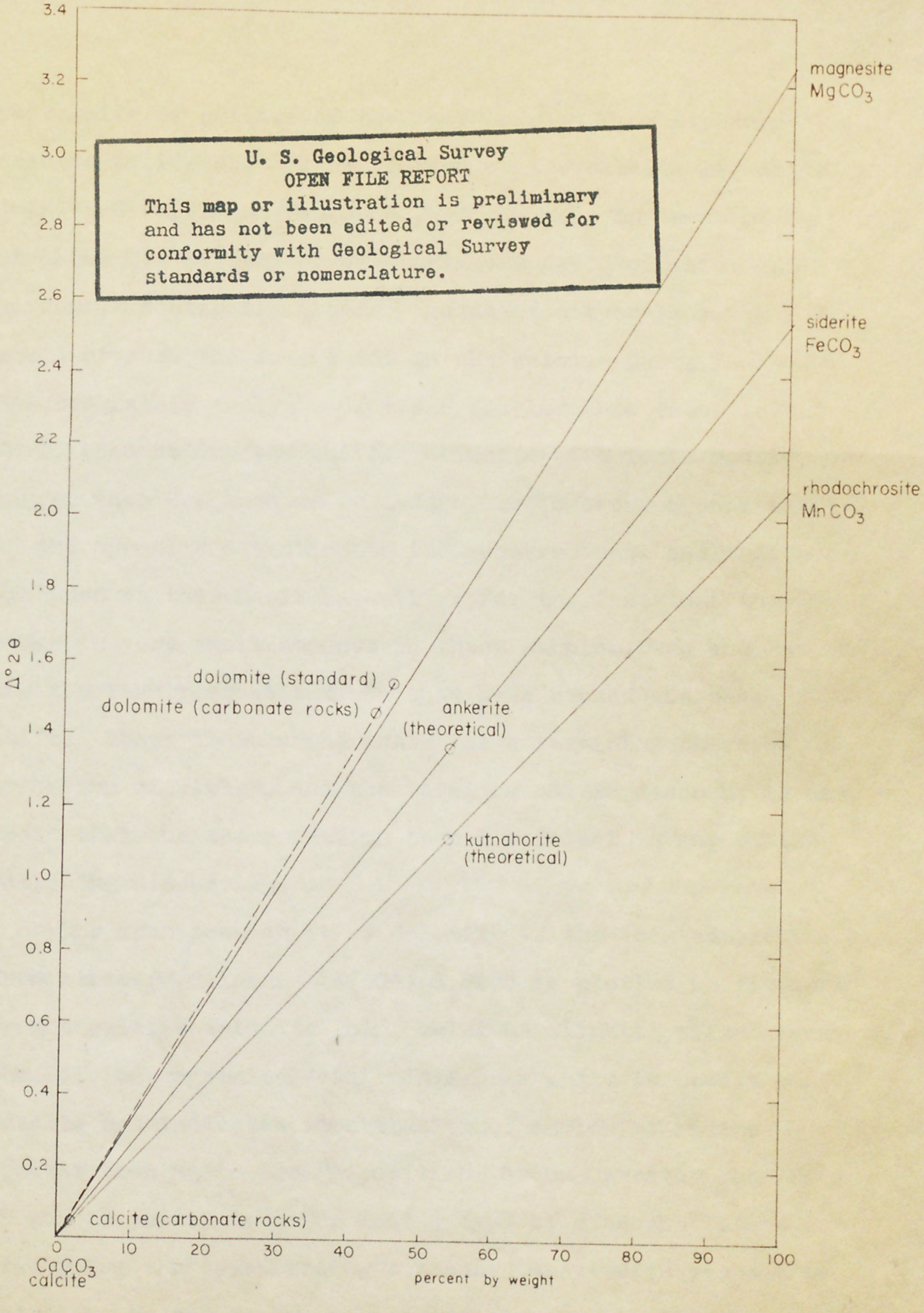

FIGURE 4. Relation of 104 X-ray peak with composition between some end-member carbonate minerals, and composition of dolomite and calcite in carbonate rock samples.

peak shift of calcite of the rock samples from standard calcite (d(104)=3.037) is plotted on the calcite-magnesite join, and represents an amount of diadochy in terms of Mg of about 0.4 percent or as equivalent $MgCO_3$ of about 1.5 percent. A slightly greater amount of either Fe or Mn could produce the same shift in the calcite peak. Spectrographic analyses of these samples show insufficient Mn to account for the shift. Elements with ionic radii larger than Ca, such as Sr and Ba, would cause a peak shift in the opposite direction to the observed one, and they are excluded on that basis as well as for the fact that they occur in very small amounts in these samples. Mg and Fe are the likely substitutions that have caused the peak shift. There is no sound basis for determining the contribution of either, and the total amount in diadochy is so small that the determination is not critical to any of the following discussion.

The mean peak shift of dolomite of the rock samples from standard dolomite (d(104)=2.887) is plotted in figure 4 on the calcite-dolomite join, which is slightly offset from the calcite-magnesite join. This peak shift is toward calcite and indicates substitution of an ion of radius greater than Mg in the Mg positions or one greater than Ca in the Ca positions. The latter type of diadochy is unlikely for the same reasons discussed above with respect to calcite. Mn and Fe are common ions larger than Mg that theoretically could produce the shift; however, using the theoretical positions of kutnahorite and ankerite in figure 4 and assuming a linear relationship, the observed peak shift of dolomite of the rock samples would require about 10 percent $MnCO_3$ or 24 percent $FeCO_3$ in substitution for Mg--neither case possible. Kutnahorite has an ordered dolomite structure (Frondel and Bauer, 1955, p. 749), and presumably ankerite does too; thus the theoretical positions plotted in figure 4 are only approximations, yet close enough for the purpose here. Ca, however, is larger than Mg and very likely occurs in excess in the dolomite, substituting for Mg in an amount of about 1 percent Ca or 2.5 percent equivalent $CaCO_3$.

The small amount of diadochy found in the dolomite and calcite of the carbonate samples studied very likely represents a stable relationship, and one that conforms, with respect to Ca-Mg diadochy at least, to general low temperature extrapolations from the high temperature relations determined by Graf and Goldsmith (1955, p. 125) and Harker and Tuttle (1955, p. 279). The amount of $MgCO_3$, approximately 1.5 percent if all the diadochy is attributed to Mg, in the calcite of these samples is similar to the general modal amount found in pre-Cenozoic calcitic fossils and to one mode in Paleozoic limestones (Chave, 1954b, p. 595 and 598), and it is markedly less than the amount commonly found in the calcite of Cenozoic fossils and modern skeletons. These data are inadequate at present for determining the conditions under which natural calcites have formed, but more work of this kind on calcites of many environments, as well as dolomites about which there are now few compositional data, offers promise of aiding the achievement of this goal. The various amounts of Mg held metastably in the calcitic skeletons of modern marine organisms have an important bearing on the significance of dolomite-calcite proportions found in the older rocks, if it is presumed that similar amounts of Mg occurred in fossils of the past and formed, with time, equivalent amounts of dolomite essentially in situ. This aspect of dolomite formation will be discussed in a later part of this report. In addition to Ca and Mg relationships, quantitative determinations of minor elements, particularly Sr, Mn, and Fe, in calcite and dolomite should be helpful. Strontium may be a valuable indicator on the basis of the work by Zeller and Wray (1956); Turekian and Kulp (1956); Kulp, Turekian, and Boyd (1952); Murray (1954); and Lowenstam (1954). The semiquantitative Sr determinations on the carbonate rocks of this section, all less than 0.1 percent and most less than 0.01 percent Sr, only show that these rocks probably contain on the average slightly less than the average value of 610 ppm for limestones (Turekian and Kulp, 1956, p. 245).

Carbonate-fluorapatite

The character of the phosphate mineral in the Phosphoria formation has been obscure because of the difficulty of obtaining pure homogeneous samples for analysis and because its composition is complex. Mansfield (1927, p. 367) suggested that carbonate (CO_3) and fluorine were chemically combined with the calcium phosphate but could not satisfactorily prove it. Subsequent analytical work by Jacob and others (1933) and Hendricks and others (1931) conclusively established the mineral to be a fluorine-apatite, and both groups noted the relationship of carbonate with the mineral. The occurrence of carbonate as a structural component of the phosphate mineral of the Phosphoria formation has been in doubt and has been part of a controversy involving the validity of carbonate-apatites in general. The problem has been to determine whether the carbonate occurs as calcium carbonate intimately mixed with the apatite, as carbonate on occluded surfaces (Hendricks and Hill, 1950), or as carbonate occupying lattice positions of the apatite structure. Silverman, Fuyat, and Weiser (1952), in an excellent study of the problem, show by several tests that although calcite is commonly intermixed with apatite, some of the carbonate, approximately 1 to 2 percent equivalent CO_2, occurs homogeneously in the apatite mineral and not on occluded surfaces. X-ray analyses by Altschuler, Cisney, and Barlow (1952) show that carbonate-fluorapatite is a homogeneous phase distinguishable from fluorapatite and hydroxyapatite. Apatite from the Phosphoria formation was tested in the latter two studies, and it is a carbonate-fluorapatite, as are other marine apatites, according to Altschuler and others (1952), in this country and other parts of the world. Although carbonate-fluorapatite is distinct chemically and structurally from other apatites, a dilemma persists as to the specific manner of occurrence of the carbonate in the structure. Trautz (1955) has made a recent general review and detailed study of the problem of the carbonate-apatites but no explanation is entirely consistent with accepted structural principles, and present terminology is inadequate for describing some of the possible relationships. This aspect of the carbonate-fluorapatite problem is only touched on in the following discussion.

Relation of carbonate-fluorapatite to the apatite mineral group

Carbonate-fluorapatite belongs to the apatite group of minerals having a general formula $A_5(XO_4)_3Z_q$. The structure of the group was first described independently by Náray-Szabó (1930) and Mehmel (1930, and 1931). They have shown that the unit cell of fluorapatite contains 10 Ca, 6 P, 24 O, and 2 F ions; or in formula $Ca_{10}(PO_4)_6F_2$. In this structure a large number of substitutions have been described, as shown in table 11, taken from McConnell (1938). Recently McConnell (1953) has added vanadium, chromium, and possibly aluminum to the list of what he considers to be adequately demonstrated substitutions for phosphorus.

Considering all of the substitutions together the following general formula is obtained:

$$(Ca,Sr,Mn,Na,K,C)_{10}/(P,S,Si,As,V,Cr,Al(?),C)_{6} -- (O,(OH),F)_{24}/(F,Cl,(OH),O)_{2}.$$

Other minerals of the apatite group belonging to the pyromorphite and svabite series (Palache, Berman, and Frondel, 1951, p.877) are chemically distinct from the ones considered in table 11 in that they represent end-members for which few naturally occurring intermediate members with the apatite series are known, particularly with regard to the diadochy of Ca and Pb.

A glance at the elements in table 12, reported as substitutions in the apatite structure, shows an unusual range in ionic size and charge. Carbon is so extremely small that, from crystal chemical considerations, it would not be expected to substitute for either calcium or phosphorus. In fact it is this consideration that precipitated the argument concerning the mode of occurrence of carbon in apatite minerals. From the study of minerals in which oxygen is the dominant anion it has been found that the ionic radius ratio of the cation to oxygen is a

Table 11

Diadochy in some minerals of the apatite group

Mineral	Formula
Fluorapatite	$Ca_{10}/(PO_4)_6/F_2$
Hydroxyapatite	$Ca_{10}/(PO_4)_6/(OH)_2$
Dahllite	$(Ca,C)_{10}/(PO_4)_6/(OH)_2$
Dehrnite	$(Ca,Na,C)_{10}/(PO_4)_6/(OH)_2$
Francolite	$(Ca,C)_{10}/(P,C)_6(O,OH,F)_{24}/F_2$
Lewistonite	$(Ca,K,Na,C)_{10}/(PO_4)_6/(OH)_2$
Wilkeite and Ellestadite	$(Ca,C)_{10}/(P,S,Si,C)_6O_{24}/(Cl,F,OH,O)_2$
Fermorite	$(Ca,Sr)_{10}/(P,As)_6O_{24}/(F,OH,O)_2$
Manganapatite	$(Ca,Mn)_{10}/(PO_4)_6F_2$

Table 12

Ionic radii* (six-fold coordination) and radius ratios of ions in apatite

Ion	Ionic radius* A	Ratio cation/oxygen
Ca^{2+}	0.99	0.71
Sr^{2+}	1.12	0.80
Mn^{2+}	0.80	0.57
Na^{+}	0.97	0.69
K^{+}	1.33	0.95
C^{4+}	0.16	0.11
U^{4+}	0.97	0.69
R.E.$^{3+}$(including Y and La)	0.85-1.14	0.61-0.81
P^{5+}	0.35	0.25
S^{6+}	0.30	0.21
Si^{4+}	0.42	0.30
As^{5+}	0.46	0.33
V^{5+}	0.59	0.42
Cr^{6+}	0.52	0.37
Al^{3+}	0.51	0.36
C^{4+}	0.16	0.11
O^{2-}	1.40	
F^{-}	1.33	
Cl^{-}	1.81	
OH^{-}	similar to O^{2-}	

* Ahrens, L. H., 1952.

principal factor in determining the coordination of oxygen ions about a cation. Table 13 shows the range of radius ratios for the different coordinations. Ions whose ratios with oxygen fall near the border of a group have been found to occur in minerals with a coordination of either group. On this basis carbon generally would be expected to have a coordination of two or three as it commonly does. McConnell (1938) proposed a structurally possible mechanism for the substitution of calcium by carbon, one in which carbon would be coordinated by three oxygens, but the mechanism does serious violence to crystal chemical principles. Carbon and phosphorus, in their respective CO_3 and PO_4 groups, each require more than one half the charge of each of their coordinating oxygens. Thus their groups cannot share oxygens as would be required in McConnell's hypothesis. In the phosphorus position carbon would be in four coordination in the center of a tetrahedron, a position at variance with the concepts mentioned above; however, Hendricks and Hill (1942) and McConnell (1952) have proposed that four CO_3 groups substituting for three PO_4 groups would be possible and would give carbon the desired threefold oxygen coordination.

McConnell's arrangement of the carbonate groups, however, would result in a positive rather than the negative birefringence apatite has, according to Trautz (1955, p. 699). Supporting McConnell's arrangement in which most of the

Table 13

Coordination of cations*

Oxygen coordination about cation	Position of oxygen ions	Radius ratio cation:oxygen
8	corners of a cube	1.-0.732
6	corners of a regular octahedron	0.732-0.414
4	corners of a square	0.732-0.414
4	corners of a regular tetrahedron	0.414-0.225
3	corners of an equilateral triangle	0.225-0.155
2	linear	0.155-0

*Evans, R. C., 1948, p. 176.

planar CO_3 groups are oriented parallel to the c axis is the fact that, according to most workers, the carbonate-containing apatites have a smaller a axis than the corresponding carbonate-free ones. An old idea that CO_3 can occupy F, Cl, or OH positions in apatite has been revived by Romo (1954). He has synthesized a carbonate-apatite that has an x-ray pattern closely similar to hydroxy-apatite, and has an infrared curve that shows the presence of CO_3 radicles and the absence of OH radicles. From this he deduces that the CO_3 replaces the OH. This kind of substitution is not important with respect to the marine carbonate-fluorapatites, however, since they commonly contain an excess of fluorine above that necessary to fill the regular lattice positions. The infrared data of Romo (1954), as well as those of Posner and Duyckaerts (1954) and of Underwood and others (1955), are important in that they provide concrete evidence of the occurrence of CO_2 in apatite as CO_3 groups, always a tacit assumption except for Gruner and McConnell's (1937, p. 213) hypothesis, which McConnell rejects in later works, that carbon substitutes for phosphorus directly and is coordinated by four oxygens.

Explanation of the occurrence of carbonate in the apatite lattice in terms of classical substitution is not entirely satisfactory; but of the possibilities the substitution of CO_3 for PO_4 groups seems to me the more likely.

Other explanations delving into the gap between true substitution and true inclusion are discussed by Trautz (1955), but in this realm knowledge is as yet insufficient to describe and test adequately the possible phenomena.

On the basis of size, K^+ and Cl^- also appear to be unlikely substitutions, respectively for Ca^{2+} and F^-; however, they seem to occur in some of the apatite minerals in appreciable amounts. Elements of the same valence but of slightly different size generally require in substitution an increase or decrease in volume of the unit cell but do not present the complications resulting from the substitution of ions of different valence. The latter requires compensating substitutions to preserve the overall electrostatic equilibrium of the structure; for example, S^{6+} and Si^{4+} for P^{5+}; or S^{6+} for P^{5+} and Na^+ for Ca^{2+}; and so on. Compensating substitutions of this kind are apparently commonplace in the apatite minerals but are little understood.

Diadochy in the carbonate-fluorapatite of the Meade Peak member

Diadochy in the carbonate-fluorapatite of the Meade Peak member has been established previously only for uranium, although the substitution of sodium for calcium has been suggested by Hendricks and others (1931). Other substitutions in significant but small amount, however, are indicated by an appraisal of the analyses of phosphorite.

A comparison of chemical analyses, table 14, of the three end-member rock types shows that phosphorite contains concentrations of sulfur, sodium, and vanadium relative to one or both of the other rock types. The mean values of the constituents of carbonate and quartz-silicate rocks are compared in turn with the respective mean values of phosphorite by a modified t test (Bennett and Franklin, 1954, p. 177). This test provides a more precise test of the difference between the means than does the ordinary "student" t test for the case in which the variances of the groups are not assumed to be equal.

The amount of sodium in the phosphorite is significantly greater (table 14) than it is in the other rock types, although the apparent excess unique to phosphorite is small. Some of the sodium, then, is believed to substitute for calcium in the apatite structure--a relationship that appears to be general for phosphorites of the Phosphoria, as shown by other unpublished analyses.

Sulfur is distinctly concentrated in phosphorite relative to carbonate rock (table 14), but not to quartz-silicate rock. It is probable that the modes of occurrence of sulfur in phosphorite and quartz-silicate rock are different. Jacob, and others (1933, p. 49) found that most of the sulfur in Phosphoria phosphorite samples occurs as soluble sulfate, whereas sulfur in the quartz-silicate rock occurs as sulfide and possibly in some other forms, as

Table 14

Comparison of the amounts of Na_2O, SO_3, and V_2O_5 in phosphorite with amounts in carbonate and quartz-silicate rocks

	percent Na_2O			percent SO_3			percent V_2O_5		
	phos.	carb.	q-sil.	phos.	carb.	q-sil.	phos.	carb.	q-sil.
	1.0	0.6	0.3	2.9	0.4	1.6	0.10	0.06	0.11
	1.2	0.8	0.4	3.5	1.0	1.1	0.15	0.07	0.08
	1.1	0.5	0.4	3.4	0.5	0.6	0.09	0.04	0.07
	0.8	0.8	0.2	2.3	1.6	3.7	0.07	0.09	0.19
	1.0	0.5	0.2	3.2	1.1	1.5	0.26	0.04	0.04
	0.7	0.6	0.4	2.4	1.7	0.8	0.08	0.07	0.04
	1.0	0.7	1.5	3.2	1.0	0.9	0.10	0.05	0.08
	1.0	1.3	1.0	3.0	0.8	0.8	0.13	0.05	0.04
	1.0	1.1	0.6	2.2	0.6	0.9	0.10	0.06	0.06
	1.1	0.8	0.8	3.5	1.7	0.3	0.11	0.06	0.02
	1.0	0.4	1.3	2.7	0.7	8.4	0.08	0.04	0.37
	0.9	1.0	1.2	3.5	0.5	1.6	0.11	0.06	0.06
	0.9	0.9	0.6	2.8	0.8	3.1	0.09	0.08	0.09
	1.2	0.9	1.2	2.9	1.6	8.6	0.06	0.08	0.36
	1.2	0.8	1.0	2.3	1.0	1.1	0.06	0.05	0.52
$\bar{X}$	1.00	0.78	0.74	2.92	1.00	2.33	0.106	0.060	0.142
comparisons									
t' (phos.-carb.)=	3.02**			11.44**			3.46**		
degrees of freedom	22.8			28.0			16.8		
t' (phos.-q-sil.)=	2.21*			0.84			0.88		
degrees of freedom	17.1			14.8			16.9		

** significant at the .01 probability level
* significant at the .05 probability level
t' modified t test (Bennett and Franklin, 1954, p. 177)

discussed further on. Soluble sulfate in phosphorite is considered to indicate diadochy of sulfur with phosphorus in the apatite, because neither gypsum nor anhydrite, the only other likely soluble sulfate compounds, has been found.

Phosphorite contains more vanadium than carbonate rock (table 14) but only as much as or possibly even less than quartz-silicate rock. Vanadium may be diadochic with phosphorus here, a substitution in apatite that McConnell (1953) considers substantiated; if so its mode of occurrence is different from that in quartz-silicate rock. More information is needed to verify this, however, because the manner of occurrence of vanadium in quartz-silicate rock is not known with certainty either.

Wilkeite and ellestadite are apatite group minerals that show the diadochic substitutions of silicon for phosphorus, and this kind of substitution is believed to occur in carbonate-fluorapatite also. Silicon in this occurrence is acid soluble silica and is shown to occur in phosphorite in this manner by the fact that the total silica in end-member phosphorite is greater than the total acid insoluble of the rock by an average amount of 1.7 percent. In contrast, the carbonate and quartz-silicate rocks contain more acid insoluble than silica, the common relationship because of the presence of elements other than silicon in insoluble silicate minerals. For comparison, the values for each rock type are the following:

	phosphorite	carbonate rock	quartz-silicate rock
A. I.-SiO_2 (acid insoluble)	-1.7%	3.4%	11.8%

The amount of soluble silica in phosphorite cannot be determined with any precision in this manner, but the value of 1.7 percent is probably a minimum estimate.

Spectrographic analyses (table 4) show that Ag, Zn, and Sr are also relatively concentrated in end-member phosphorites. The disposition of Ag and Zn in the phosphorite is not known, but Sr likely occurs in the apatite structure diadochic with Ca -- a common relationship and one that also appears to be general for all phosphorites of the Phosphoria. Why strontium favors apatite as against calcite, however, is not known.

Of the elements described in the preceding paragraphs as possibly occurring to some extent in the apatite structure of the phosphate mineral in the Meade Peak member, the substitution of Si and Na appears to be best substantiated and significant in amount. Assuming that Na^+ and Si^{4+} are diadochic, respectively, with Ca^{2+} and P^{5+}, other substitutions of cations of higher valence than phosphorus and calcium or of anions of lower valence than oxygen are necessary to preserve the electrostatic equilibrium of the apatite structure. Thus sulfur diadochic with phosphorus tends to satisfy this demand, as would fluorine in substitution for oxygen. The excess of fluorine found in the phosphate rocks over that required for the theoretical composition of fluorapatite may well be explained in this manner; that is, fluorine, diadochic with oxygen, is present in amount necessary to balance, at least partially, the substitutions of ions of lower valence for calcium and phosphorus, such as sodium and silicon. Considering the elements discussed above as the ones most probably occurring as substitutions in the apatite structure a general formula would be as follows:

$$(Ca,Na,Sr,U)_{10}/(P,Si,S)_{6-x}(O,F)_{24-3x}(CO_3)_x/F_2$$

~~The~~ phosphate mineral names

Collophane and francolite are the mineral names that have been applied, respectively, to isotropic and anisotropic phosphate material of the Phosphoria formation, though chemical differences, if any exist, have not been detected. As McConnell (1950, p. 18) and Palache, Berman, and Frondel (1951, p. 885) suggest that collophane be used to designate any crypto-crystalline phosphatic material for which specific mineralogic information is not known, the use of collophane for the phosphate mineral of the Phosphoria formation is no longer desirable.

McConnell (1938, p. 9) suggests that francolite is a suitable name for an apatite which contains an appreciable amount of carbon dioxide and more than 1 percent fluorine.

The carbonate-fluorapatite of the Meade Peak member falls well within the definition; for a species name, however, it is not inclusive enough for a mineral in the apatite group -- a group that is noted for the number and amount of ionic substitutions in its minerals. Should the diadochy described above exist, the phosphate mineral of the phosphatic shale member would be compositionally intermediate between francolite, dehrnite, and wilkeite and ellestadite as shown in table ~~9~~ 11. Because no adequate name is available, the phosphate mineral in the Meade Peak member is here called descriptively carbonate-fluorapatite, or simply apatite where it is the only phosphate mineral of reference.

~~The~~ S submicrocrystalline character of carbonate-fluorapatite

The common mode of occurrence of carbonate-fluorapatite in the Meade Peak member is as submicrocrystalline isotropic masses. As x-ray analysis shows it to be well developed crystalline material, its submicrocrystalline and isotropic character is due to the random aggregation of submicroscopic particles. Vol'fkovich and others (1952), in an electron-microscope study of natural phosphates, found the diameter of the smallest particles to be several hundred angstroms. A possible explanation for this form of development can be derived from the inherent character of the mineral. Crystal growth is a surface phenomenon, depending upon surface forces and their distribution. It seems possible that the asymmetry of forces developed on a crystal surface because of ionic substitutions such as discussed above, of different sizes and charges, is sufficient to restrict crystal growth to relatively small size -- particles containing relatively few unit cells. It might well be due to the effect of stong and small ions of high polarizing power on anions that are easily polarized. Thus the forces on a crystal surface would be quite different from those in the interior. Carbon, silicon, phosphorus, and sulfur, in particular, would cause pronounced asymmetry at the surface, polarizing the anions, oxygen and fluorine, to the extent that they make the principal but weak contribution to the surface energy. A similar phenomenon is described by Weyl (1951, p. 14) about which he says "the equilibrium surface may deviate sufficiently from the ideal surface to make further crystal growth improbable". Trautz (1955, p. 708) visualizes a coprecipitate concentrated along certain layers of the host serving to break the coherence of the structure and limiting crystal size.

Feldspars

Much progress has been made in the past several years toward an understanding of the origin of feldspars. This is due in large measure to the fundamental work of

Bowen and Tuttle (1950) on artificial alkali feldspars and Tuttle and Bowen (1950) on high albite and high modifications of other sodic plagioclases. X-ray techniques that they developed for determining composition and high and low modifications have served to simplify and spur on the study of natural feldspars. An additional x-ray technique described by Smith and MacKenzie (1955) provides precise information about the phases comprising single alkali feldspars. X-ray data, obtained by these several procedures, together with chemical and optical data on many feldspars of somewhat well defined origins (Tuttle, 1952a and 1952b; Tuttle and Keith, 1954; MacKenzie and Smith, 1955 and 1956; and Baskin, 1956) now permit precise identification of feldspar types; and, as data like these accumulate, the environments of origin become more precisely defined. Although there is a great deal more to learn about feldspars, it is possible now to gain much information about the origin of rocks that contain feldspars, such as the sedimentary rocks reported on here, by the identification of the specific type or types contained therein. With this in mind nearly half the samples of this section were studied by x-ray powder analysis and nearly all in thin section. The fine grain size of the materials, nearly all of silt size except the apatite pellets, greatly restricts optical work and makes mineral separations prohibitively difficult, but nevertheless this study of the feldspars, particularly the x-ray analysis of acid insolubles of the samples, has yielded some interesting and useful information even though not entirely complete nor conclusive.

The feldspars were identified mainly from the x-ray powder charts of acid insolubles that consist, in addition to the feldspar, mostly of quartz and some illite-muscovite. The presence of quartz and illite-muscovite was undesirable, but fortunately, in this particular mineral mixture, the coincidence of some peaks did not prevent the identification of the feldspar. More difficulty, as might be imagined, is encountered where there are two feldspars, as there are in most of the samples here; but even in such cases, reasonable identifications are possible. Two feldspars and two modes of occurrence have been found. In one mode of occurrence, orthoclase occurs as the only feldspar present; whereas in the other orthoclase and albite occur together. Microcline has been identified in thin sections of many samples but is minor in amount and not detected by x-ray. In figure 5 x-ray patterns of samples P-6 and P-28 are examples of the orthoclase and orthoclase-albite occurrences. The orthoclase of sample P-6 is close to its end-member composition as indicated by the fact that its $\bar{2}01$ peak is located at or very close to 21° (angle of 2θ using Cu radiation), even though the strong quartz peak at that position obscures the weaker orthoclase peak. The

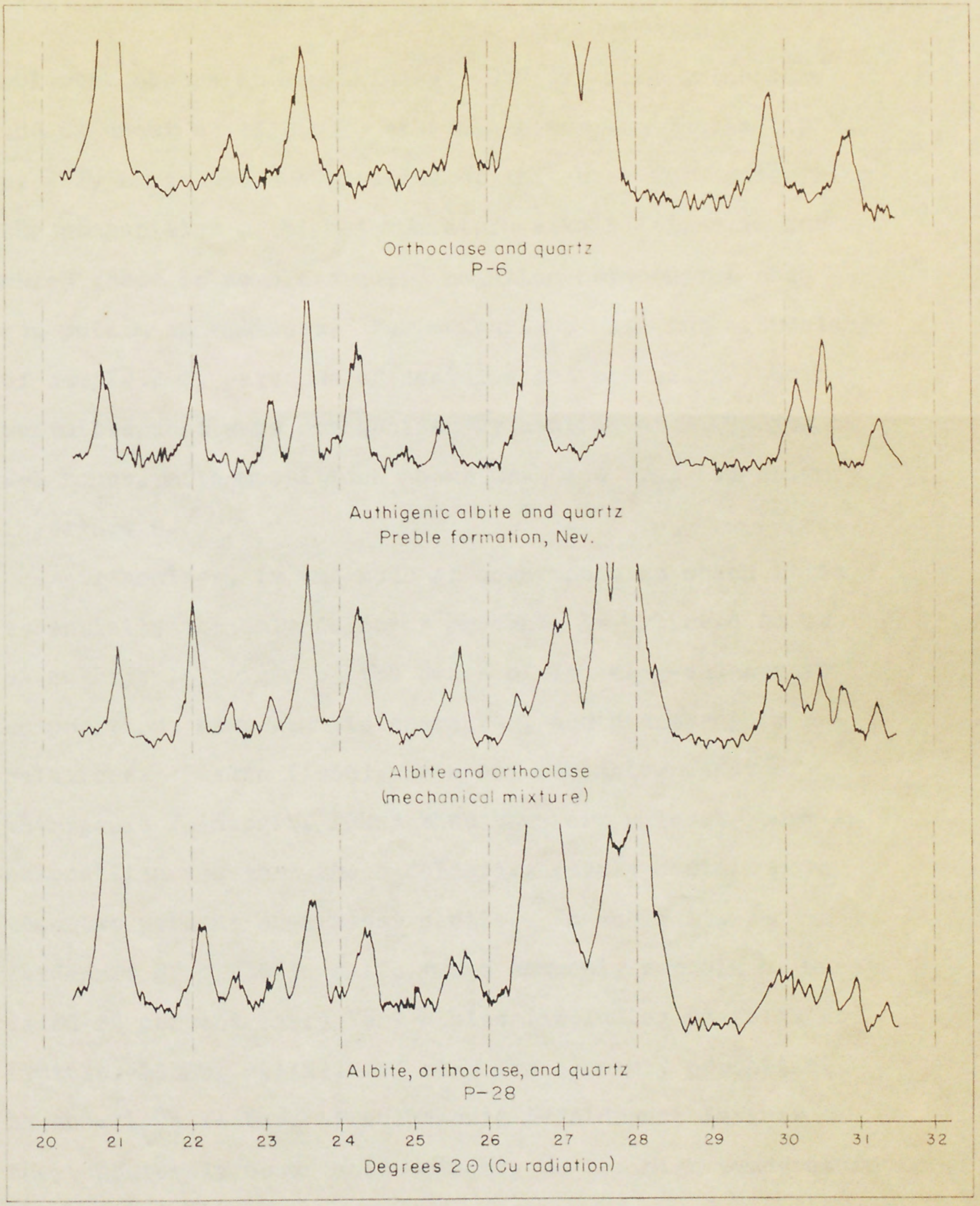

Figure 5. Partial x-ray patterns of albite and orthoclase and mixtures of the two. A quartz peak near 21° obscures an orthoclase peak. A strong quartz peak obscures orthoclase and albite peaks between about 26.5° and 27°.

$\bar{2}01$ peak occurs at approximately 21° for pure orthoclase and at about 22° for pure albite. Bowen and Tuttle (1950, p. 491) have used the position of this peak for determining the composition of high temperature alkali feldspars for which there is complete solid solution between the soda and potash end-members. For comparison with the orthoclase of sample P-6, patterns of sanidine and orthoclase, both perthites that were homogenized by heating at 950°C for 2-3 hours, of compositions about Or_{50} and Or_{75} are shown in figure 6.

Orthoclase, in the mode of occurrence in which it is essentially the only feldspar present, is believed to be of authigenic origin on the bases of its near-end-member composition, nonperthitic character, and petrographic relations. Baskin (1956), in a comprehensive study of authigenic feldspars, found that they are uniquely pure in composition and that the K-feldspars rarely contain more than two percent equivalent albite. In contrast, K-feldspars of plutonic salic rocks commonly contain as much as 20-35 percent equivalent albite (including Ca-feldspar) (Tuttle, 1952b, p.111), and also are commonly perthitic. An anomalous feature of authigenic K-feldspars is that they apparently occur more commonly as the high temperature monoclinic form than as the expected low temperature triclinic microcline. Baskin (1956, p. 151) considers that authigenic monoclinic K-feldspar forms metastably. Evidence

of authigenic development in thin section is suggested by the occurrence of orthoclase in irregularly-shaped patches that can be considered cement, and by the inclusions of carbonaceous material that must have been enveloped by the orthoclase in its growth. Many grains, however, do not show any definitive features of origin--they range in shape from anhedral to subhedral and contain few to many inclusions of bubbles, illite, and carbonaceous and iron oxide materials.

The samples in which orthoclase and albite occur together are more difficult to interpret. In figure 5 a pattern of a mechanical mixture of orthoclase and albite is presented for comparison with the pattern of P-28. The similarities of the two patterns are apparent, disregarding, of course, the two strong quartz peaks of P-28 at approximately 21° and 26.5°; yet a comparison like this is not sufficient in itself for identification purposes, and a detailed study of the position of peaks that are present or absent of all possible feldspars must be made. Without doubt the feldspar present, other than orthoclase, is a plagioclase, but its identification as albite is not certain. The choice is only between albite and oligoclase, however, and albite is favored by the x-ray and optical data. The unresolved or poorly resolved x-ray peak at about 28.3° is characteristic of albite. This peak shifts to higher angles and is clearly resolved in plagioclases more calcic than albite, and it is one of a pair of peaks used by Goodyear and Duffin (1954, p. 319) for determining the anorthite content of plagioclases. Indices of refraction and extinction angles favor albite, though neither of these was determined precisely enough for positive identification.

The occurrences of orthoclase and albite together pose some interesting problems that are not resolved here: their mode of occurrence, petrographically, is similar to that of orthoclase in the one-feldspar-rocks, and the orthoclase in both modes of occurrence is considered of authigenic origin. Authigenic origin of the albite is not as clearly established, because knowledge of its precise composition is lacking, but the petrographic similarities of the occurrence of albite and orthoclase suggest that the albite is probably of authigenic origin, too. If the feldspars in these rocks, then, are mostly of authigenic origin, one is faced with the problem of explaining their different occurrences. Orthoclase occurs alone in the rocks comprising about the lower one-quarter of the section, and in some of the quartz-silicate rocks of this part of the section it may occur in amounts of as much as 15 to 20 percent--the most of any rocks in the entire section. In the upper three-quarters of the section, most of the rocks contain orthoclase and albite, although occurrences of orthoclase alone are common. There is no apparent correlation between the mode of feldspar occurrence and the major rock types. The amount of feldspar in a rock, however, is roughly proportional to the amount of quartz. Thus it would seem that the constituents from which the feldspars were formed were derived ultimately from the same source as the quartz. Volcanic glass is an appealing source material for the feldspars and is often cited as a possibility, Honess and Jeffries (1940, p. 17) for example, but is not well substantiated. The rare occurrence of biotite in a few samples and the characteristics of some quartz suggest a volcanic origin for some of the material, but this evidence is not conclusive.

Although an authigenic origin of the feldspars is favored here, an important alternative interpretation of the occurrence of two feldspars is possible and cannot be excluded on the basis of the present data. It is possible that the orthoclase-albite association is actually an orthoclase cryptoperthite, i.e., a perthite of orthoclase and albite phases, as detected by x-ray, which appears to be a homogeneous feldspar under the microscope. This alternative is not readily excluded by petrographic data since twinning is not common, and where it is developed it is often fuzzy. Since perthites can be homogenized by heating at temperatures above the solvus and below the solidus (Bowen and Tuttle, 1950, p. 497), some of the samples containing two feldspars were tested by this means. Homogenization was nearly complete but a couple of modified albite peaks persisted. Utilizing the position of the $\bar{2}01$ peak, apparent Or compositions ranged from about Or_{75} to Or_{45}. This test is not definitive here, however, because it was found that finely ground mechanical mixtures of orthoclase and albite, treated in the same manner, reacted similarly.

Quartz and microcrystalline quartz

Quartz occurs in all beds of the section and microcrystalline quartz in many of them. The total amount of quartz and microcrystalline quartz, as estimated from the chemical analyses, ranges from a few percent to about 50 percent. Microcrystalline quartz makes up only a small proportion of the total, although in beds P-16 and P-56 thin interbeds are composed nearly entirely of microcrystalline quartz.

Most of the quartz occurs as discrete anhedral particles that tend to be equidimensional though subangular in shape, but a marked variation in shape is shown by the particles that are lath-shaped or splinter-like. They have a length to width ratio greater than about 3 to 1 and generally have extinction inclined to the long dimension. Weaver (1955, p. 168) suggests that lath-shaped quartz in some samples of the Phosphoria in Montana is of volcanic origin, and that the particles are similar to the quartz paramorphs after tridymite described by Ray (1947) and

Wager and others (1953). Inclined extinction of the particles noted here is similar to that shown by the quartz paramorphs, but inclined extinction would also occur where elongation was determined by the rhombohedral cleavage, the type of fracturing Ingerson and Ramisch (1942, p. 597) found was favored in some quartz crushing experiments. Authigenic quartz crystals tend to be elongate due to the strong development of the prism form, but they then exhibit parallel extinction. Organic quartz spicules and spines are nearly always composed of microcrystalline quartz in Phosphoria rocks. It thus seems that the lath-shaped quartz particles are either quartz paramorphs of volcanic origin or are fractured particles elongated in the direction of the rhombohedral cleavage but data are insufficient at present to decide between the two possibilities.

Inclusions in quartz are common and of medium amount. Most of them are bubbles up to several microns in diameter but generally about 1 micron or less. Their distribution is mostly irregular though some occur along planes, giving the common bubble or dust chain appearance. Carbonate occurs as apparent inclusions in a wide range of amount, because its relationship to quartz is one of replacement. Illite is common as replacement inclusions in some beds. The iron oxide-carbonaceous material occurs as inclusions around the border zone of some particles. Other rare included minerals are zircon (figure 7), and fine needles of rutile(?) (bed P-70).

An occurrence of quartz in very small veins in bed P-107 (figure 8) shows an unusual combination of properties. Its index of refraction is slightly less than Canada balsam, and it shows strong irregular extinction like microcrystalline quartz; yet it has a good crystal outline. X-ray analysis verifies that it is quartz.

Microcrystalline quartz occurs mostly as matrix material, that is, it is mixed intimately with the iron oxide-carbonaceous material and the clay minerals. In such occurrences discrete particles or masses of microcrystalline quartz are difficult to define, and estimates of amount cannot be made from thin sections. However, its occurrence is distinct in some carbonate rocks, forming small segregations of irregular form. In these carbonate rocks the refractive index of the microcrystalline quartz is less than Canada balsam.

Aside from its mixture with other materials, microcrystalline quartz is typically full of bubbles, though the concentration of bubbles is variable. The bubbles are believed to be liquid-filled cavities as shown by their moderate relief and low refractive index with respect to quartz. The refractive index of the microcrystalline quartz is distinctly less than Canada balsam in some occurrences and slightly greater in others. Folk and

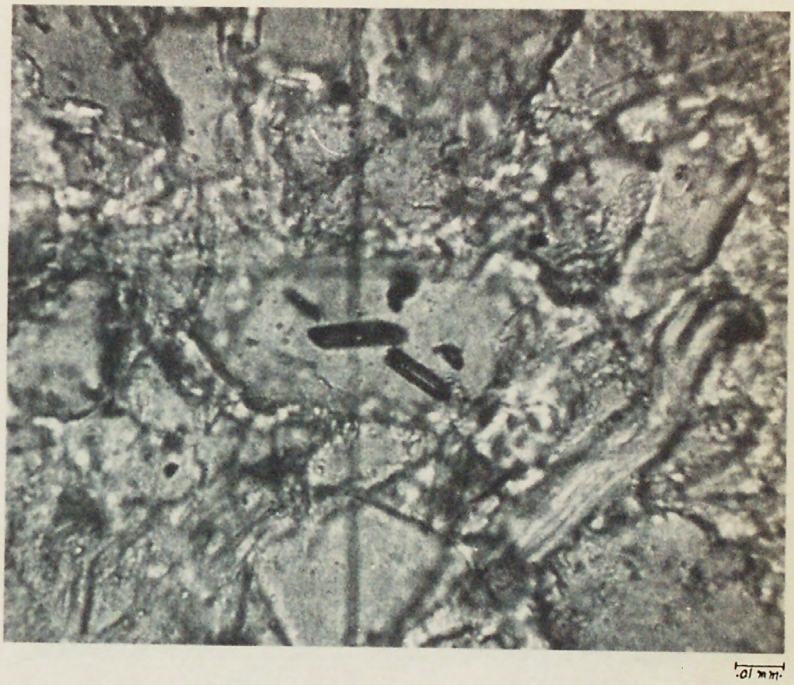

Figure 7. Zircon inclusions in quartz particle and curved muscovite lath to the right of the quartz. Other particles are carbonate and quartz. Bed P-70.

Weaver (1952) show that the lowering of the refractive index of microcrystalline quartz with respect to normal quartz is a direct function of the abundance of liquid-filled cavities in the microcrystalline quartz.

Mica group

Muscovite and biotite are the mica minerals present in the section. Two petrographic types of muscovite, defined somewhat arbitrarily on the basis of size and mode of occurrence, probably represent at least two of the polymorphs of muscovite determined by Yoder and Eugster (1955). Although fine fractions of the samples have not been sufficiently pure to identify the polymorphs by x-ray with precision, the muscovite in the clay fraction of sample P-101 is apparently mostly the 1 Md polymorph, or what is here called illite - the very fine-size mica. The differential thermal analysis pattern is characteristic also of illite. The other petrographic type present as large laths, is probably a different muscovite polymorph, but, without specific information, it is called simply muscovite in further descriptions.

Muscovite has been identified in nearly all the beds of the section. It occurs as discrete laths that commonly have a length of 0.05 mm to 0.15 mm and a ratio of length to thickness of about 10:1. Cleavage lines are generally well expressed and the laths show various degrees of "freshness".

Some are sharply rectangular with straight regular borders and others are irregular and ragged, particularly at the ends of the laths. It is not uncommon to find laths that have been bent or broken during compaction of the sediment (figure 9). Strain developed at the points of bending results in the lowering of interference colors and irregular extinction. There are few to many inclusions and they are mostly iron oxide-carbonaceous material that occur along cleavage planes or along the margin of the laths. Other inclusions are carbonate and in one instance zircon. The bent and broken laths and the zircon inclusions in one particle suggest that the muscovite is exogenic.

Illite is petrographically the very fine-grained mica that occurs in and makes up a considerable portion of the rock matrix. Generally it is so mixed with iron oxide-carbonaceous material and microcrystalline quartz that its character is largely indiscernible; in aggregates, however, its characteristic relief and interference colors are distinctive. In contrast to muscovite at least part of the illite is authigenic, as shown by its development in and along the margins of quartz and feldspar particles.

Biotite is rare, at least in recognizable form. In the three samples in which it was found, P-3, P-82, and P-99, it is strongly altered. The biotite is considered here as volcanic in origin and indicative of the occurrence of an unknown amount of pyroclastic material in the

section. This interpretation is based on the fact that in a review of descriptions of tuffs and bentonites, biotite is nearly ubiquitous in occurrence. In addition, because of biotite's poor resistance to weathering at the earth's surface, it is commonly found only in rapidly deposited sediments, represented by graywackes and arkoses. Biotite has been found in the Phosphoria at one other locality, the Kelly Gulch section in southwestern Montana (Weaver, 1955, p. 172).

Kaolin group

Kaolinite is used in the broad sense as that group of clay minerals, other than the chlorites, which show the typical x-ray basal reflection (001) with a spacing of about 7.15Å. It occurs in many of the beds but only in very small amount. In thin section it is easily recognized by its characteristic occurrence as "books" of medium relief and its low interference colors. In one bed several "books" are aligned end to end in such a way as to suggest that they had been derived from muscovite--that a lath of muscovite had been altered to kaolinite before deposition and had been broken during the compaction of the sediment. In other places kaolinite is found as relatively large aggregate particles.

It is noteworthy that only illite and kaolinite clay minerals have been identified in this section, although it is possible that small amounts of others may have been overlooked. Mixed layer illite - montmorillonite has been found in one sample at Trail Canyon, Idaho, and Herr (1955) found it to be common in some Montana samples; and montmorillonite has been identified in samples of the Phosphoria in Montana by Weaver (1955, p. 175), Rooney (1956), and Herr (1955).

Iron sulfides

Pyrite has been identified only in rock of the "vanadiferous zone", beds P-71 through P-75, which contains the most sulfur of any beds of the section. Pyrite probably occurs in small amount in most of the other beds, although it has not been found in them by x-ray or in thin section. The "vanadiferous zone" samples taken from an adit were unweathered, whereas the other samples contain iron oxides that probably have been derived in large part from pyrite in weathering. The pyrite in the "vanadiferous zone" was detected by x-ray. It is not identifiable in thin section but apparently comprises part of the black opaque amorphous-appearing matrix material of the rock which is presumably an intimate mixture of carbonaceous material and sulfide. This same rock may contain another sulfide, since hydrogen sulfide is evolved when the sample is treated with hydrochloric acid. Pyrite and marcasite are unaffected by the acid, but pyrrhotite or a simple iron sulfide would produce such a reaction. Pyrrhotite is an unlikely constituent of these rocks. It is more likely that the material is similar to that found in some modern marine sediments by Emery and Rittenberg (1952, p. 791), which reacted in the above manner, and which they suggest is hydrotroilite ($FeS \cdot nH_2O$) or melnikovite (a cryptocrystalline FeS_2). Another possibility is that the reaction is with sulfur-containing organic compounds rather than iron sulfide.

Iron oxides

The identification of the iron oxide minerals is possible in only a general way because of their very finely particulate state. An exception is the iron oxide occurring as small globules, usually in swarms in which some of the globules are spherical in shape. These are blood red or opaque in transmitted light and blood red in reflected light, and have high relief. Though other optical properties cannot be determined because of their small size and strong coloration, the mineral is believed to be hematite.

Most of the iron oxide occurs as finely disseminated brown particles mixed with black organic material. This is designated limonite in its broad usage as including all of the hydrous and hydrated iron oxides. This material is ubiquitous and, along with the carbonaceous material, is responsible for the coloring of the rocks.

Sulfur compounds

Sulfur has several modes of occurrence in these rocks. As discussed previously, it occurs in pyrite and possibly as a simple iron sulfide; and it is believed to occur in apatite diadochic with phosphorus. Some probably occurs in organic compounds that compose the carbonaceous material. Some occurs as gypsum in weathered rock of the "vanadiferous zone", derived presumably in most part from the oxidation of pyrite.

Jacob and others (1933, p. 48), on the basis of chemical analyses of phosphate rock of the Phosphoria, list five forms of sulfur: sulfate soluble in 1:4 HCl, sulfate insoluble in 1:4 HCl, H_2S evolved with 1:4 HCl, sulfide insoluble in 1:4 HCl, and organic sulfur. The results of these analyses showed that most of the sulfur occurs as sulfate soluble in HCl, followed in order of amount by organic sulfur. The other forms were of minor amount. These findings tend to confirm that sulfur occurs in apatite - SO_4 substituting for PO_4 - as suggested in the discussion of apatite mineralogy. Gypsum or anhydrite would be other common forms of soluble sulfate. Evolution of H_2S with HCl suggests the presence of a simple sulfide as discussed previously, and Jacob's insoluble sulfide would be pyrite or marcasite.

An acid insoluble sulfate mineral, suggested by

Jacob's determination of acid insoluble sulfate, has not been recognized here; however, W. W. Rubey (written communication) found that sulfur in some other "vanadiferous zone" rock of western Wyoming occurred largely as acid insoluble sulfate, conceivably as alunite although not specifically identified.

Carbonaceous material

Little is known of the chemical character of the carbonaceous material, though part of it is bituminous as indicated by its odor. Sulfur is undoubtedly a component of the carbonaceous material, but it is not known how much occurs in organic compounds rather than in iron sulfides. The carbonaceous material is black and opaque in concentrations but brown in disseminations. It gives the rock its black color, and the blackness of a rock is rough indication of the amount of carbonaceous material the rock contains. Thus, the carbonate rocks are generally the lightest in color and contain the least carbonaceous material.

Accessory minerals

Fluorite, titanite, and leucoxene, tourmaline, and zircon are common but minor constituents of the rocks. Fluorite occurs mainly in phosphate rock, though most of the phosphate rocks do not contain fluorite. A single occurrence was found in dolomite, bed P-42. Fluorite is readily identified by its high negative relief and isotropic character. In phosphate rock it occurs both within carbonate-fluorapatite pellets and between them. The fluorite is purple or colorless but mostly colorless; the two colors may occur in the same rock.

Titanite is relatively abundant. Its high interference colors, high relief, and strong dispersion are distinctive. White semitranslucent particles are tenatively identified as leucoxene. Tourmaline is less abundant. It generally is brown in color but some is green or grayish-blue. Tourmaline particles range in shape from irregular to subhedral form. Zircon occurs in its typical rounded prismatic form.

PETROGRAPHY

Rock types

Rocks of the phosphatic shale member are of three principal end-member types--carbonate rock, phosphorite, and quartz-silicate rock. In general their physical character is similar. All are fine-grained--modal size of silt,/ -- except those phosphorites composed of pellets and oolites that are of sand size. All are dark colored, black and dark shades of gray and brown. In order of darkest to lightest they are, respectively, some of the quartz-silicate rocks, phosphorite, and carbonate rock. All are thin-bedded, measured in tenths of a foot, except some carbonate beds of a foot or more. With the exception of a few of the carbonate rocks and phosphorites they weather to a typical shale, small and thin plates of quartz-silicate rock and phosphate rock and small irregularly-shaped chunks of carbonate rock.

Composition

Carbonate rock is composed largely of dolomite and calcite, and is subdivided to dolomite rock and limestone for specific purposes, but the two are best grouped together for general comparisons. Phosphorite is composed predominantly of the mineral carbonate-fluorapatite. The quartz-silicate rock is composed largely of quartz, feldspar, muscovite, illite, and kaolinite. The amounts of these latter constituents have not been determined individually so that their group total is represented by the acid insoluble chemical determination. The rigorous acid insoluble determination involves solution, oxidation, and strong ignition so that only the very resistant quartz and silicate minerals remain; and of these there is some loss in solution and ignition, presumably from muscovite, illite, and kaolinite. This loss is indicated by comparison of A.I. and the summation of SiO_2, Al_2O_3, K_2O, and Na_2O wherein the summation of the main silicate constituents exceeds the A.I. by approximately two percent in the fifteen rocks of highest quartz-silicate content. This figure does not include structural or absorbed water lost in ignition above 105° C. Thus the quartz-silicate content of the rocks as represented by the A.I. determinations is in general a minimum value.

Range of mixtures of end-member rock types

Only the end-member rocks have been considered up to this point, but in order to show the relationship of their principal mineral components in all of the rocks of the section, the components are plotted on a ternary diagram in figure 10. The three components, carbonate (calcite plus dolomite), carbonate-fluorapatite, and quartz-silicate have been recalculated to represent one hundred percent for all beds of the section not composed of interbedded lithologies.

As can be seen in figure 10, the rocks tend to cluster toward the apices of the triangle; that is, rocks of end-member composition are more common than those of intermediate composition. The quartz-silicate component mixes with carbonate and carbonate-fluorapatite in about all proportions, though the intermediate mixtures are uncommon. However, mixing of carbonate and carbonate-fluorapatite appears to be restricted; the two components do not tend to occur with one another in proportions less than about 3:1. Such a restriction is indicated by not only the left central barren zone of figure 10 but also the lack of rocks

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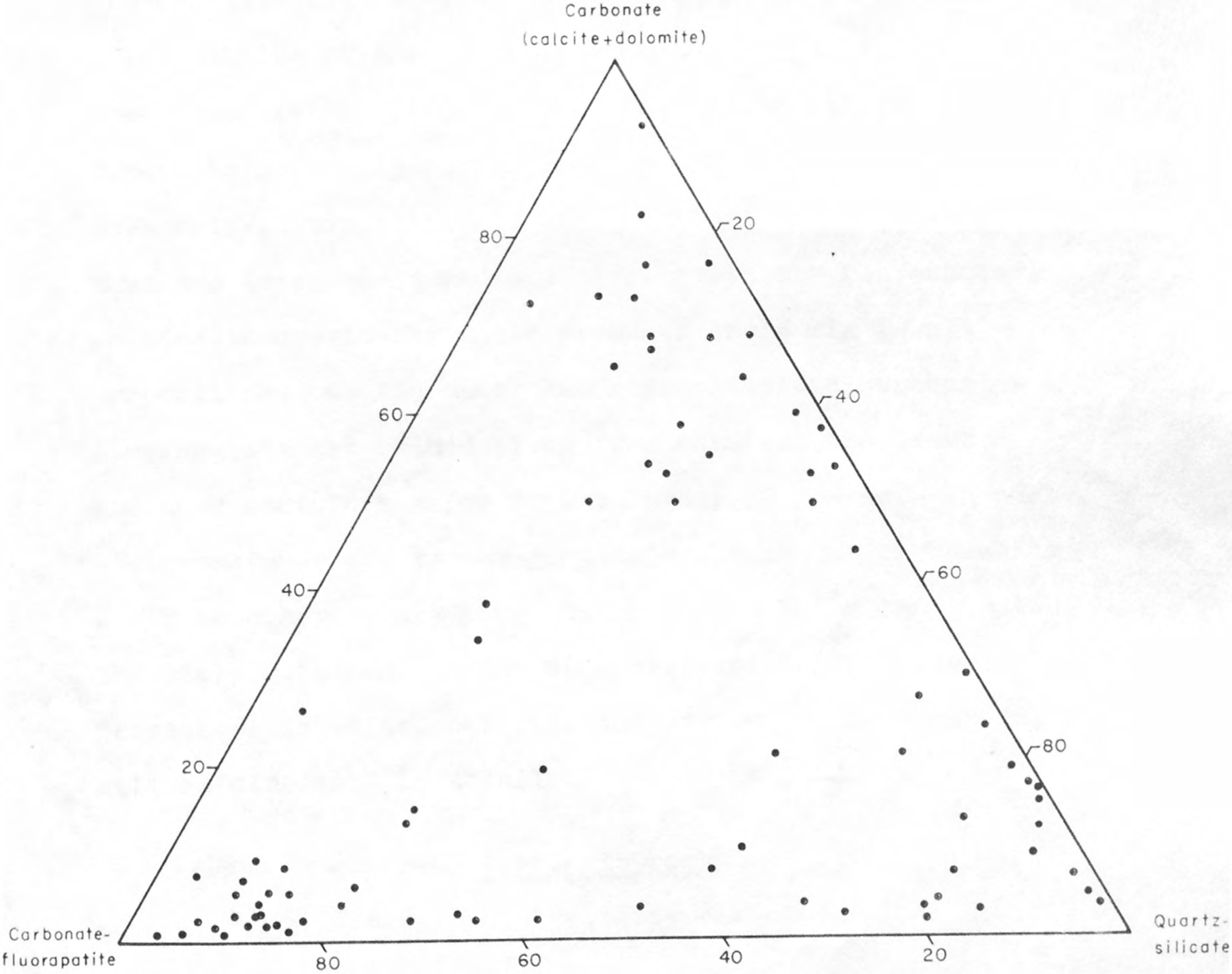

Figure 10.—Ternary plot of principal mineral components representing end-member rock types recalculated to 100 percent of all beds except those composed of interbedded lithologies

that would compositionally fall in the central zone of the triangle if proportions of carbonate and carbonate-fluorapatite less than 3:1 tend to be prohibitive. The relationships of the three components that have just been described are understandable if the quartz-silicate component is primarily exogenetic and the carbonate and carbonate-fluorapatite are endogenetic (precipitates). Thus two independent modes of derivation are represented, so that theoretically their products could mix in all proportions. On the other hand carbonate and carbonate-fluorapatite are both derived from chemical processes, and they contain a major ion, calcium, in common. In such a circumstance the two components would not be expected to occur together in all proportions. In a following section the phase relations of the minerals derived from chemical processes, dolomite, calcite, and carbonate-fluorapatite, will be discussed in detail.

Carbonate rock

Petrographic types of carbonate

The dominant mode of occurrence of the carbonate minerals is as sub-equidimensional, anhedral, inclusion-filled, pale brown particles. Variations from this type of carbonate are marked but continuous, and cannot be distinctively categorized, except for the carbonate which has filled fractures, replaced quartz, feldspar and muscovite, and that which constitutes fossil shells or fragments of shells. The carbonate occurring as veins and as a replacement of minerals, other than carbonate-fluorapatite, is distinguished from the modal type carbonate by its lack of color and by its relative lack of inclusions. The carbonate of shells of foraminifera and shell fragments of brachiopods or pelecypods is characterized by its fineness of grain, shape, and structure. These latter two carbonate types make up a very small proportion of the total carbonate.

✓ Texture

Carbonate rocks are composed of particles or grains of carbonate and other minerals that produce a granular texture (figure 11). There is essentially no matrix. Size and shape of the carbonate particles are frequently difficult to determine, because discrete particles are not easily defined. Physical boundaries around particles are often discontinuous or indistinct, and particles largely defined by physical boundaries may not be homogeneous with respect to optical properties. In contrast carbonate microfossils and fossil fragments which occur in significant amount in some of the rocks that contain much calcite, are sharply defined.

The common size of the carbonate particles lies in the range of 20 to 60 microns in diameter. The smallest particles that can be resolved are about 2 microns, and the

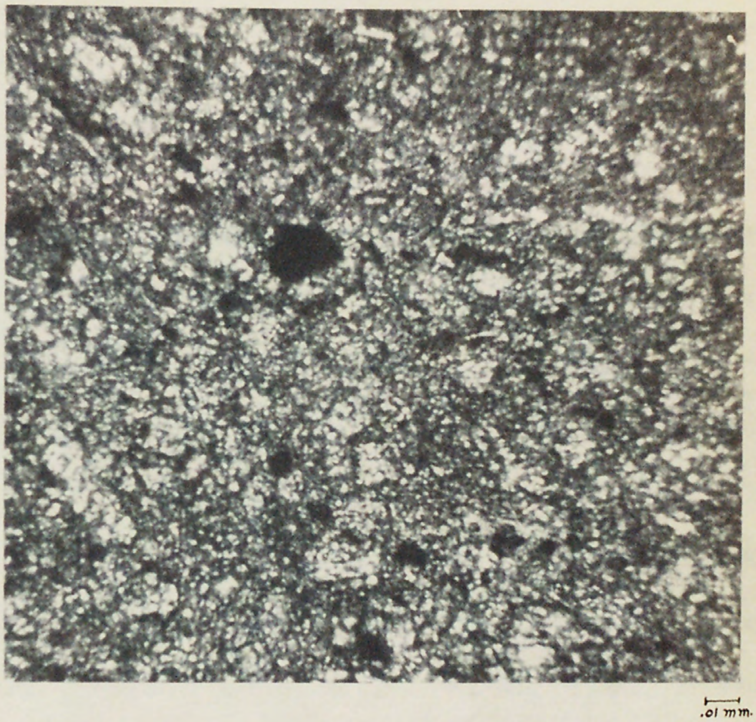

Figure 11. Granular texture of carbonate rock composed of anhedral particles of dolomite and calcite, 51 percent dolomite and 22 percent calcite. Bed P-107.

largest carbonate particle found, not including shell material, is about 300 microns. The size distribution is approximately seriate with a single mode, except for bed P-42 where relatively large phenocrysts are set in a much finer-grained matrix with few, if any, intermediate-sized particles. A few beds show a marked uniformity of size; that is, a small size range and a distinct modal group, analogous to that in well sorted beds of detrital material.

Both dolomite and calcite occur most commonly as sub-equidimensional anhedral particles, a mode of occurrence that reflects upon their tendency to crystallize as rhombohedrons. Variations from the sub-equidimensional anhedral form tend, for calcite, toward greater irregularity of shape accompanied by increase of particle size; and for dolomite toward greater euhedralism along with increase in size. Shell material contributes to the irregular shape of some calcite; however, the irregular shape of other calcite, as in bed P-66, is due to secondary growth which has resulted in the incorporation of other mineral particles within the calcite particles. Euhedral dolomite particles, as rhombs, are not common but are striking in their occurrence, as in figure 12, in which the rhombs are like phenocrysts, much larger than any of the surrounding particles. In bed P-56, (figure 13) the dolomite has been reorganized into large subhedral particles whose unequal development is the result of mutual interference in growth.

Most of the carbonate rock textures reflect two main stages of modification of a primary accumulation of very small particles: (1) Aggregation and primitive reorganization: and (2) Advanced reorganization.

The stage of aggregation and primitive reorganization is one in which the physical boundaries of the particles are vague and discontinuous, and one in which groups of particles have attained a degree of optical homogeneity. Particles separated by a physical boundary may have nearly the same optical orientation, giving rise to the common phenomenon of migrating extinction that is observed in thin section under crossed nicols with rotation of the stage. In such instances the darkness of extinction passes uniformly from particle to adjacent particle, indicating a gradual change in orientation of the particles that is not affected by apparent physical discontinuities. This phenomenon is interpreted to indicate that a marked reorganization of the carbonate particles has occurred, one in which particle growth, apparently by accretion of adjacent particles, is imperfectly attained.

Advanced reorganization is indicated by an increase in particle size; a tendency for euhedral development, except where the particles mutually interfere in growth; and by the attainment of the greatest degree of physical and optical homogeneity of all the carbonate particles. Included iron oxide-carbonaceous material occurs in some instances as relatively large segregations within the particles or as concentrations along their borders, a mode of occurrence that represents an attempt by the particles to exclude foreign particles during their reorganization. In rare instances other minerals were included during the carbonate reorganization.

Inclusions

Inclusions in dolomite and calcite particles are common and generally abundant. Due to the aggregate character of most of the carbonate particles, the instances in which an aggregate is composed of one large and several small particles may be considered as instances of carbonate inclusions in carbonate particles. In addition to carbonate inclusions, there are generally many bubbles, presumably liquid inclusions, and very finely divided dark brown material that is believed to be mostly carbonaceous matter and iron oxides and, in some instances, brown isotropic carbonate-fluorapatite. The dark brown material is always present but ranges considerably in amount. It accounts for the weak brownish-colored darkness of the carbonates. Where it occurs in large amount the nature of the carbonate is obscured to a considerable degree. Where it occurs in small amount and is finely disseminated throughout the carbonate, the coloring and darkening is hardly perceptible except where it may be contrasted with clear colorless vein calcite.

Only in bed P-66 have other minerals occurred as inclusions in the carbonate. Here calcite has been reorganized into some large irregularly-shaped masses that have enclosed quartz, feldspar and muscovite particles.

Replacement

Carbonate replacement of other minerals seems not to have occurred on a large scale, though a significant amount has occurred in bed P-80. In this bed the replacement of brown isotropic carbonate-fluorapatite by calcite is distinct in that relict pelletal outlines have been preserved, and in some places ragged apatite masses occur as nuclei within the relict pellets. Also, the replacement calcite within the globular outline is strongly brown-colored as compared to the calcite enclosing the relict pellets.

Replacement has taken place on a small scale in nearly all beds. The most common carbonate replacement is of quartz, occurring as projections and embayments along the quartz particle boundaries. Feldspar and muscovite have been replaced by carbonate in the same manner but not as frequently. The carbonate replacing these minerals is colorless and stands out sharply in contrast to the regular carbonate.

Replacement of carbonate has been noted in only one bed, P-56, where microcrystalline quartz has replaced the corner of a dolomite rhomb, and the rhomb-corner outline has been preserved.

Cleavage and twinning

Cleavage is weakly developed and is generally found in only the larger carbonate particles. Twinned particles are uncommon in the section as a whole, but are abundant in some beds such as P-28 and P-79.

Phosphorite

Petrographic types

Most of the carbonate-fluorapatite is submicrocrystalline, brown, inclusion-filled, and optically isotropic. Light brown anisotropic apatite occurs as bands on oolites that show the extinction cross, indicating a radial orientation of the crystallites in the bands. Most fish scales and fragments of bone and/or tooth are also composed of this type of apatite, but orientation of the crystallites, although not radial, is indicated by wavy extinction. Others contain colorless apatite probably due to recrystallization. Colorless and inclusion-free anisotropic apatite frequently occurs as small segregations in pellets and oolites. Apatite euhedra have been found in veins in the phosphorite and, in one instance, in a local matrix of microcrystalline quartz (figure 14).

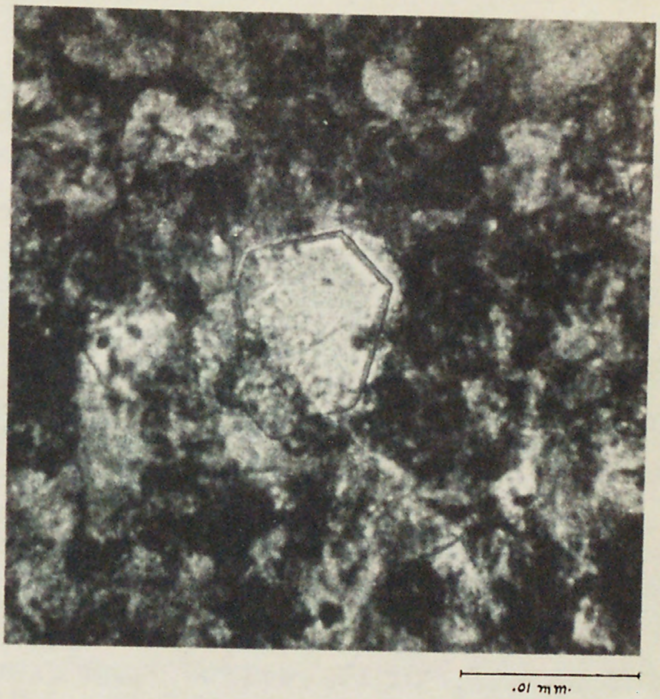

Figure 14. Carbonate-fluorapatite crystal in matrix of microcrystalline quartz, iron oxide, and carbonaceous material. Bed P-16.

Texture

There are two principal textures of the phosphorites, microphanite and pelletite -- textural terms used in an unpublished rock classification by McKelvey, Gulbrandsen, and Sheldon. Microphanite is composed mainly of interlocking, sutured, mosaic, subhedral or euhedral crystals less than 0.0625 mm. Although the apatite microphanite considered here is composed of submicrocrystalline particles, there can be little question but that the relationship between the individual crystallites is of the kind described in the above definition. Pelletite, figure 15, is composed mainly of well sorted spherical or sub-spherical aggregates with no internal structure that have a modal size of 0.0625-2.0 mm. Oolite, figure 16, is the equivalent term of pelletite except that the aggregates have a concentric internal structure. Only in beds P-1 and P-97 is the oolite texture predominant. Pelletite is a more common texture than microphanite. Phosphorites may contain only pellets, but those that contain oolite grains contain pellets too. Mixtures of microphanite with pelletite and oolite occur in many beds, but where microphanite is in small amount it is considered as cement. Pellets are indistinct in some phosphorites, representing a texture intermediate between microphanite and pelletite, and such incompletely developed aggregates are called incipient pellets.

Very nearly all of the carbonate-fluorapatite is submicrocrystalline in size. The remainder is macrocrystalline and consists of small anhedral to euhedral crystals. Pellets and oolites, aggregates of submicrocrystalline apatite, range in shape from spherical to markedly elongate. Those that are elongate have their axis of elongation remarkably parallel in some beds, although in others a preferred orientation is absent. The pellets and oolites are well rounded, even those whose outline is irregular. Their common size is generally much larger than that of other mineral particles in a bed. For the member as a whole their modal size is in the range of about 0.1 to 0.5 mm., and the maximum is about 5.0 mm. Fish scales and fragments of bone and tooth commonly are measured in tenths of a millimeter.

Inclusions and color

Pellets and oolites may contain inclusions of any of the major minerals in the rocks but tend to contain few or none. Small segregations of colorless anisotropic apatite are common but few occur in one pellet or oolite. Some fluorite is present in this manner also. Nuclei of fish scales and bone or teeth fragments in the aggregates are rare except in bed P-1.

The submicrocrystalline apatite ranges in color from a light brown to a very dark brown. The coloration is commonly splotchy and is due to the presence of finely divided iron oxides and carbonaceous material. Upon heating the apatite to 1,000° C. most of the color and carbonaceous material is lost, leaving only reddish brown iron oxide as a residue of the included material.

Development of pellets and oolites

Apatite microphanite represents an unmodified accumulation of apatite. A post depositional formation of aggregates from such a primary accumulation of apatite is indicated in those rocks that show incipient pellets. Complete pelletization is not recognized with certainty, but some of the pelletites that don't show evidence of pelletization prior to deposition may be of this derivation. Pelletization prior to deposition is indicated by the presence of pellets in carbonate and quartz-silicate rocks; by the occurrence of quartz and silicate minerals interstitially to pellets that do not contain those minerals as inclusions; and by the occurrence of apatite cement between the pellets.

The development of oolites is not well understood and only a few observations about them will be made here. None of the oolites are completely banded from center to edge. In a sense, then, they all must have nuclei, even though most of the nuclei consist of structure-less apatite. Other nuclei are organic apatite fragments and, rarely, quartz grains. The oolites most likely developed prior to deposition at their final resting place, and they probably have a complex or varied earlier history of formation. Development of the remarkably uniform and delicate banding seems to demand conditions such that the entire surface of an oolite was free to accrete new material evenly and essentially simultaneously. Growth while the oolite is spinning in suspension or rolling gently on the bottom may be the explanation, but it is difficult to conceive of how uniform banding concordant with the irregular shape of some oolites could develop in this manner, particularly by a bottom rolling mechanism. It may be that the bands of oolites are not accretionary but due to reaction and recrystallization of the outer portion of pellets, a scheme suggested by Lowell (1952, p. 35).

Quartz-silicate rock

Texture

Quartz-silicate rock contains two elements of texture, grains and matrix. The grains are dominantly quartz, feldspar, and muscovite; and the matrix is composed largely of illite and some microcrystalline quartz mixed with iron oxide-carbonaceous material. The matrix materials are very finely divided and intimately mixed. Variations in amount of the matrix components relative to each other occur to the extent that individual ones dominate in particular samples; e.g., rocks of the vanadiferous zone, beds P-71 to P-75, contain much carbonaceous material and finely divided pyrite that causes thin sections of the rock to be nearly opaque and obscures other mineral relationships. Carbonate minerals and apatite occur in a wide range of proportions with the quartz-silicate constituents, as shown earlier. Pellets of apatite are generally large relative to other grains of the quartz-silicate rocks and produce a distinct bimodal size distribution.

The grains of the rock are mostly of coarse silt size, modal size in the range of 0.02 to 0.05 mm. Muscovite occurs typically as lath-shaped particles that range in lengths from about 0.05 to 0.15 mm. and have a common ratio of length to thickness of about 10:1. Quartz and feldspar tend to be equidimensional and sub-angular to sub-round, and both, but particularly feldspar, may be subhedral to euhedral. Additional description of the characteristics of these minerals and other constituents in the quartz-silicate rocks is included in the mineral descriptions of an earlier section.

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The constituents comprising the rocks of the Meade Peak member are broadly classed as exogenetic or endogenetic. The major part of the quartz-silicate suite of minerals is exogenetic, derived principally as detritus but possibly in part as pyroclastics. The occurrences of this mineral group are the result primarily of physical processes. The group of major constituents composed of apatite, dolomite, and calcite is endogenetic, and its occurrences are largely the result of chemical processes. The occurrences of these two groups were shown previously to be essentially independent of one another, and attention is directed here to chemical processes involved in the formation of the endogenetic group - apatite, dolomite, and calcite. Other endogenetic constituents, such as carbonaceous material, sulfide, some illite and feldspar, and many minor constituents, have been described to the extent possible at this time in other parts of this report.

The chemical composition of this section of the Meade Peak member, as noted earlier, is unusual in that phosphorus and fluorine are abnormally abundant. These elements occur in the mineral carbonate-fluorapatite, which is the most abundant mineral in the member. Apatite is also one of a group of chemically related minerals - apatite, dolomite, and calcite - that comprises more than 50 percent of the total mineral composition. The occurrences of these three minerals in the rocks at this locality and the associations of the minerals on a broader scale provide a basis for investigating their modes of formation.

Nature of rock type changes in the member

The member is composed of three principal rock types, some of which contain exceptional amounts of their characterizing minerals, as explained previously. The rock strata, most commonly beds 0.5 to 2 feet in thickness, occur in an unsystematic alternation of one upon another. As determined from the columnar section, plate 1, there are 56 alternations or changes of rock type and 57 rock units (determined by grouping adjacent beds with the same rock name). The 13 quartz-silicate units do not appear to preferentially overlay or underlay either of the other types. Carbonate rock (23 units) and phosphorite (21 units) overlay one another about the same number of times. Also, there is no favored sequence or triplet of the three rock types. Where adjacent beds are of different composition, the difference is large. It is unusual for a group of beds to show uniform progressive change. Qualitatively the mineral composition of the member is the same throughout--the different rocks are due to different proportions of the major minerals. In addition, the number of major minerals is small. These features indicate that highly selective physical and chemical processes prevailed during the time that the rocks of the Meade Peak member were formed, and that specific conditions prevailed for considerable lengths of time in order to produce the thicknesses of the individual rock units. The relations noted above provide no obvious key to the origin of the phosphorites and carbonate rocks, beyond indicating an intimate association of the rock types, but the features conform in general to the hypothesis explored further on which considers the relationship of vertical lithologic changes at a locality to lateral changes or facies of rock units.

Range and distribution of calcium contents of the rocks in the member

Apatite, dolomite, and calcite are chemically related minerals that have two ions in common, calcium ion and carbonate ion; although carbonate occurs in the apatite in only small amounts, calcium is a major component of all three minerals and is the most abundant oxide (26.9 percent CaO) of all the constituents in the member. A frequency diagram (figure 17) shows that CaO contents are essentially symmetrically distributed with one distinct mode. This is taken to signify that calcium was supplied continuously and uniformly as sediment in one or more of its three mineral phases, and that the amount concentrated at any one time was dependent upon the amount of dilution by quartz-silicate detrital material. Thus the modal class of concentration of calcium represents the most common or prevalent condition, and variations from that to the right are toward greater concentrations of calcium minerals and

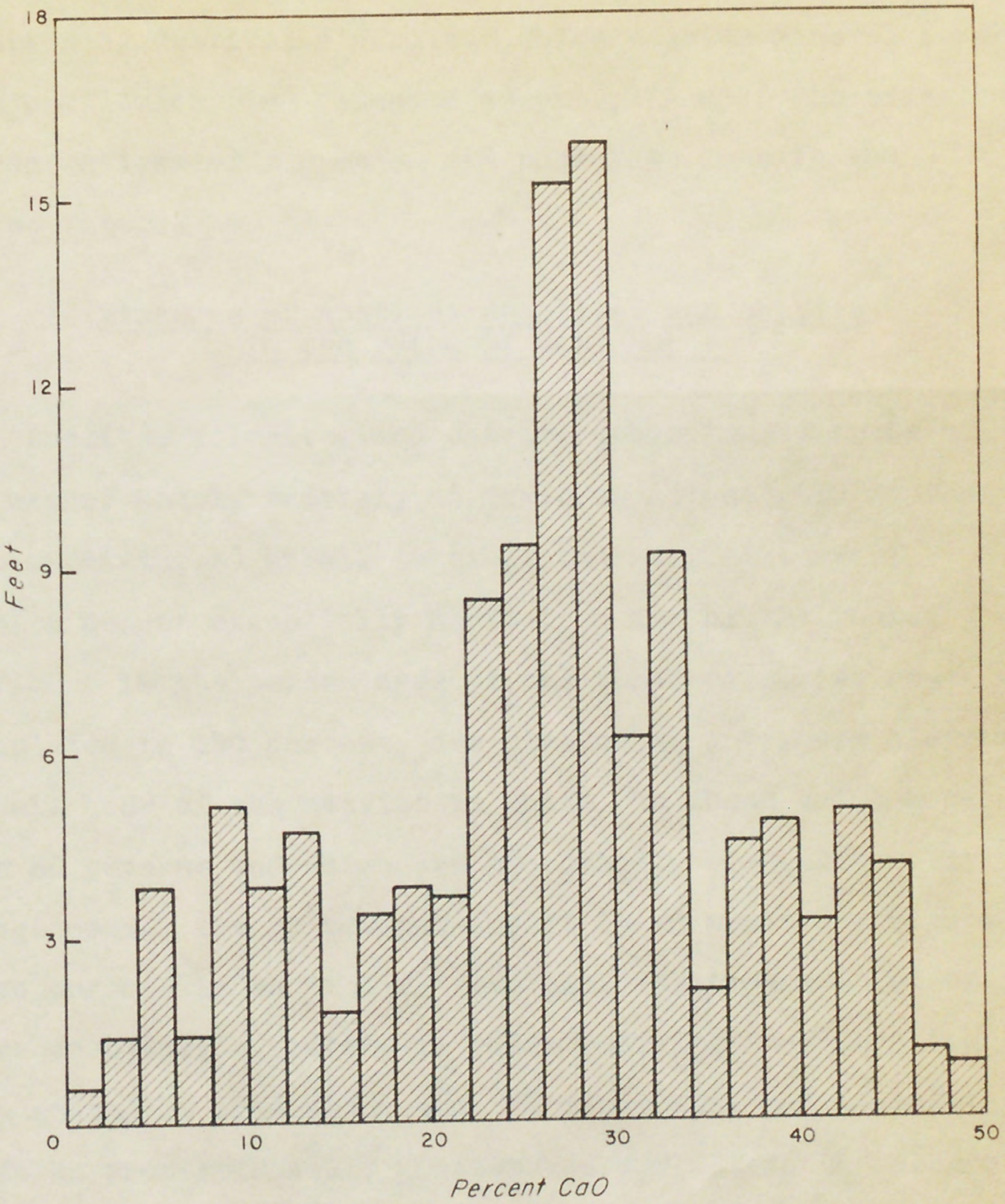

Figure 17.—Frequency of occurence of CaO in all beds of phosphatic shale member. Expressed as total feet of rock in 2 percent classes

to the left toward lesser concentrations and greater dilution by detrital minerals. Which calcium mineral formed at a particular time depended essentially upon the effective concentrations of magnesium and phosphate ions in the marine waters.

Mixtures of apatite, dolomite, and calcite in the rocks of the member

Apatite, dolomite, and calcite occur in the rocks of the member nearly entirely as mixtures of one with another (binary mixtures) or all together (ternary mixtures). Apatite occurs essentially alone in a few of the rocks. In figure 18 the percentages of the three minerals, recalculated to 100 percent, are plotted on a ternary diagram for all beds of the section in which the three total more than 50 percent and which are essentially compositionally homogeneous. The 50 percent cutoff is an arbitrary figure whose purpose is to exclude from consideration samples of lower endogenetic content in which modifications resulting from secondary processes, such as diagenesis and weathering, would be proportionately greater and would tend to obscure primary compositions. Calcite that occurs along fractures and joints in the rocks is a known contaminant of this kind. It is also known that the samples selected here only approximate the ideal of a homogeneous rock, and therefore, the rocks are not precise representatives of discrete primary mineral mixtures. It is not likely, however, that the

effects due to lack of complete homogeneity of the rocks and to secondary processes are large enough in most cases to obscure primary relationships entirely.

The samples shown in figure 18 are distributed along the dolomite-apatite and dolomite-calcite edges of the triangle. There are two principal groups of samples. Samples of the larger group are composed essentially of apatite, and samples of the other group in the dolomite corner are essentially dolomite-apatite mixtures. Samples distributed along the dolomite-calcite edge cover nearly the entire range of dolomite-calcite proportions. The near absence of points along the calcite-apatite edge and in the central part of the diagram suggests that there is an antipathetic relationship between calcite and apatite. The two groups of samples, described above and which include a majority of all the samples, represent the dominant types of mineral associations in the section. The dolomite-calcite mixtures represent the only other principal mineral association, but they cover a large range of mineral proportions.

Broader relations of mineral associations

All the features of the member just described are concerned with differences of mineral phases; and an hypothesis explored here attributes these differences to compositional changes of sea water. This hypothesis, although considered here with respect to the rocks of a part of one Phosphoria section, is suggested also by some aspects of the overall mineral associations of the Permian rocks in Idaho and Wyoming. Facies changes eastward from southeastern Idaho to central Wyoming, with respect to the constituents of concern here, are phosphorite to carbonate to anhydrite. If this is actually a continuous series, as stratigraphic data suggest, it might result from a continuous eastward increase in salinity, or salinity gradient, of the Permian sea. Thus Scruton (1953, p. 2506) ascribes the possible formation of lateral facies of carbonate, anhydrite, and salt to a salinity gradient; and Campbell (1955) considers this hypothesis as a possible explanation of the carbonate to anhydrite facies change of the Permian rocks in the Big Horn Basin of north-central Wyoming. A real genetic relationship between phosphorite, carbonate, and anhydrite facies - all of which have calcium as a common ion of their characterizing minerals - is suggested further by the fact that the Permian phosphorites of the Ural Mountains region of Russia have carbonate and gypsum facies (Kazakov, 1938). The occurrence of phosphorite and gypsum in Jurassic deposits in Mexico (Rogers, and others, 1956, p. 85), in Cretaceous-Tertiary deposits in the Atlas Mountains of North Africa (Visse, 1952, p. 17, 20), and in Upper Cretaceous deposits in Israel (Bentor, 1953, p. 97) may be additional examples, but the facies relationships of these deposits are unknown. Since neither anhydrite nor gypsum occurs in Coal Canyon, only phosphorite and carbonate facies are treated here.

Basic hypothesis of the formation of dolomite, calcite, and carbonate-fluorapatite

As a basic hypothesis, the occurrences of dolomite, calcite, and carbonate-fluorapatite in the rocks of the member are considered to represent approximately the solid phase or phases in equilibrium with the sea water from which they formed. The three minerals are chemical compounds that have two ions in common so the conditions for the formation of the minerals must be interrelated. Thus the carbonate rocks and phosphorites represent accumulations of primary precipitates whose mineral proportions are due to the specific conditions prevailing at any one time. The proof of such an hypothesis must show, as a minimum requirement, that the occurrences of the minerals singly or as mixtures are possible relationships in terms of theoretical requirements and are possible with respect to pertinent experimental data. The hypothesis assumes that equilibrium conditions were attained between sea water and the minerals formed from it. Common experience, however, has shown that in low temperature reactions, such as those considered here, equilibrium is frequently not attained and that unstable or metastable compounds are formed; e.g., Brooks and others (1950) have shown that metastable phases of calcium carbonate and its hydrates are reproducible under some conditions. One kind of mineral association is reasonably explained in this manner, but equilibrium is implicit in the general hypothesis.

The requirement of circulating sea water

The minerals dolomite, calcite, and carbonate-fluorapatite together make up more than fifty percent by weight of the total mineral content of the Meade Peak member; the weight of the carbonate minerals is about equal to that of apatite. Although the carbonate minerals occur in large amount throughout the geologic column, apatite is relatively rare. In order to emphasize the magnitude of the amount of phosphate in the Phosphoria formation as a whole, McKelvey, Swanson, and Sheldon (1953, p. 56) calculated that the formation contains about 1.7×10^{12} metric tons of P_2O_5, an amount that is more than five times the 0.32×10^{12} metric tons of P_2O_5 in the total volume of ocean and sea water of $1370. \times 10^6$ km^3 (Sverdrup and others, 1942, p. 15 and 220). These figures serve to show that oceanic circulation over a long period of time is a prerequisite to the deposition of such an immense amount of material, and that the total volume of oceanic waters, so to speak, must have passed over this locus of deposition many times in order to form the Phosphoria formation. The importance of oceanic circulation to the development of large phosphorites is recognized also by

Kazakov (1937 and 1938). He postulates that cold phosphate-rich upwelling currents become saturated and precipitate phosphate on shelf areas as the water's temperature and pH increase and its CO_2-content decreases upon rising to the surface.

The role of organisms

Animals and plants play a dual role in the formation of rock, directly contributing skeletal and shell material as sediment and affecting the overall physical-chemical environment by their life processes and decomposition after death.

As a whole, skeletal and shell material make but a small contribution to the carbonate rocks and phosphorites of the Meade Peak member, but the amount is significant in some--shell fragments in limestone beds and bone fragments, fish scales, and teeth in phosphate rock. Though some carbonate shell material has been reorganized in various degree, no petrographic evidence suggests large scale reorganization of this kind in either the carbonate or phosphate rocks.

Though organisms thus probably did not play an important direct role in the formation of the Meade Peak sediments, they may have played an important indirect one through their affect on the physical-chemical environment. The elements phosphorus, carbon, and calcium--major elements in the carbonate and phosphate minerals--are elements essential to the metabolism of animals and plants. Those elements are extracted from sea water by organisms and returned after their death. Thus life abounds near the surface of the sea in water rich in nutrients, and carbonate and phosphate minerals might not form other than as hard parts of the animals and plants; however, upon death the elements are returned to solution and conditions may become favorable for precipitation of the minerals. Probably the best known hypothesis today for the origin of the phosphate in the Phosphoria formation is the one proposed in detail by Blackwelder (1915) in which precipitation of phosphate resulted from the dissolution of phosphate of masses of animals killed in a catastrophic manner. An excellent large scale study of mass mortalities associated with "red tides" by Brongersma-Sanders (1948) lends credence to the possibility that such a mode of formation may be significant in the origin of some phosphate.

The physical-chemical conditions of sea water, however, are basic to the formation of the carbonate and phosphate minerals, regardless of the indirect or intermediate role that animals and plants may play. And it should be noted, too, that the minerals composing the hard parts of plants and animals are closely similar to the minerals that are formed as precipitates. Thus the basic hypothesis proposed in this study for the formation of the carbonate and phosphate minerals applies in general to both the organic material and precipitate modes of origin.

The system, dolomite--calcite--carbonate-fluorapatite--sea water

Experimental study of the system, dolomite--calcite--carbonate-fluorapatite--sea water, as a whole, has not been made; and most of the available data that pertain to the system only treat relationships of the individual minerals with sea water. Inferences made here about the system are based on mineral solubilities, the nature of general phase relations, and indicated phase relations in the rocks of the member.

As an approximation, sea water is treated as a single component. Although the chemistry of sea water is complex, its gross effect upon the formation of dolomite, calcite, and carbonate-fluorapatite is considered constant. In general sea water is remarkably uniform in the proportions of its dissolved constituents but varies significantly in its total salinity (Forchhammer, Natterer, and Dittmar in Sverdrup and others, 1942, p. 166; and Rubey, 1951, p. 1125). Average sea water (Rubey, 1951, p. 1126) at 8° C. has a salinity of 35 g/kg. Deviations of temperature and salinity toward higher values that have been observed in today's oceans and connecting seas range up to 35° C. for temperature and 42 g/kg. salinity (Emery, 1956, p. 2359, 2361), although the extreme surface salinity in the oceans proper is only about 37 g/kg. (Sverdrup and others, 1942, p. 126). Even though the salinity variations are not large, Trask (1936) found that the development of calcium carbonate was favored in the ocean waters that had the higher salinities. Larger compositional changes are postulated for Permian sea waters in this investigation of the formation of apatite and the carbonate minerals, and are indicated to have occurred in the extreme case by the large scale development of gypsum and anhydrite on the east side of the basin.

Solubility of calcite

The solubility of calcite has been studied extensively. Miller (1952), in an excellent general study, has reviewed nearly all of the significant earlier solubility determinations. He suggests that failure to control carefully the CO_2 concentration accounts for many of the discrepancies in calcite solubility data. Miller (1952) and Faust (1949) have summarized the most recent data bearing on part of the system $CaO-CO_2-H_2O$.

Some of the more comprehensive and important theoretical and experimental work on the solubility of calcite in sea water and the affect of major physical chemical variables upon the solubility has been done by Garrels and Dreyer (1952), Miller (1952), Revelle (1944), Sverdrup and others (1942), Smith (1940), Wattenberg (1936), Wattenberg and Timmerman (1936), and Trask (1936). Calculated solubility products in sea water, although not in close agreement, are all of the same order of magnitude, 10^{-6}, a value of sufficient precision for the purpose of comparison with dolomite and apatite determinations. The solubility of calcium carbonate in sea water is affected in the following ways:

1. Solubility increases with increase in total pressure on the system.
2. Solubility increases with increase in total amount of CO_2; as Garrels and Dreyer (1952) point out, however, the increase is due to the decrease in pH--at constant pH the solubility decreases with an increase in CO_2 concentration.
3. Solubility decreases with an increase in salinity due to loss of CO_2, though an increase in salinity (ionic strength), particularly by the addition of ions other than Ca and CO_3, generally results in increased solubility.
4. Solubility decreases with increase in temperature.
5. Solubility decreases with increase in pH.

The variables important in determining $CaCO_3$ equilibrium are, in part at least, not entirely independent, particularly the relationship between pH and CO_2 concentration, as the latter is the principal control of pH in sea water. In solution CO_2 forms the radicles HCO_3^- and $CO_3^=$.

These in conjunction with those of boron and phosphorus make up what is called the alkalinity or "excess base" of sea water, and give it a large buffer capacity (Moberg and others, 1934) that tends to limit the variation of pH to a small range.

Most solubility product determinations indicate that sea water in general is saturated or nearly saturated with calcium carbonate; and considering the factors that affect the solubility, supersaturation and conditions favorable for precipitation generally occur in near-surface waters that are relatively of high temperature, low pressure, and low CO_2 concentration.

Solubility of dolomite

The solubility of dolomite has not been studied as extensively as calcite, and much of what is known is due to the works of Mitchell (1923), Klähn (1928), Bär (1932), Halla (1935), Yanat'eva (1949,1950,1954, and 1956), Yanat'eva and Danilova (1956), and Sveshnikova (1952). An excellent review of the dolomite system has been made by Faust (1949) and Faust and Callaghan (1948).

Halla (1935) has determined the solubility product of dolomite at 25° C. under a partial pressure of CO_2 of about one atmosphere; and, of most importance, he has calculated the thermodynamic equilibrium of the following reaction:

$$2CaCO_3 + Mg^{++} = CaMg(CO_3)_2 + Ca^{++}$$

$$\Delta F = -1150 \pm 50 \text{ cal. at } 25^\circ \text{ C. in sea water}$$

$$\text{with } \frac{Ca^{++}}{Mg^{++}} = 0.197$$

The attainment of equilibrium can be questioned because Halla did not experimentally determine the reversibility of the reaction. If only the sign of the free energy value for the above reaction in sea water is correct, however, it indicates that dolomite is the stable phase under those conditions, that it represents the solid phase in equilibrium with the solution from which it formed and for which the system is at its lowest energy state. Halla shows that the principal factor in determining the equilibrium of the reaction is the ratio of the concentrations $\frac{Ca^{++}}{Mg^{++}}$ in solution. The value of the solubility product for dolomite determined by Halla is $3. \times 10^{-17}$ (25° C.)

An approximate check of this solubility product is provided by the data of Klähn. The average solubility of three essentially pure dolomites in CO_2 - free water at 15-20° C. is 0.023 g/1000 ccm. of solution (Klähn, 1928, p. 537), and the solubility product calculated from that value is $8. \times 10^{-16}$. Klähn did not achieve complete equilibrium in his determinations, but the error involved is probably not great. Even so, a greater solubility of dolomite would increase the difference between the values of Halla and Klähn, and thus these values only give an order of magnitude of the dolomite solubility product.

Klähn (1928) found that dolomite was less soluble than calcite in CO_2 - free water at 15-20° C. Dolomite is also less soluble than calcite in solutions at 25° C. under a CO_2 pressure of 1 atm. (Yanat'eva, 1949 and 1954; and Sveshnikova, 1952). At a CO_2 pressure of 0.0012 atm., however, Yanat'eva (1954) found a dolomite solubility greater than calcite. This indicates, according to Yanat'eva that dolomite is incongruently soluble (the elements or radicles in solution are in different proportion than in the solid compound) at low CO_2 pressures, and it supports Bär's (1932) earlier hypothesis of an congruent-incongruent solubility dependent on CO_2 concentration. Halla (1936) contends that this is an impossible relationship simply on the basis of the nature of equilibrium constants and that only temperature could produce a change from one condition to the other. And Yanat'eva (1956) did in fact find that dolomite was incongruently soluble above 65°-66° C. at 1 atm. CO_2 pressure and that calcite was the stable phase in saturated solutions of 1:1 Ca-Mg mole ratio. This problem is of particular importance in diagenetic and metamorphic reactions and more determinations are needed in the experimentally difficult low CO_2 pressure range to clarify it. The argument is not critical, however, to the considerations here of primary relationships.

The solubility of dolomite is affected by other variables in the same way as calcite. Between 70° and 0° C. and at 1 atm. CO_2 pressure dolomite solubility increases in NaCl solutions up to 2 percent in concentration (Yanat'eva, 1949).

If dolomite is the stable phase in average sea water with respect to calcite over the range of sea water temperatures, as suggested by the data of Halla (1935) and Yanat'eva (1956), a calcite precipitate would be expected to change with time, as long as it remained in contact with sea water, to dolomite. Such a process would be what is generally called penecontemporaneous dolomitization. Thus the amount of dolomitization would be directly related to the length of time calcite was in contact with sea water, and the time factor would be related to the rate of sedimentation and subsidence. This method of dolomitization has been suggested by Faust and Callaghan (1948, p. 60 and 63).

Solubility of carbonate-fluorapatite

The solubility of carbonate-fluorapatite in any type of solution has not been determined except by Graham (1925, p. 324) who measured the solubility of phosphate rock of the Phosphoria formation and other naturally occurring phosphate rock mixed with limestone in various salt and acid solutions, presumably at room temperature. Some early work on the solubility of calcium phosphate in water and salt solutions was performed by Cameron and Siedel (1904), Cameron and Hurst (1904), and Sendroy and Hastings (1927). Rivière (1941) determined the solubility of calcium phosphate in sea water at several pHs and concentrations of CO_2. Dietz, Emery, and Shepard (1942) used the data of Sendroy and Hastings to calculate a solubility product for $Ca_3(PO_4)_2$ in sea water at 38° C. of 3.73×10^{-25} and concluded that sea water is nearly saturated with phosphate. Since carbonate-fluorapatite is presumably the stable phosphate compound in sea water, its solubility product would be even less than the one calculated for tricalcium phosphate.

Important work with regard to the relations of phosphate in sea water has been done by Kazakov (1937, 1938, and 1950) and Kazakov and Sokolova (1950). Kazakov studied the system $CaO-P_2O_5-HF-H_2O$ at the 25° C. isotherm over a range of low concentrations to determine the solid phases formed and the regions in which they are stable. The liquid phase in equilibrium with fluorapatite at a pH of around 8 was determined to contain 0.100 mg/l of P_2O_5 and 1.0-10.0 mg/l of F, values that he holds to be similar to those in ocean waters of the upper and middle part of the shelf. The CaO content of the liquid phase, however, is disturbingly far below its amount in average sea water. In the system mentioned above, it is noteworthy that Kazakov found only one phosphate mineral, fluorapatite, to be stable in the range of compositions that approximate those found in sea water. The phosphate mineral of the phosphatic shale member is carbonate-fluorapatite, but, of course, Kazakov found only fluorapatite in his experiments because CO_2 was not a component of the system; he assumed that the effect of CO_2 would not greatly change the conditions except that the solid phase would be carbonate-fluorapatite. On this point Rivière (1941) found that calcium phosphate in sea water solutions transforms to a "phosphocarbonate".

Kazakov (1937 and 1938) and Krumbein and Garrels (1952, p. 9) note that the factors affecting the solubility of calcium carbonate affect the solubility of the rock phosphate compound in the same way. Thus it appears that a change in conditions that would favor the precipitation of carbonate minerals would also favor the precipitation of carbonate-fluorapatite, although, of course, they need not precipitate together.

Explanation of phase relations in the system

The studies described above provide data that deal mostly with the individual relationships of calcite, dolomite, and apatite with sea water, and furnish but little information about mutual relationships of the compounds. Possible mutual relationships can be described qualitatively, however, in terms of simple phase equilibria.

The system has four components. If temperature and pressure are constant, the system may be completely described in terms of the phases that may be present at various compositions of the total system. A theoretical example of such a system will serve to illustrate some of the possible relationships. Let the four components be three compounds with common ion, A-B-C, that do not form double compounds, and water that does not form hydrates with any of the compounds. The following states of the system or associations in the system are possible:

1) 1 phase - all solution
2) 2 phases - 1 compound plus solution
3) 3 phases - 2 compounds plus solution
4) 4 phases - 3 compounds plus solution.

A general course of crystallization upon evaporation of an unsaturated solution could result in the sequential appearance of one, two and three solid phases (compounds A, B, and C). The phase that appears first depends upon the total composition of the unsaturated solution. Two solid phases, i.e., A+B, B+C, or A+C, could form as the first precipitate, but the range in unsaturated solution compositions for which this could occur is small in comparison to that for one solid phase formation. Also, if two compounds precipitate together, the ratio of their amounts is likely to change as evaporation proceeds. Three solid phases could form at the same time only from one specific composition of solution. This composition is the invariant point of the system, the conditions under which the system is completely and rigorously defined. The kind of crystallization described here represents a differentiation of a solution by the continual removal of water, and the stage of differentiation attained depends on the amount of water removed from the system. Another kind of crystallization occurs if one of the compounds, A, for example, is continuously added to a solution that is saturated with respect to A. Although obvious, it is important to note that A will begin and continue to precipitate as long as the addition of A is the only change imposed on the system.

These phase relations for a four component system are the simplest possible, and it is unlikely that the mineral relations in natural systems are as uncomplicated. The general principles, however, provide a basis of understanding of the kinds of factors that may play a part in the formation of common ion mineral associations.

Phase relations of dolomite, calcite, and carbonate-fluorapatite in the rocks of the Meake Peak member

The mineral mixtures of dolomite, calcite, and carbonate-fluorapatite in the rocks of the Meade Peak member may be examined in the light of the principles involved in phase equilibria. The mineral mixtures shown in figure 18 and discussed previously are considered to represent essentially three principal kinds of mineral association: apatite alone, dolomite-apatite, and dolomite-calcite. No true primary ternary mixtures, in terms of phase relations, are represented, or cannot be recognized if any exist, because of the very wide range of proportions of the minerals in the apparent ternary mixtures.

The large apatite-alone group of samples indicates that apatite was the first and only mineral formed under the conditions and for the period of time in which those beds were deposited. This could result from a first stage differentiation of sea water or by the addition of phosphate by a special means.

The only other distinct group of samples occurs in the dolomite corner of figure 18 and consists essentially of dolomite-apatite mixtures, although a few samples near the dolomite-calcite boundary are better considered as mixtures of dolomite and calcite. The dolomite-apatite mixtures are interpreted to represent the stage following the single phase precipitation of apatite in which dolomite and apatite form together. A high ratio of dolomite to apatite would be expected in this circumstance because of the much larger amount of carbonate than phosphate in sea water. This group of samples and the apatite-alone group together make up a majority of all the samples and represent the dominant types of mineral associations in the section. The other samples of dolomite and apatite mixtures not included in these groups have to be considered in this hypothesis as products of special processes.

Dolomite and calcite mixtures cover a wide range of proportions that is not readily explained in terms of simple phase relations, but metastable precipitation probably can account for the associations. Under conditions in which dolomite is the single solid phase in equilibrium with some composition of sea water, calcite could precipitate metastably and change with time, while in contact with sea water, to dolomite, the stable phase. In this manner, the amount of dolomite formed is a function of the time the calcite is in free contact with sea water, and all proportions of dolomite and calcite are possible.

Conclusions on phase relations and modes of formation of dolomite, calcite, and carbonate-fluorapatite

From the foregoing considerations, it seems likely that the mineral mixtures of dolomite, calcite, and carbonate-fluorapatite in the rocks of the Meade Peak member can be explained in part by phase relations. Although the interpretations are largely speculative, because of the lack of critical criteria for evaluating the effect of many factors within and outside the system, three principal generalizations are postulated for the modes of formation of the three minerals from sea water.

(1) Precipitation by increase in total salinity, due to evaporation. Starting with a mass of sea water in a state of near saturation with respect to one or more of the three solid phases, dolomite, calcite, and carbonate-fluorapatite, and assuming a fixed temperature and pressure, precipitation of one or more phases will occur upon the removal of water and the consequent increase in concentration of the three compounds in the same proportion as they occur in the primary mass of sea water. With continuing loss of water, the course of precipitation would be like that described previously in the explanation of the phase relations--probably one solid phase first, then two, and conceivably all three solid phases if the differentiation proceeds that far. This method of precipitation is a likely one if a mass of sea water moves into an environment in which loss of water by evaporation is the principal change in the system. If the solid phases formed from this moving mass of sea water are deposited directly under their area of formation, the deposits would show an ideal lateral gradation in composition in the direction of movement of the water mass from that composed of only one mineral to mixtures of two minerals in changing proportions to a final deposit of three minerals in fixed proportion (figure 19).

Scruton (1953) has described this kind of precipitation in terms of a salinity gradient that can be established

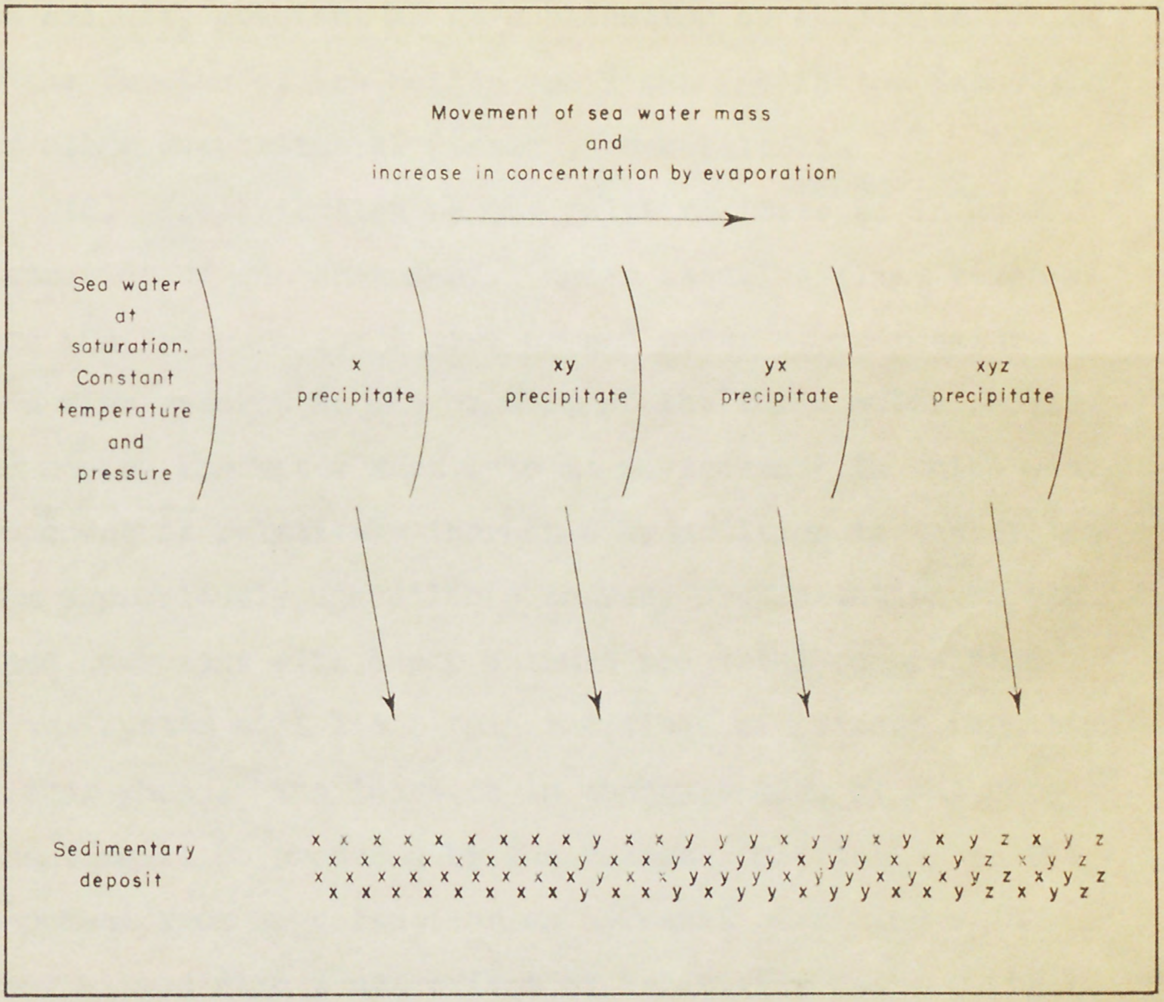

Figure 19.—Formation and deposition of dolomite, carbonate-fluorapatite, and calcite from moving mass of sea water by decrease in amount of total solution (evaporation)

in inland seas and which could produce lateral facies of limestone, anhydrite, and salt. Lang (1937, p. 885) and Richter-Bernburg (1955) have also utilized the concept of the salinity gradient as an explanation of evaporite facies in the Permian of New Mexico and Texas and in the Zechstein and other evaporites of Germany, respectively.

(2) Precipitation by the relative increase in concentration of one component. Again assuming fixed temperature and pressure for a mass of sea water at near saturation with respect to one or more of the three solid phases, and moving the water mass into an environment in which one component is relatively increased by addition to the system from a previously unavailable source, precipitation of the added component will occur because the total composition of the system will lie within the field of primary formation of that phase. The increase in concentration of one component could be produced by the release to solution of the component from organisms, or as a result of mixing with other waters with a net effect of relatively raising its concentration. In this case only that one solid phase will form and continue to form as long as the conditions defined above prevail. Figure 20 illustrates this concept. Organisms, particularly phytoplankton, would be a probable cause for this type of formation by returning to solution in death the components they extracted by their life processes. For example, the rapid dissolution of phosphorus

would precipitate immediately as apatite.

(3) Precipitation by change in temperature and pressure. In previous discussions of phase relationships these two variables have been considered to be constant for the purpose of simplification. Aside from the direct effect of temperature and pressure upon the kind of mineral structure that can form, they affect the composition of sea water by helping to control CO_2 equilibrium which, in turn, plays a large part in determining the pH of sea water. As mentioned previously the effect of changes in temperature and pressure upon the solubility of the three minerals is qualitatively the same, increasing temperature and decreasing pressure decreasing the solubility of the minerals. On that basis and to the extent that temperature and pressure effects can be treated independently of concentration, the course of precipitation as a result of increasing temperature and decreasing pressure would be similar to type (1) above, but the effects would be small by comparison and more by way of modification than control.

The relationship of modes of formation (1) and (3) to rock facies is plain. If the locus of differentiation in a current of sea water remains stationary for a considerable period of time, continuous deposits will form, which from one place to another are grossly different in composition. The different compositions will constitute distinct facies of the depositional unit. However, the locus of differentiation may not be expected to remain stationary; more likely it will shift around, though favoring one position on a frequency basis. A shifting locus of differentiation would mean shifting facies, so a vertical section at any one place would represent a recapitulation of lateral facies changes. Thus the phosphorites and carbonate rocks of the Coal Canyon section may represent various lateral facies, and of course, these rocks have served as the basis for the development of this thesis. Rocks composed mostly of apatite and rocks of dolomite-apatite mixtures are the most abundant types, and it is suggested that the latter may be lateral facies of some phosphorites. A possible example of this kind is illustrated by the compositional change in the well defined lower phosphate zone between the southeastern Idaho area and Coal Canyon. The lower phosphate zone in southeastern Idaho is about 6 feet thick and is one of the principal high grade economic zones in the Meade Peak member. There it is composed largely of carbonate-fluorapatite, a small amount of quartz and silicate minerals, and only a trace of carbonate minerals. At Coal Canyon this interval, beds P-8 through P-15, contains about the same amount of quartz and silicate minerals, but dolomite occurs in large amounts at the expense of carbonate-fluorapatite.

Sharp contacts between beds and marked changes in the proportions of minerals, as described previously, are understandable on the basis of the principles presented; for example, the change from apatite precipitation alone to a dolomite and apatite mixture would be sharp and the proportion of dolomite to apatite would be high.

Mode of formation (2) is an appealing explanation of the origin of phosphorites when some other factors are considered. The phosphorites are dark brownish-gray to black and contain appreciable carbonaceous material. This suggests, along with the fine grain size of associated detrital material, that the rocks were formed in a low part of the Phosphoria sea basin where circulation was poor and the water deficient or low in oxygen. A low part of the basin would also contain sea water of greater salinity (density) than that in higher parts, if a significant range of salinity was produced in the Phosphoria sea waters by evaporation. Such bottom water would certainly be saturated with respect to apatite if it is assumed that normal sea water is nearly so. Under these circumstances, as mentioned before, phosphorus added to the system by the decomposition of dead organisms would precipitate as apatite. Apatite formed by this scheme would likely not be a first precipitate but would follow one or both of the carbonate minerals.

The formation of apatite just described can be explained as well, however, in surface waters as those on the bottom. If a salinity gradient exists in the surface waters, a saturation point would be reached whereby any phosphate given up by deceased organisms, whose death could also be due to increased salinity, must be precipitated. In this instance apatite would be a first rather than a late precipitate, and sea water differentiation could even continue as in mode of formation (1).

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APPENDIX

A method of x-ray analysis for determining the ratio of calcite to dolomite in mineral mixtures

Introduction

The need of a method for readily determining the proportion of calcite to dolomite in rocks is well known. Differentiation by optical means in thin section is rarely possible. Staining methods are not general in application--depending in large part on characteristics of the rock other than carbonate composition. The use of x-ray for determining the proportion of calcite to dolomite in carbonate rocks is apparently not common, and a method of measurement has been described only recently (Tennant and Berger, 1957) and since this work was done. Several workers, however, have quantitatively utilized relative diffraction intensities in measuring the proportions of carbonate compounds in artificial mixtures (Stolkowski, 1948; Faivre, 1944; and De Keyser and Degueldre, 1950).

The method described here has been designed and tested for a particular series of closely related rock types. Its general application is not known; however, the procedure for testing the significance of the method is applicable to other rock types.

Design of the experiment

The experiment was designed to test the usefulness of relative x-ray diffraction intensities of calcite and dolomite as a means of estimating their percentage ratios in carbonate rocks of the Meade Peak phosphatic shale member of Coal Canyon, Wyoming. To do this, sixteen artificial mineral mixtures were prepared of compositions similar to those of the carbonate rocks of the phosphatic shale member. The composition of the mixtures was considered in two parts, carbonate mineral composition and background mineral composition. Calcite and dolomite were each at four levels of concentration, 5, 20, 35, and 50 percent, providing a convenient 4x4 factorial plot (table 1). The background mixtures were eight types composed of a range of mineral proportions of quartz, apatite, muscovite, K-feldspar, and Na-feldspar (table 2). As an example, type IIB background mixture is composed of 10 percent muscovite, K-feldspar, and Na-feldspar in the proportion, 0.50:0.25:0.25; and 90 percent quartz and apatite in the proportion, 0.35:0.65. These mixtures were randomly assigned to the sixteen mixtures of calcite and dolomite; thus each background mixture was used twice. The purpose of the background mixtures and their randomization was to determine if they had any effect upon the peak intensities of calcite and dolomite; or in other words, if there was any interaction. The total composition of

TABLE 1

4x4 factorial plot

% Dolomite				
5	1 C=10 IIB=90	2 C=25 IIC=75	3 C=40 IIC=60	4 C=55 IID=45
20	5 C=25 IID=75	6 C=40 IC=60	7 C=55 IC=45	8 C=70 IA=30
35	9 C=40 IIA=60	10 C=55 ID=45	11 C=70 IID=30	12 C=85 IIA=15
50	13 C=55 IB=45	14 C=70 IA=30	15 C=85 ID=15	16 C=100
% Calcite	5	20	35	50

C= % Calcite + % Dolomite

IA.....IID= % Background Mixture

TABLE 2

Mineral proportions in background mixtures

	I							II						
	95%				5%			90%				10%		
	%				%			%				%		
	90	65	35	10	50	25	25	90	65	35	10	50	25	25
A	a			q	m	k	n	a			q	m	k	n
B		a	q		m	k	n		a	q		m	k	n
C		q	a		m	k	n		q	a		m	k	n
D	q			a	m	k	n	q			a	m	k	n

q= quartz

a= apatite

m= muscovite

k= K-feldspar

n= Na-feldspar

each mixture is listed in table 3.

The 4x4 factorial type statistical design makes possible the testing of the following hypotheses:

(1) Are the differences between the ratios of peak heights of calcite and dolomite due to the difference in amounts of calcite and dolomite?

(2) Are the peak height ratios useful as a measure of the ratio of calcite to dolomite?

Preparation of the mixtures

The minerals were ground to pass a 325-mesh sieve. The proportions assigned to each mixture were weighed on an analytical balance to three decimal places. A volume of water approximately twice that of the mixtures was added, and these combinations were mechanically shaken for two hours. X-ray mounts were made on regular glass slides from these water mixtures with the aid of an eye dropper and rapidly dried in an 80° C. oven.

Procedure of analysis

Samples were run on the Norelco x-ray spectrometer, using copper radiation. The peaks selected for measurement were those representing diffraction from comparable planes of calcite and dolomite, peaks at approximately 29.4 and 30.9 degrees 2 θ, respectively. They were selected because they are the peaks of greatest intensity for

Table 3

Mineral composition of mixtures

% by weight

	calcite	dolomite	quartz	apatite	muscovite	total feldspar
1	5	5	28.4	52.6	4.5	4.5
2	20	5	43.9	23.6	3.75	3.75
3	35	5	35.1	18.9	3.0	3.0
4	50	5	14.2	26.3	2.25	2.25
5	5	20	60.9	6.6	3.75	3.75
6	20	20	37.0	20.0	1.5	1.5
7	35	20	27.8	15.0	1.1	1.1
8	50	20	2.9	25.6	0.75	0.75
9	5	35	5.4	48.6	3.0	3.0
10	20	35	38.6	4.2	1.1	1.1
11	35	35	24.3	2.7	1.5	1.5
12	50	35	1.4	12.1	0.75	0.75
13	5	50	15.0	27.8	1.1	1.1
14	20	50	2.9	25.6	0.75	0.75
15	35	50	12.8	1.4	0.4	0.4
16	50	50	-	-	-	-

both calcite and dolomite; they are relatively free of interference from peaks of other minerals in the mixtures; and they are close together. Measurement of the peaks was in recorder chart units (4 lines to the inch) from a baseline determined primarily by the background line between 14° and 20°. This part of the traverse was relatively free of peaks and provides the best indication of the background trend. The total traverse was from 38° to 4°.

Control of the x-ray procedure was kept at a minimum. On the spectrometer only the slit openings and the assurance of a warmed machine were controlled conditions. The amplitude and damping were varied purposely. Sample runs were made in groups on different days and at different times of the day. The order of the runs was randomized using a table of random numbers. Peak height measurements, peak height ratios, and percentage ratios for the mixtures are listed in table 4.

Statistical treatment. The analysis of variance.

Logarithms of the ratios were used in this type of treatment in order that the plot of the ratios of the peak heights against the percentages be a linear function. The plot of the logarithms of these values on arithmetic paper (figure 1) clearly indicates a straight line trend as shown by the calculated least squares line.

Table 4

Measured peak heights and ratios

	Peak height calcite*	Peak height dolomite*	Log of peak height ratios[f] calcite/dolomite	Log of percentage ratios[f] calcite/dolomite
1	0.95	1.05	1.9566	2.0000
2	3.75	1.25	2.4771	2.6021
3	4.60	1.05	2.6415	2.8415
4	7.10	0.90	2.8971	3.0000
5	1.60	4.25	1.5752	1.3979
6	2.70	2.65	2.0086	2.0000
7	2.20	4.25	1.7143	2.2430
8	6.80	3.60	2.2068	2.3979
9	0.60	4.15	1.1614	1.1553
10	3.85	5.35	1.8561	1.7566
11	4.50	4.70	1.9809	2.0000
12	7.60	4.80	2.1987	2.1553
13	0.95	5.15	1.2648	1.0000
14	3.45	7.70	1.6513	1.6021
15	4.50	5.30	1.9289	1.8451
16	5.15	5.30	1.9877	2.0000

* Measurements in recorder chart units.

[f] Logarithms of 100 times the ratios.

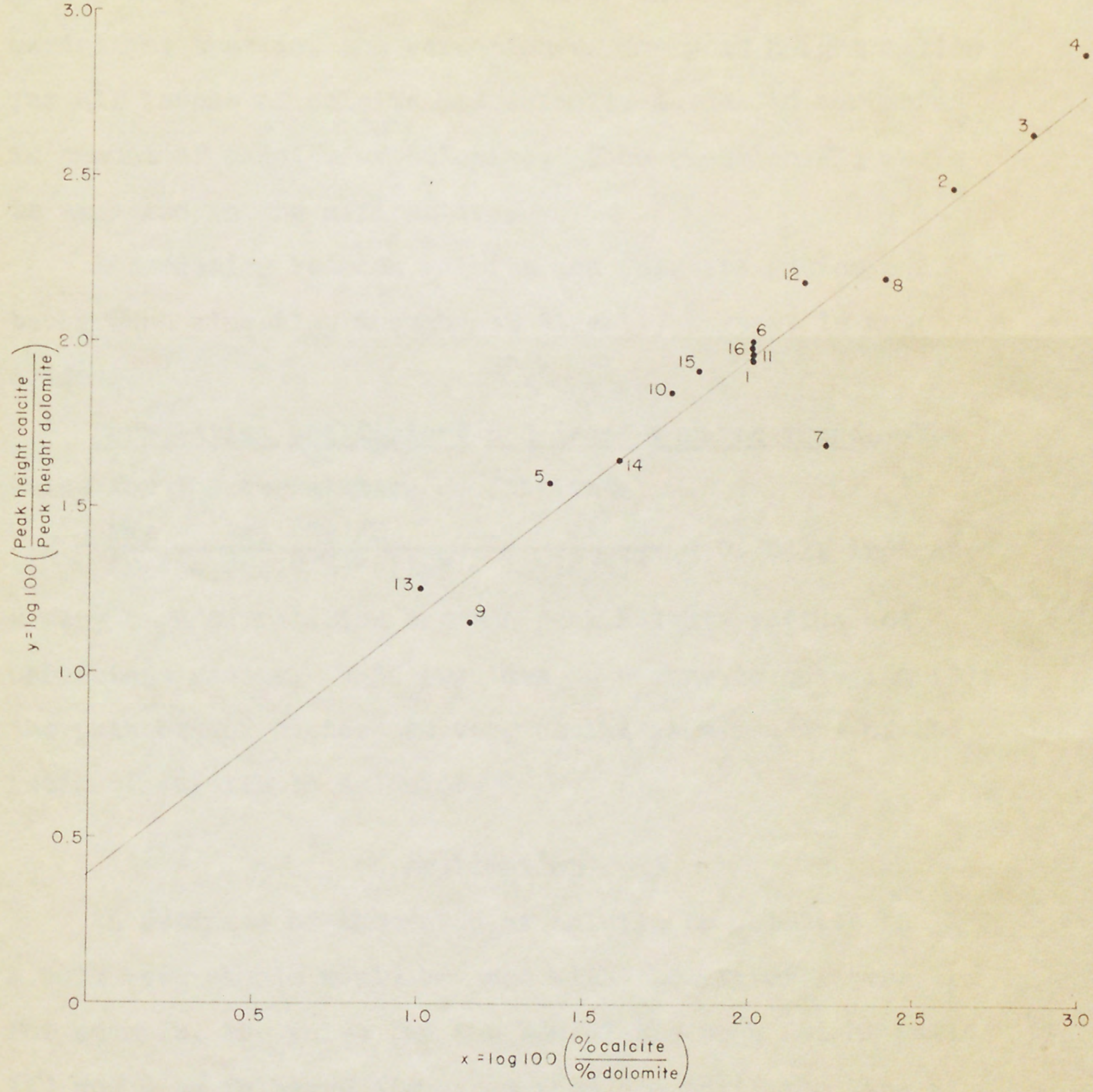

FIGURE 1. Peak height ratios of calcite to dolomite plotted against percent ratios.

The analysis of variance is shown in table 5. The variance ratio (F) indicates that there is less than 1 chance in 100 that the ratio would be exceeded by random variation; that is, the variation of the peak height ratios for all levels of calcite and dolomite is due to variation in amount of calcite or dolomite. Thus question (1) above is answered in the affirmative.

Interaction between calcite and dolomite ratios and background minerals, though not directly tested, is not evident.

Correlation Coefficient and least squares trend.--The value for the correlation coefficient,

$$r = \frac{Sxy - (Sx)\ (Sy)/N}{(Sx^2 - (Sx)^2/N)^{1/2}\ (Sy^2 - (Sy)^2/N)^{1/2}} = 0.9541,$$ indicates

a very high correlation between peak heights ratios and percentage ratios. This provides an answer to question (2); the peak height ratios are very useful as a measure of the ratio of calcite to dolomite.

Application

An estimate of the ratio of calcite to dolomite in a bulk rock sample would be made with the use of figure 1. For example, the value for the log of the peak height ratio (Y) would be followed along the abscissa until the line of least squares $y = 0.3921 + 0.7885$ was intersected. The value (X) read on the abscissa at that point would be the estimate of the log of the percentage ratio of calcite to

Table 5

Analysis of variance

Source of variation	Items	D. F. (n-1)	Formulas for S.S.	S.S.	M.S.	F	$P_{.01}$
calcite levels	4	3	$\frac{S_1^4(S_1^4 x)^2}{4} - C.T.$	1.4611	0.4870	23.6	6.99
dolomite levels	4	3	$\frac{S_1^4(S_1^4 x)^2}{4} - C.T.$	1.5204	0.5068	24.6	6.99
remainder		9	$S_1^{16}x^2 - C.T. - S.S._{dol} - S.S._{cal}$	0.1852	0.0206		
total	16	15	$S_1^{16}x^2 - C.T.$	3.1667	0.2111		

Where:

D.F. = Degrees of Freedom (n-1)
S.S. = Sum of Squares
M.S. = Mean Square = S.S./D.F.
$F_{cal} = M.S._{cal}/M.S._{remainder}$
$F_{dol} = M.S._{dol}/M.S._{remainder}$
C.T. = Correction Term = $(S_1^{16}x)^2/16$

dolomite in the rock.

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