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The Vanadiferous Zone of the Phosphoria Formation in Western Wyoming and Southeastern Idaho

U. S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1465



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By V.E. McKELVEY, J.D. STROBELL, JR., and A.L. SLAUGHTER

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THE VANADIFEROUS ZONE OF THE PHOSPHORIA FORMATION IN WESTERN WYOMING AND SOUTHEASTERN IDAHO

By V.E. MCKELVEY, J.D. STROBELL, JR., and A.L. SLAUGHTER

ABSTRACT

A black shale in the upper part of the Meade Peak Member of the Permian Phosphoria Formation contains an average of 0.8 to 0.9 percent V_2O_5 or more over a large area in western Wyoming and southeastern Idaho. In 1942 and 1943, this vanadiferous zone was sampled at numerous localities in the region by the U.S. Geological Survey, the Wyodak Coal and Manufacturing Co., and the U.S. Bureau of Mines.

At Sublette Ridge, 1 mi east of the Idaho State line in Lincoln County, Wyoming, the vanadiferous zone lies about 50 ft below the top of the Meade Peak Member in the nearly vertical eastern limb of a north-striking anticline. The full thickness of the vanadiferous zone in the explored part of Sublette Ridge contains about 1.9 million tons of indicated subeconomic resources above drainage level. The richer upper part contains about 1.35 million tons. In the Paris-Bloomington area of Bear Lake County, Idaho, in the eastern foothills of the Bear River Range about 1 mi west of the towns of Paris and Bloomington, the Phosphoria Formation and associated rocks lie in the Paris syncline, which plunges about 15° N. The western limb of the syncline is overturned; the beds near the trough are nearly vertical, but, high on the limb, they dip as little as 20° W. The vanadiferous zone is about 35 ft below the top of the Meade Peak Member and about 5 ft below the upper phosphate zone. The zone consists of three beds: a shale, a phosphorite, and a siltstone, in ascending order.

Estimates of measured, indicated, and inferred subeconomic resources of vanadium in the Paris-Bloomington area have been prepared for the shale bed, the shale and phosphorite beds combined, and the full thickness of the vanadiferous zone. Measured resources for the full zone are estimated to be 600,000 tons averaging 10.8 ft in thickness and 0.93 percent V_2O_5 ; indicated resources are 4,000,000 tons averaging 10 ft in thickness and 0.9 percent V_2O_5 ; inferred resources, within the area sampled, are 50 to 75 million tons averaging 10 ft in thickness and 0.6 to 1.0 percent V_2O_5 .

The vanadiferous zone appears to be the product of primary deposition from upwelling water in a reducing marine environment below wave base in a water depth of 100 m or so. These deposits formed on the outer continental shelf on the western side of the North American craton at low latitude, where deep, cold, nutrient-rich seawater came to the surface as a result of divergent upwelling in a tradewind belt.

The vanadiferous zone in western Wyoming and southeastern Idaho contains about 41 million tons of indicated subeconomic resources averaging about 0.9 percent V_2O_5 . Inferred resources are many times larger. Eventually, these inferred resources may prove to be an important source of vanadium and several other metals.

INTRODUCTION

A black shale containing 0.8 to 0.9 percent V_2O_5 over a large area was discovered by W.W. Rubey of the U.S. Geological Survey (USGS) in 1938 in the upper part of the Meade Peak Member of the Permian Phosphoria Formation in the Salt River Range of western Wyoming (Rubey, 1943, 1958). This vanadiferous zone, as it came to be called informally, was sampled by the USGS in 1942 at numerous localities in the adjoining region (McKelvey, 1946); it was sampled in more detail in late 1942 and 1943 by the Wyodak Coal and Manufacturing Co., agent for the Metals Reserve Co., in the Paris-Bloomington area of Idaho (McKelvey and Strobell, 1955) and in the Sublette Ridge area of Wyoming. The U.S. Bureau of Mines (USBM) also explored the zone in Sublette Ridge (Allsman and others, 1949a) as well as in the Salt River Range (Allsman and others, 1949b) and investigated means of recovering the vanadium (Ravitz and others, 1947). Information on the geology, composition, and magnitude of the vanadiferous deposits in the Salt River Range was summarized by Love (1961).

These published data are herein supplemented by additional information acquired in the 1942-1943 investigations of the Sublette Ridge and Paris-Bloomington deposits, along with some interpretations of the regional extent, composition, and origin of the zone based in part on subsequent studies (for example, McKelvey and others, 1953, 1959; Gulbrandsen, 1960; Desborough, 1977; E.C.T. Chao, J.A. Minkin, and J.M. Back, written communication, 1986).

REGIONAL EXTENT

The vanadiferous zone has been found within an area of about 4,500 mi² in western Wyoming, southeastern Idaho, and northeastern Utah (figs. 1, 2). In Wyoming and Utah, the zone is a readily identifiable

VANADIFEROUS ZONE OF THE PHOSPHORIA FORMATION, WYOMING AND IDAHO

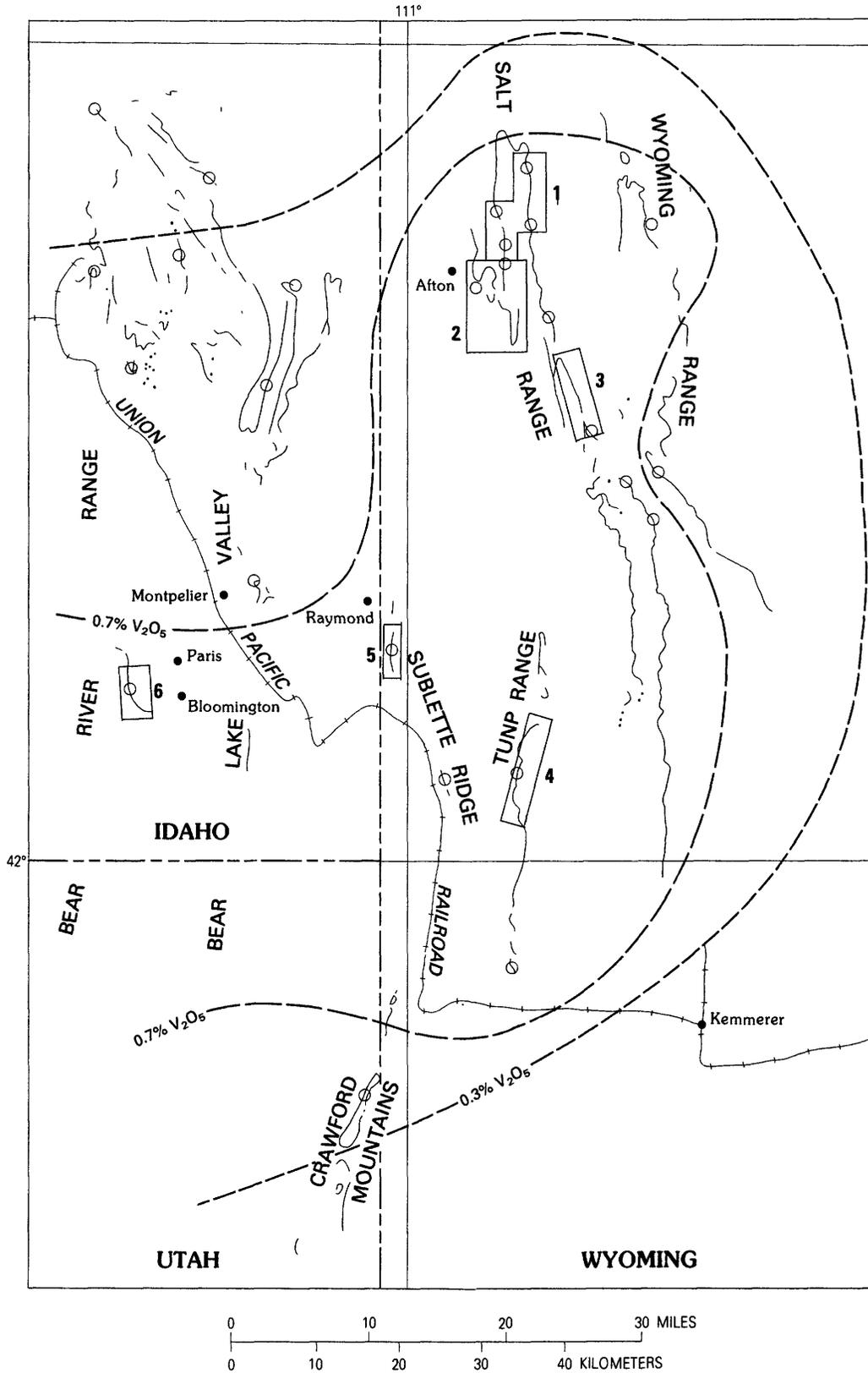


FIGURE 1.—Approximate areal extent of the vanadiferous zone in the upper part of the Meade Peak Member of the Phosphoria Formation, defined on the basis of the area within which a thickness of 3 ft or more contains 0.3 percent V_2O_5 or more (shown by short-dash line). Shown also is the area within which one bed or more contains 0.7 percent V_2O_5 or more (long-dash line). Outcrops of the Phosphoria Formation are shown by thin lines, and the location of samples for which analyses are shown on figure 2 are marked by open circles. The areas outlined are (1) Swift Creek-McDougal Pass, (2) Afton, (3) Labarge Creek, (4) Tunp Range, (5) Sublette Ridge, and (6) Paris-Bloomington.

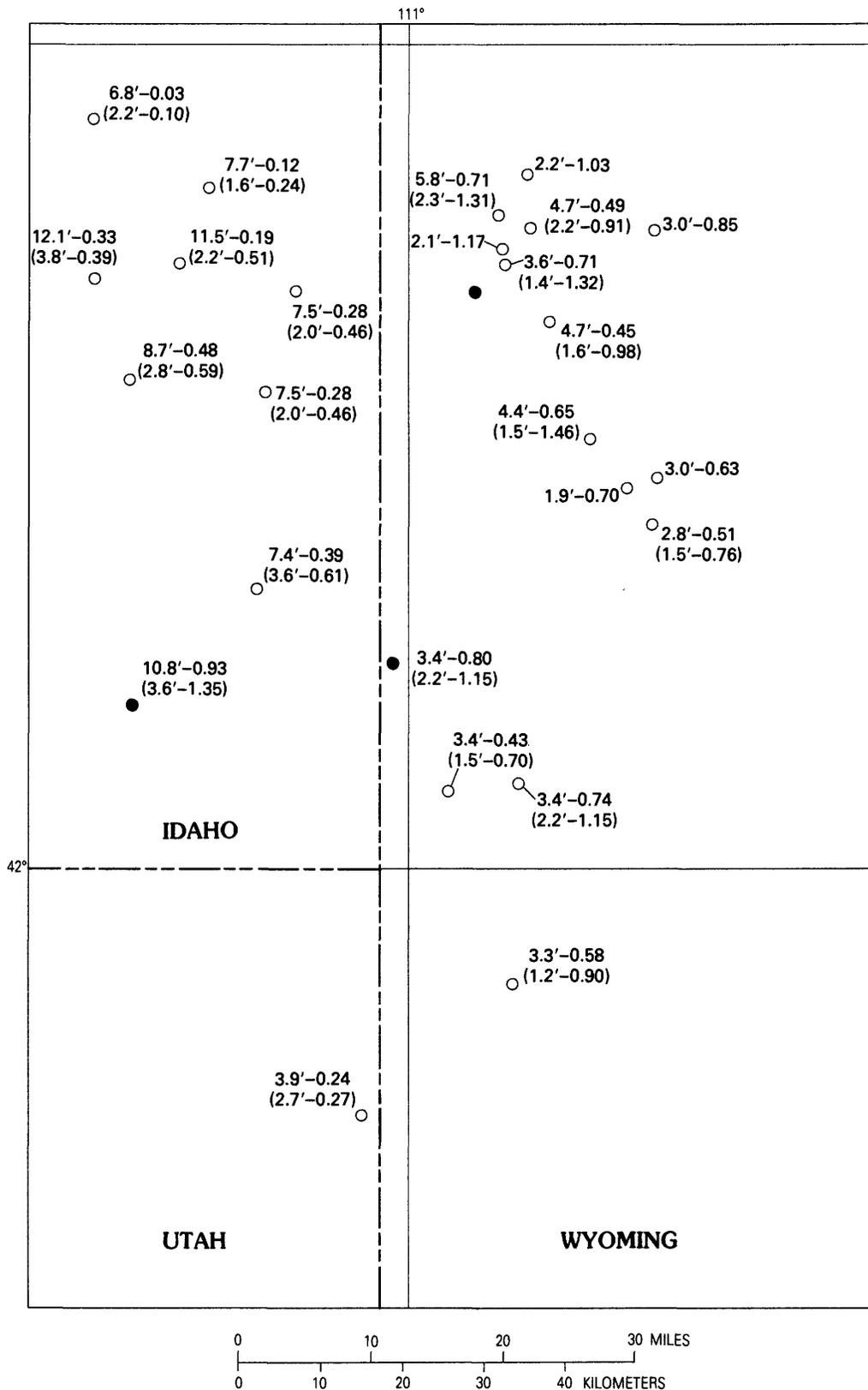


FIGURE 2.—Selected V₂O₅ analyses from the vanadiferous zone (see fig. 1 for position of samples on outcrops of the Phosphoria Formation). Only locations having unfaulted exposures, unaffected by deep weathering, are shown; where available, values of samples taken from the higher grade part of the zone are shown in parentheses. Analyses from locations indicated by solid circles rather than open circles are based on the average of many samples collected by the USBM (Afton area) and the Wyodak Coal and Manufacturing Co. (Sublette Ridge and Paris-Bloomington areas).

stratigraphic unit 2 to 6 ft thick, consisting of non-phosphatic hard black mudstone that weathers to soft black shale containing conspicuous orange coatings along joint and bedding planes. It is 30 to 100 ft below the base of the Rex Chert Member of the Phosphoria Formation and essentially at the base of the upper phosphate zone of the Meade Peak Member.

In Bear Lake County, Idaho, the zone is 6 to 15 ft thick and also lies at the base of the upper phosphate zone, 25 to 40 ft below the Rex Chert Member. Unlike the zone in Wyoming, it contains a few to several percent P_2O_5 . The beds are soft and black in weathered exposure, but their phosphate content gives them an appearance different from that of their Wyoming correlatives. Farther north, in Caribou County, the P_2O_5 content increases to 20 to 25 percent, and the zone is not distinguishable lithologically from the upper phosphate zone. The presence of the zone is generally indicated by V_2O_5 analyses in the range of about 0.35 to 1.0 percent over a thickness of a few feet.

The areal limits of the zone are known only approximately. It is present in the Tump Range to the east of Sublette Ridge, where it is about 3 ft thick and contains 0.75 to 0.9 percent V_2O_5 . It is also present in the northern Crawford Mountains of Utah, an occurrence lithologically quite similar to the one farther north but containing much less vanadium. Southward and eastward, the beds of the vanadiferous zone either tongue out or grade into other lithic units; they are not identifiable on the basis of either lithology or vanadium content in the Wasatch or Uinta Mountains. A similar change in facies occurs to the east and north of the Wyoming Range; the zone is not identifiable in the Wind River Mountains, the Gros Ventre Range, or the Snake River Range. The vanadiferous zone may extend westward for some distance, but its vanadium content west of Bear Lake Valley in southeastern Idaho is so low that the zone is not identifiable as such.

A comparison of figures 1 and 3 shows that the vanadiferous zone extends over that part of the Meade Peak Member richest in organic C, P, V, and Ag. However, the zones highest in vanadium lie to the east and south of the carbon-, phosphorous-, and silver-rich zones.

The Salt River Range near Afton, Wyo. Sublette Ridge, and the Paris-Bloomington area were selected for further exploration within the area underlain by the vanadiferous zone because of their potential minability, judged on the basis of the vanadium content of the zone and the relatively uncomplicated structural settings. Should exploitation of the vanadiferous zone become economic, however, they would not be the only possibly minable areas.

SUBLETTE RIDGE DEPOSITS

Sublette Ridge lies in the western part of Lincoln County, Wyoming, about 1 mi east of the Idaho State line. It is a northward-trending ridge of mountainous relief on the eastern side of Thomas Fork Valley. Raymond Canyon, the main point of entry to the deposit, is about 2 mi east of Raymond, Idaho. The Union Pacific Railroad at Border, Wyo., is about 7 mi by road from Raymond Canyon.

During the winter of 1942-1943, the Wyodak Coal and Manufacturing Co. and the USBM undertook exploration programs. Fifty-four trenches spaced 200 to 1,000 ft apart were dug, and 13 tunnels and a shaft were driven.

GEOLOGY

Vanadium is present in small amounts in many of the beds of the Meade Peak Member of the Phosphoria Formation, but only the vanadiferous zone, lying about 50 ft below the top of the member, contains amounts of possible economic interest. The Meade Peak Member is underlain by the Grandeur Member of the Park City Formation and overlain by the Rex Chert Member of the Phosphoria Formation.

These formations occur on the eastern limb of the Sublette anticline, the axis of which strikes north along the western front of Sublette Ridge. The western limb of the anticline has been downthrown by normal faulting, and most of it is buried beneath Holocene and Tertiary(?) alluvium in Thomas Fork Valley. A part of the western limb is exposed in the northern part of the area east of the fault for a short distance. The Phosphoria Formation extends over a strike length of 6.5 mi in Sublette Ridge but is concealed by younger rocks for a distance of 1.5 mi north of Petereit Gulch. The beds are nearly vertical along the flank of the anticline but dip as low as 45° in places near the crest. Numerous faults marked by small displacements cut the vanadiferous zone.

VANADIFEROUS ZONE

The vanadiferous zone in the Sublette Ridge area consists of seven layers of black mudstone overlain by a hard, massive, fossiliferous limestone about 2 ft thick and underlain by an equally hard and massive but locally lenticular limestone. The beds are soft and fissile near the surface, but, about 40 ft beneath the surface, they abruptly become hard and massive; the layers there are separated from one another by barely discernible cracks. Orange coatings, probably the

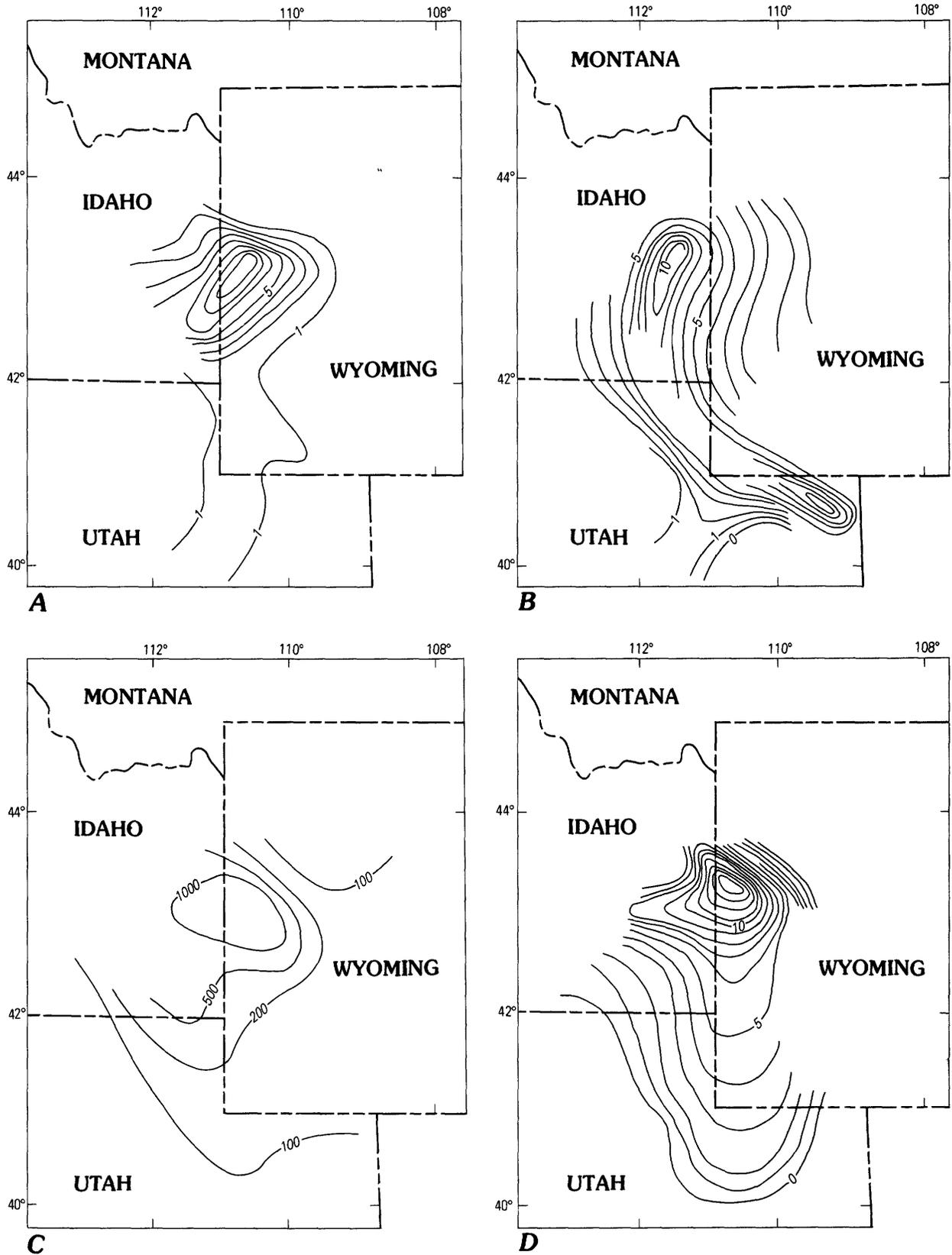


FIGURE 3.—Average concentrations of (A) organic C (in percent), (B) P (in percent), (C) V (in parts per million), and (D) Ag (in parts per million) in the Meade Peake Member of the Phosphoria Formation (after Maughan, 1976, 1980).

result of pyrite oxidation, are prominent on bedding and joint surfaces of the weathered rocks. Although weathering produced the effects just described, it did not mobilize the vanadium in this area, for the vanadium content is essentially the same in both fresh and weathered parts of the zone.

The full vanadiferous zone is 2.5 to 4.3 ft thick and averages about 3.4 ft. Most of the vanadium is concentrated in the upper 1.5 to 2.5 ft of the zone. The V_2O_5 content of the whole zone ranges from 0.45 to 1.05 percent and averages about 0.8 percent. During the early stages of the work, it was assumed that the shaly nature of the rocks would require mining the full width of the zone between the hanging-wall and the footwall limestone beds; consequently, the zone was sampled as a unit in most of the trenches (pl. 1). After hard, unweathered rock was encountered in underground workings, attention was given to mining only the upper, more vanadiferous part of the zone, which averages about 1.05 percent V_2O_5 over a width of 2.25 ft.

The individual layers of the zone are remarkably continuous stratigraphically, and their vanadium contents are similar throughout the area (pl. 2). In fact, essentially the same sequence is found some 40 mi to the north in the Afton area, where the same rich central part of the zone (pl. 1) is 0.5 to 1.0 ft thick and averages 1.6 percent V_2O_5 (maximum 2.5 percent) (Love, 1961), about the same as the values found in Sublette Ridge. Although these layers are recognizable in the field on the basis of physical properties, the distinctions between them are slight, and they were not recognized during the 1942 reconnaissance sampling when the zone was generally sampled as a unit. It seems likely that these same layers are also present at

other localities in western Wyoming where the zone has been found.

The USBM reported partial analyses of several samples, as table 1 shows (Ravitz and others, 1947). The locations and thicknesses represented by these samples were not reported, but, because the V_2O_5 content is in the range of 0.52 to 0.92 percent, it is assumed that they represent the full thickness of the zone. The analyses suggest that the main constituents of the rocks are quartz-silicate minerals, organic matter, carbonate minerals, and pyrite.

Relatively complete chemical analyses were made by the Tennessee Valley Authority on all of the beds of the Meade Peak Member sampled in 1947 by a USGS field party in Coal Canyon,¹ about 1 mi south of Raymond Canyon (McKelvey and others, 1953). Analyses for the beds of the vanadiferous zone and the hanging-wall and footwall limestones are shown in table 2. Gulbrandsen (1960) determined the vanadiferous beds to be quartz-silicate rocks containing grains of quartz, feldspar, and mica in a matrix of illite, organic matter, pyrite, and dolomite. Because of its odor, he believed part of the organic matter to be bituminous. Spectrographic analyses of minor elements in two of the beds of the zone are listed in table 3.

Desborough (1977) later collected samples from the vanadiferous zone in Coal Canyon intended to correspond to the same beds sampled in 1947 and had them analyzed for the constituents shown in table 4. On the basis of electron microprobe, optical, and chemical studies, he concluded (Desborough, 1977, p.

¹Now shown as Rose Canyon on the USGS topographic map of the Geneva 7½-min quadrangle.

TABLE 1.—Partial chemical analyses (in wt percent) of the vanadiferous zone at Sublette Ridge, Wyo. (from Ravitz and others, 1947)

[LOI, loss on ignition; n.d., not determined]

	Lot 1-2	Lot 1-3	Lot 1-4	Lot 1-9	Lot 1-10	Lot 6-5
V_2O_5	0.65	0.52	0.77	0.53	0.92	0.74
P_2O_5	2.9	2.6	.9	2.1	.8	1.4
SiO_2	52.3	43.8	46.5	42.2	49.0	44.0
Fe_2O_3	3.9	4.0	4.2	3.4	3.9	3.6
Al_2O_3	9.5	12.7	12.2	11.6	12.7	10.9
CaO	7.1	9.9	6.5	10.4	5.2	7.8
S	n.d.	4.1	4.1	3.4	4.0	4.0
CO_2	n.d.	6.5	5.8	6.2	4.6	4.7
Organic C	3.9	10.7	10.9	9.2	8.5	4.7
MoO_301	.02	.02	.01	.02	.02
TiO_29	.7	.7	.7	n.d.	n.d.
LOI	11.6	n.d.	n.d.	n.d.	19.5	20.3

TABLE 2.—Chemical analyses of the vanadiferous zone and adjacent limestones (in wt percent) at Coal Canyon, Wyo. [U and Se determinations by the U.S. Geological Survey; all others by the Tennessee Valley Authority under the direction of J.H. Walthall (McKelvey and others, 1953; Gulbrandsen, 1960). AI, acid insoluble; LOI, loss on ignition; n.d., not determined; no entry, not analyzed]

	Bed 70 ²	Vanadiferous zone ¹					Bed 76 ³
		Bed 71	Bed 72	Bed 73	Bed 74	Bed 75	
CaO	36.40	15.60	4.20	4.20	6.05	8.40	50.22
MgO	1.8	1.4	2.9	2.7	2.3	1.9	1.8
CO ₂	29.3	6.4	5.6	5.1	5.9	5.0	40.2
P ₂ O ₅80	6.30	.5	.20	.34	2.73	.36
SiO ₂	22.98	37.36	52.58	45.64	41.64	47.18	4.82
Al ₂ O ₃	2.6	7.1	9.7	9.6	9.8	8.6	1.1
Fe ₂ O ₃	1.2	3.3	4.4	4.0	3.9	3.4	.5
Na ₂ O	1.10	1.27	1.30	.99	.78	1.25	.60
K ₂ O70	2.11	2.85	2.78	2.55	2.12	.72
TiO ₂05	.28	.36	.23	.18	.52	.03
V ₂ O ₅06	.14	.37	1.45	1.75	.52	.06
S as SO ₃60	9.4	8.4	10.6	12.5	8.6	.44
H ₂ O29	.37	.32	.52	.83	.51	.13
AI	27.6	46.66	65.75	56.38	51.2	59.30	5.90
LOI	30.90	17.4	16.6	22.6	24.9	16.7	41.1
U0005-.0004				
Se	n.d.	.009	.010	.015	.015	.015	n.d.

¹Beds 71 through 75 are from base to top of vanadiferous zone.

²Footwall limestone.

³Hanging-wall limestone.

1) that "V is in, or associated with, organic material and minor amounts of V are in Ti-Fe oxysulfide and an unidentified Fe sulfide; Cr is in a 10A mica. Zn and Cd are in sphalerite; Se is in pyrite; S is in pyrite,

sphalerite, and organic material; Ti is in TiO₂ and Ti₂Fe(SO₃O₂; and Mo is in powellite."

TABLE 3.—Minor elements (in ppm) in two beds of the vanadiferous zone at Coal Canyon, Wyo.

[Semiquantitative spectrographic analyses by Harry Bastron, cited by Gulbrandsen (1977). n.d., not detected]

Element	Bed P-72	Bed P-73
Ag	7	10
B	70	100
Ba	300	300
Be	n.d.	1
Co	7	7
Cr	500	1,000
Cu	70	100
Ga	10	15
Mn	200	150
Mo	150	300
Ni	200	700
Pb	20	20
Se	15	15
Sr	150	150
V	5,000	7,000
Y	50	30
Yb	7	20
Zn	700	15,000
Zr	300	300

Agreement among these analyses for minor elements, made by different methods on different samples, leaves much to be desired, but they nevertheless support an interesting observation: a sizable group of elements—Ag, Cd, Cr, Cu, Ga, Mo, Ni, and Zn—roughly follow V in their concentrations. As table 3 shows, for example, an increase in V by a factor of 1.4 from bed P-72 to P-73 is paralleled by a 1.43 increase for Ag and Cu, a 1.5 increase for Ga, a 2.0 increase for Cr and Mo, and a 3.5 increase for Ni. (The 21.4 factor of increase shown for zinc may be a gross error; the value of 700 ppm shown for bed P-72 probably should be 7,000 ppm.)

In a further attempt to define the site of the vanadium, E.C.T. Chao (written communication, 1985) undertook a study of a doubly polished thin section prepared by Cheryl Edwards from a chip of sample VEM 42-47 from the zone in Coal Canyon. He reported that:

The pyritiferous, carbonaceous black shale, VEM 42-47, is a very fine-grained shale with most grains less than 50 micrometers in size. It contains several larger (up to a few tenths of mm) fossil fragments. The dominant minerals are as follows: Quartz (many with less than 10 micrometer size pyrite inclusions), detrital calcite (both single crystal fragments and aggregates), illite (platy micaceous clay),

TABLE 4.—Analyses of selected constituents of the vanadiferous zone at Coal Canyon, Wyo. (from Desborough, 1977)

	Bed 72-CC	Bed 73-CC	Bed 74-CC	Bed 75-CC
Total C, ¹ in percent	9.24	8.13	8.16	14.08
Carbonate C, ² in percent	1.34	1.63	1.16	1.28
Organic C, ³ in percent	7.9	6.5	7.0	12.8
Total S, ⁴ in percent	3.38	3.03	3.38	4.34
V, ⁵ in percent	.09	.14	.19	.95
Zn, ⁶ in percent	.05	.09	.09	.69
Cd, ⁶ in percent	n.d.	.007	.01	.07
Ag, ⁶ in ppm	6.	5.	6.	10.
Ti, ⁷ in ppm	3,000.	2,000.	2,000.	2,000.
Mo, ⁸ in ppm	50.	100.	70.	300.

¹Combustion, gasometric CO₂.

²H₃PO₄ digestion.

³Difference between 1 and 2.

⁴Combustion.

⁵Colorimetric.

⁶Atomic absorption.

⁷Semiquantitative six-step spectrographic.

⁸X-ray fluorescence.

sphalerite (both single crystal fragments and in fine-grained aggregates), and abundant pyrite both granular and framboidal.

In addition, this black shale contains very fine grained (10 μm) or less in grain size) lithic fragments of clay lenses consisting of quartz and illite in a brownish dark matrix. The black shale also contains fairly abundant thin lenses and fragments of semifusinite (tentatively identified by its optical characteristics), a maceral of the inertinite group of coal. It also contains several opaque minerals, unidentified minerals such as a K-Al-silicate of low birefringence, rutile, zircons, plagioclase feldspar, and other accessory minerals. Authigenic secondary overgrowths on quartz have been observed but they are extremely rare. Based on two qualitative analyses, the V is contained in fragments of semifusinite. One grain without sphalerite, the other with inclusions of sphalerite. This suggests that semifusinite (an aromatic hydrocarbon of terrestrial plant origin) is the host of V in this rock. This would support George Desborough's earlier finding.... Phosphorus is present in the fossil fragments.... This black shale contains an unusual amount of sphalerite with traces of cadmium, in isolated grains and in fine aggregates, apparently of sedimentary origin. The presence of framboidal pyrite, detrital calcite, phosphatic fossil fragments, and coaly fragments (and its V content) provide clues to the depositional environment... (anaerobic environment with dominant marine influence).

On the basis of its nonfluorescence in ultraviolet illumination, most of the organic matter is judged to be semifusinite. Because of its fine-grained mineral impurities, however, it is not uniform in composition. The electron microprobe analyses shown in table 5 were made by J.A. Minkin and J.M. Back (written

communication, 1986) and selected from 25 such analyses of randomly selected semifusinite areas in the doubly polished thin section of VEM 42-47. The electron beam focuses on an area a few micrometers in width, so that the analysis reflects the composition of any impurities present. Because the electron microprobe does not detect light elements, such as carbon and hydrogen, the difference between the total shown and 100 percent can be assumed to be largely organic matter. Chao grouped these analyses on the basis of their composition, as table 5 shows. For example, analyses having a low total of inorganic constituents are assumed to be nearly pure semifusinite; potassium is assigned to illite; iron is assigned to pyrite, and excess sulfur is assumed to be organic; phosphorus is assumed to be in apatite.

These analyses show that the vanadium in the semifusinite is likely to be in more than one form. Some of it clearly is in organic matter, since the nearly pure semifusinite contains appreciable amounts of vanadium. Because the highest amounts—up to 4.2 percent V₂O₃ (5.1 percent V₂O₅)—are in the areas composed mainly of illite, however, some vanadium may be attached to that mineral. Some may also be in apatite, although the areas containing apatite also contain the lowest amounts of vanadium. The presence of appreciable amounts of vanadium in association with the unidentified minerals of groups 6 and 7 in table 5 suggest that it may be in or attached to one or more other minerals also.

TABLE 5.—Selected electron microprobe analyses (in percent) of semifusinite areas in sample VEM 42-47 from the vanadiferous zone of the Meade Peak Member of the Phosphoria Formation at Coal Canyon, Wyo.

[J.A. Minkin and J.M. Back, analysts; characterization of groups by E.C.T. Chao (written communication, 1986). n.d., no data; --, not present]

	Group 1 ¹	Group 2 ²			Group 3 ³	Group 4 ⁴	Group 5 ⁵	Group 6 ⁶	Group 7 ⁷
		A	B	C					
SiO ₂	0.13	38.54	39.4	38.5	27.6	20.46	0.11	64.0	24.8
Al ₂ O ₃	--	16.04	16.6	15.7	12.0	11.61	--	10.8	9.6
CaO.....	.43	.16	.4	.66	.96	.45	14.03	.20	11.6
Na ₂ O.....	--	.17	.11	.14	.11	.01	.40	.11	.22
K ₂ O.....	.12	4.29	3.5	3.9	3.3	1.01	.16	2.3	2.8
FeO.....	.10	.82	1.2	6.5	19.7	3.32	.08	.42	.89
MgO.....	.19	1.81	2.0	3.6	3.9	.56	.27	.7	8.6
TiO ₂	1.02	.3	.20	1.75	.77	.07	.05	3.7	.27
MnO.....	.07	.02	.03	.10	.12	.05	.04	.04	.08
V ₂ O ₃	1.38	2.98	4.2	3.4	3.9	1.06	.75	1.56	2.54
S.....	9.28	3.58	4.1	5.4	15.0	10.59	5.91	1.53	1.30
P ₂ O ₅06	.09	n.d.	n.d.	n.d.	.09	10.17	n.d.	n.d.
Total.....	12.78	68.8	71.74	79.65	87.36	49.28	31.97	85.36	62.7

¹Nearly pure semifusinite. Six samples in group show V₂O₃ range of 1.23 to 2.22 percent.

²Semifusinite having appreciable illitic clay, quartz, and low to moderate pyrite content. Four samples in group show V₂O₃ range of 1.6 to 4.2 percent.

³Semifusinite having moderate illitic clay and high pyrite content. Three samples in group show V₂O₃ range of 1.96 to 3.9 percent.

⁴Semifusinite having high organic sulfur, moderate ash, and moderate pyrite. Four samples in group show V₂O₃ range of 1.46 to 2.51 percent.

⁵Semifusinite containing apatite. Four samples in group show V₂O₃ range of 0.65 to 1.08 percent.

⁶As yet unidentified mineral containing Si, Al, Ti, K, and Mg. One sample.

⁷As yet unidentified mineral(s) characterized by moderately high Si, high Ca and Mg, and moderate Al. Two samples show V₂O₃ range of 1.05 to 2.54 percent.

RESOURCES

The Wyodak Coal and Manufacturing Co. estimated that the vanadiferous zone in the explored part of Sublette Ridge contains about 1.9 million tons above drainage level averaging about 0.8 percent V₂O₅. Experimental stoping indicated that the upper 2.25 ft of the zone, averaging 1.06 percent V₂O₅, could be mined separately by the shrinkage method of mining. This uppermost part of the zone contains about 1.35 million tons.

The feasibility of mining these rocks commercially has not been demonstrated. Hence, these quantities can be classed as indicated subeconomic resources.

PARIS-BLOOMINGTON DEPOSITS

The Paris-Bloomington area of Idaho is in Bear Lake County, in the eastern foothills of the Bear River Range. It is about 1 mi west of the towns of Paris and Bloomington and 10 mi southwest of the Union Pacific Railroad at Montpelier. The hills are low and rounded, local relief being about 500 ft. They are cut by four eastward-flowing streams—from north to south, Hammond Creek, Slight Creek, Paris Creek, and Bloomington Creek—that head in the mountains to the west.

From March to December 1943, the Wyodak Coal and Manufacturing Co., agent for the Metals Reserve Co., sampled the Paris-Bloomington deposits in nearly 2,500 ft of underground workings and in six trenches

and short adits. For its part in this project, the USGS prepared a geologic strip map of the area adjacent to the trace of the vanadiferous zone and a geologic map of the area underlain by the zone, both later published at scales of 1:4800 and 1:12,000, respectively (McKelvey and Strobell, 1955). The average thicknesses and vanadium contents of the beds of the zone in surface and underground workings are shown on these maps, as are the locations of geologic and geographic features mentioned in this report.

GEOLOGY

Rocks exposed in the area include the Phosphoria Formation (Permian), the overlying Dinwoody, Woodside, and Thaynes Formations (Triassic), and the underlying Grandeur Tongue of the Park City Formation (Permian) and the Wells Formation (Pennsylvanian and Permian). Brigham Quartzite and Ute(?) Limestone (Cambrian) are in fault contact with these rocks along the Paris overthrust (Armstrong and Cressman, 1963). Tertiary conglomerate, sandstone, and gravel overlie and conceal these Mesozoic and Paleozoic rocks, especially in the southern part of the area. Alluvium, slope wash, and talus of Quaternary age mantle much of the area.

The Phosphoria Formation is divided into the Meade Peak Member, about 200 ft thick, and the overlying Rex Chert Member and cherty shale members, about 250 ft in combined thickness. The top of the vanadiferous zone is about 35 ft below the Rex Chert

Member and about 5 ft below the upper phosphate zone of the Meade Peak.

The Phosphoria Formation and associated formations lie in the asymmetrical Paris syncline, whose axial plane dips about 35° W.; the axis plunges about 15° N. south of Paris Canyon but flattens northward to about 5° or less. The western limb of the syncline is overturned; its beds are nearly vertical near the trough of the syncline, but, high on the limb, they dip as little as 20° W. The beds on the eastern normal limb dip 10° to 35° N.-NNW.

The beds on the western limb are tightly squeezed and decrease in thickness with increasing distance above the trough. At vertical distances of 1,000 to 2,500 ft above the trough, large parts of the incompetent formations are cut out by reverse faults, which are nearly parallel to the bedding. Because of the northward plunge of the syncline, these bedding faults increase in abundance at the surface and progressively appear in stratigraphically higher beds. Thus, a bedding fault cuts out most of the Meade Peak Member at the surface north of Paris Canyon, but no such faults of any size are known in the member south of it.

Four major transverse faults displace the Meade Peak Member as much as 1,000 ft. Minor transverse faults, many of less than 5 ft displacement, and drag folds that cause local thickening or thinning of the beds are abundant on the overturned limb of the syncline. The beds on the normal limb are little disturbed but in places are warped or broken by faults of a few feet displacement.

The Paris thrust plate once overlay the entire area but has been eroded back to the west. South of Sleight Canyon, its margin now lies 500 to 2,000 ft west of the Meade Peak Member on the overturned limb. North of Sleight Canyon, however, the Paris thrust plate overlies the entire Phosphoria Formation as well as the Dinwoody and Woodside Formations. The Paris fault plane dips westward 45° in Bloomington Canyon and decreases northward to 5° at Hammond Creek.

VANADIFEROUS ZONE

The vanadiferous zone is composed of three beds: in ascending order, a shale, a phosphorite, and a siltstone (table 6). These beds are stratigraphically continuous throughout the area. Small amounts of vanadium are found in other beds of the Meade Peak Member, mainly in and near the lower and upper phosphate beds and in the beds adjacent to the vanadiferous zone. Although these adjacent beds are locally enriched as a result of weathering, other beds in the Meade Peak Member for the most part contain less than 0.2 percent V_2O_5 .

TABLE 6.—Average thicknesses and V_2O_5 contents of the beds of the vanadiferous zone, based on all available samples

[All vanadium analyses for the Paris-Bloomington deposits made by W.E. Ryan of the Wyodak Coal and Manufacturing Co.]

Bed	Average thickness, in ft	Average V_2O_5 content, in percent
Siltstone.....	4.30	0.87
Phosphorite.....	2.20	.54
Shale.....	3.4	1.38
Total.....	9.9	.97

The shale bed (the lower part of the zone) is black, medium hard, and fissile. The upper 1 ft contains some thin oolitic phosphorite layers, and the lower 6 to 8 in are in places more coarsely bedded and blocky. In the lower part of a winze in Paris Canyon, about 200 ft below adit level, the whole bed is calcareous, hard, and less fissile. Where the rock is moderately weathered, it is soft and clayey, bedding is indistinct, and its color is dark brown to tan. Lenses of black massive siltstone are found locally in the shale bed, particularly in the upper part. They range from 0.3 to 3 ft thick and from 1 to 25 ft long. Most of these lenses are soft and earthy, but, in places, some are hard and calcareous, and the change from hard to soft may be abrupt. The shale bed in the Paris-Bloomington workings, including the lenses, averages 3.4 ft in thickness and 1.38 percent V_2O_5 . It also contains about 12 percent P_2O_5 . Most of the lenses contain less than 0.2 percent V_2O_5 .

The phosphorite bed is black, massive, hard, and coarsely oolitic and has some shaly siltstone interbedded in the upper half. Where the bed is weathered, it is soft and dark brown to tan, crumbly in the lower part and clayey in the upper part. A few oolite lenses occur between the massive and shaly parts of the bed; they range from 0.5 to 1 ft thick and are generally less than 10 ft long. The average thickness of the phosphorite is 2.20 ft, and its average V_2O_5 content is 0.54 percent; the P_2O_5 content is about 23 percent.

Lenses of siltstone 0.5 to 3.0 ft thick and as much as 80 ft long locally occur at the contact of the phosphorite and the siltstone beds. The V_2O_5 content is generally low but may be high locally as the result of secondary enrichment.

The siltstone bed is black, medium hard, blocky, and well bedded. Individual layers are 2 to 8 in thick. A soft, shaly layer as much as 1 ft thick is locally developed at the top of the bed. In the lower part of the Paris Canyon winze, the bed is massive, hard, and somewhat calcareous. Where it is weathered, it is soft, clayey, and dark to light brown. Its average thickness is 4.3 ft, and its average V_2O_5 content is 0.87 percent; it contains about 3 percent P_2O_5 .

The beds adjacent to the vanadiferous zone are mainly siltstone. Unweathered beds stratigraphically below the zone are hard and calcareous and form a good hanging wall for mining where the zone is on the overturned limb of the syncline. Where these beds are weathered, however, they are soft and require much timbering to hold as a hanging wall. The siltstone stratigraphically above the zone is hard, massive, oolitic, and yellowish brown and contains about 16 percent P_2O_5 . On the normal limb of the syncline, this bed forms the hanging wall and, in most of the workings, will hold for only a day or two without support.

Several partial chemical analyses of the vanadiferous beds are shown in tables 7 through 10. The major constituents of the zone are, in order of abundance, silica, organic matter, calcium, phosphate, and alumina. Quartz-silicate minerals and organic matter are the dominant components of the shale and siltstone beds, although carbonate minerals make up 15 to nearly 30 percent of the shale bed in the lower part of the Paris Canyon winze. Organic matter seems to make up about a quarter of the rock, but little is known as to its nature. Some of the rock has an odor of petroleum, and part of the organic matter may be hydrocarbon. Whatever its form, it is readily combustible; the stockpiles at the 14 South incline caught fire spontaneously in January 1944 and burned vigorously.

Most of the phosphorite bed is composed of carbonate fluorapatite, approximately $Ca_{9.7}Mg_{.1}Na_{.2}(PO_4)_{5.6}(CO_3)_{.1}(CO_3F)_{.3}F_{.2}$, according to Gulbrandsen (Manheim and Gulbrandsen, 1979). This mineral is probably also the site of the lesser amounts of phosphate in the shale and siltstone beds.

Minor constituents of the zone include Fe, S, K, F, Na, Ti, and Mg, in approximate order of abundance. Much of the iron is in hydrous oxides in the weathered rocks and in sulfides in the fresh rocks. Some of the sulfur may be in organic matter. Potassium and sodium, as well as some of the iron and magnesium, are probably present in silicate minerals. Most of the magnesium is probably combined with calcium in dolomite. The fluorine is in the carbonate fluorapatite.

Beds P-142 and P-143 (table 10) are from the upper part of the shale beds, and P-148 is from the phosphorite; the other samples are from the siltstone in the upper part of the vanadiferous zone. Several things in these analyses are worth noting. One is the large amount of organic matter in all the beds. Another is that 49 elements (counting organic matter as carbon) have been detected in the zone. Many of the elements are present in relatively uniform amounts—mostly a few or a few tens of parts per million—and show no

marked relation to vanadium in their variation (for example, As, Be, Co, Dy, Er, Eu, Ga, Gd, Hg, Ho, Mn, Pb, Pr, Re, Sc, Sm, Ti, Y, Yb, and Zr), but several other elements do seem to follow vanadium in concentration variations (for example, Ag, Cd, Cr, Mo, Ni, Se, Sn(?), Tl, and Zn). The distribution of the highest values does not correspond exactly, however. For example, although beds P-142 and P-143 contain the most V and the most Ag, Cu, and Sn as well, bed P-151 contains the most Cd, Mo, Ni, and Tl and by far the most Zn; bed P-154 contains the most Se by far; bed P-156 contains as much Cu as bed P-142 and more Cr than all other beds.

Table 11 shows estimates of the average and maximum contents of minor elements concentrated in the vanadiferous zone in amounts that are more than 10 times their averages in continental crust. The average concentration factors of Cd, Mo, Se, Ag, Tl, V, and Zn are greater than 30; Cd, Sc, and Ag show exceptionally high concentration factors of 2,350, 11,000, and 230, respectively. The maximum concentration factors of Cd and Se are more than twice these average values, and maximum values for Mo, Tl, V, and Zn are hundreds of times larger than their averages in continental crust.

Earth Sciences, Inc., which did some experimental mining in Bloomington Canyon in the 1970's, reported that the vanadiferous shale bed there averaged 4.1 ft thick and contained 1.0 percent V_2O_5 , 13.7 percent P_2O_5 , 0.0115 percent U_3O_8 , 0.0225 percent Se, 0.05 percent Mo, 3.6 percent S, 20.1 percent C, 0.6 percent H, 0.6 percent N, 18.8 percent CaO, 13.8 percent SiO_2 , 4.3 percent Al_2O_3 , 2.0 percent combined H_2O , 8.0 percent free H_2O , 13.3 percent undetermined, and 37.7 percent loss on ignition (De Voto and Stevens, 1979). The uranium content, as well as the phosphate content, is much higher than it is in the vanadiferous zone in western Wyoming.

EFFECTS OF WEATHERING ON THE VANADIFEROUS ZONE

The effects of Holocene weathering on rocks of the vanadiferous zone have been relatively minor. They involve partial oxidation of organic matter and pyrite, some leaching of carbonate and a consequent enrichment of phosphate, a change in color from black to dark brown, formation of orange coatings on joints, a change (in hardness) from hard to soft, and a change from massive to thin bedded or fissile. As we mentioned for the Sublette Ridge deposits, such weathering does not appear to have mobilized the vanadium. Weathering in phosphatic beds has caused an increase in phosphate that is proportional to a decrease in carbonate and organic matter; because much of the

VANADIFEROUS ZONE OF THE PHOSPHORIA FORMATION, WYOMING AND IDAHO

TABLE 7.—Partial composition (in wt percent) of the vanadiferous zone and adjacent beds in the Paris-Bloomington area, Idaho

[Analyses made under the direction of N. Herz, Homestake Mining Co. AI, acid insoluble; LOI, loss on ignition; sp. gr., specific gravity; N, none; tr, trace; --, not present; ?, presence uncertain; no entry, not analyzed]

	Paris adit		Paris winze		Northern drift, Consolidated mine, no 1 x-cut	14 South incline		16 South incline, 90 ft in	Average ¹
	259 ft Portal	in	144 ft down	202 ft down		40 ft in	73 ft in		
Phosphatic siltstone									
V ₂ O ₅	0.34 ⁴		0.14		0.49 ⁴		0.17		0.28
Ni					.01 ⁴				
CaO	23.8 ⁴		30.0		15.4 ⁴		31.5		25.2
P ₂ O ₅	15.1 ⁴		10.8		13.0 ⁴		26.7		16.4
AI	20.9 ⁴		24.0		51.7 ⁴		16.0		28.1
LOI	20.5		24.6		10.0 ⁴		11.8		16.7
"Apatite" ²	39.3 ⁴		28.1		33.8 ⁴		68.9		42.5
CaCO ₃ ³	6.9 ⁴		28.0		.. ⁴				
Sp. gr.	2.70 ⁴		2.71		2.52 ⁴		2.80		2.68
Siltstone									
V ₂ O ₅	0.86		0.65	0.58 ⁴	0.93	0.68	0.93		0.78
Ni	N ⁴		tr ⁴	N ⁴			N ⁴		
CaO	5.6		9.0	6.7 ⁴	3.7	6.7	3.7		5.9
P ₂ O ₅	3.4		3.3	5 ⁴	3.3	4.0	3.3		2.9
AI	65.4		58.1	56.8 ⁴	60.1	58.7	59.4		59.7
LOI	19.9		21.1	20.1 ⁴	24.9	22.6	28.8		22.9
"Apatite"	8.8		8.6	1.3 ⁴	8.6	10.4	8.6		7.7
CaCO ₃	2.0		8.2	10.7 ⁴	..	2.5	..		
Sp. gr.	2.31		2.23	2.13 ⁴	2.16	2.22	2.11		2.19
Phosphorite									
V ₂ O ₅	0.45	0.51	0.38	0.42	0.49	0.37	0.55	0.50	0.46
Ni	N	N	tr	tr	tr	tr	tr	tr	tr
CaO	38.2	38.8	32.6	25.6	20.7	25.4	28.4	27.8	29.7
P ₂ O ₅	29.1	25.8	20.6	19.5	23.4	24.4	22.1	23.0	23.5
AI	14.2	20.0	22.4	29.8	21.6	17.8	19.1	19.6	20.6
LOI	5.7	10.3	13.6	13.8	10.3	14.4	19.2	13.6	12.6
"Apatite"	75.7	67.08	53.6	50.7	60.8	63.4	57.5	59.8	61.1
CaCO ₃	..	?	?
Sp. gr.	2.94	2.72	2.50	2.66	2.60	2.62	2.34	2.77	2.64
Shale									
V ₂ O ₅	1.68	1.06	0.96	1.01	1.32	0.87	1.38	1.37	1.21
Ni		.017	.34 ⁴	tr	.02	tr	tr	.02	
CaO	15.1	18.5	26.6	21.7	16.8	22.8	18.2	22.1	2
P ₂ O ₅	11.9	12.3	7.7	10.1	11.0	17.2	14.5	16.5	12.6
AI	40.2	24.6	17.0	19.1	25.0	21.3	20.3	17.2	20.0
LOI	17.4	35.3	34.9	34.7	38.5	27.7	37.2	24.6	32.5
"Apatite"	30.9	32.0	20.0	26.3	28.6	44.7	37.7	42.9	32.9
CaCO ₃	..	4.1	29.3	15.0	4.1
Sp. gr.	2.37	2.13	2.07	2.13	1.93	2.24	1.91	2.31	2.14
Siltstone (calcareous and phosphatic)									
V ₂ O ₅	0.15	0.15			0.20	0.27	0.60	1.67	0.51
CaO	40.0	30.8			29.4	21.1	19.1	18.0	26.4
P ₂ O ₅	2.2	4.2			3.8	12.7	14.9	13.7	8.6
AI	7.6	6.1			6.4	9.8	10.8	22.5	10.5
LOI	41.3	42.8			43.3	48.8	47.2	37.3	43.4
"Apatite"	5.6	11.0			9.9	33.0	38.7	35.6	22.3
CaCO ₃	66.4	45.0			43.5	7.7
Sp. gr.	2.50	2.28			2.30	1.97	1.91	2.25	2.20
Soft lens in shale bed									
V ₂ O ₅		1.20					0.96		1.08
CaO		17.8					5.6		11.7
P ₂ O ₅		10.7					6.2		8.4
AI		25.4					13.2		19.3
LOI		34.3					69.4		51.8
"Apatite"		27.8					16.1		21.9
CaCO ₃		6.6				
Sp. gr.		2.12					1.55		1.84
Hard lens in shale bed									
V ₂ O ₅		0.29			0.29				0.29
CaO		26.6			25.8				26.3
P ₂ O ₅		4.2			2.7				3.4
AI		5.6			3.5				4.5
LOI		44.0			44.8				44.4
"Apatite"		10.8			7.1				8.9
CaCO ₃		38.0			39.6				38.8
Sp. gr.		2.41			2.42				2.41
Soft lens between phosphorite and siltstone beds									
V ₂ O ₅					0.99				0.99
CaO					24.8				24.8
P ₂ O ₅					7.6				7.6
AI					18.1				18.1
LOI					32.3				32.3
"Apatite"					19.8				19.8
CaCO ₃					26.4				26.4
Sp. gr.					2.37				2.3

¹ Average of analyses shown in this table.² "Apatite" here is assumed to be 10CaO·3P₂O₅·CO₂·CaF₂. The amounts of "apatite" and CaCO₃ shown are calculated by converting all the P₂O₅ to "apatite," adding the CaO necessary to satisfy the P₂O₅ and F, and converting the remaining CaO to CaCO₃.³ Insufficient CaO present to satisfy the proportions called for in the "apatite" formula.⁴ Sample from only part of the bed.

TABLE 8.—Partial chemical analyses (in wt percent) of the vanadiferous beds in the Paris-Bloomington area, Idaho

[Analyses by the U.S. Bureau of Mines (Ravitz and others, 1947). LOI, loss on ignition; n.d., not determined]

	Lot 6-6 ¹	Lot 6-10 ¹	Lot 6-11 ²	Lot 6-12 ³	Lot 6-13 ⁴	Paris composite ⁵
V ₂ O ₅	0.91	1.17	0.86	0.49	1.60	0.69
P ₂ O ₅	11.3	10.3	3.0	22.8	12.8	13.1
SiO ₂	23.8	30.2	45.4	16.8	15.0	23.4
Fe ₂ O ₃	2.2	3.0	1.7	2.3	1.4	1.8
Al ₂ O ₃	10.1	11.1	10.2	4.3	4.7	6.8
CaO	13.8	12.6	3.6	30.2	17.4	17.4
S	3.2	2.0	2.1	1.2	4.6	2.8
CO ₂	3.2	.6	.4	.7	.6	.6
Organic C	17.1	12.6	14.4	8.5	25.7	16.0
MoO ₃02	.02	.02	<.01	.07	.03
TiO ₂3	.3	.6	.2	.2	n.d.
LOI	27.7	24.8	27.7	16.2	41.2	30.0

¹Full thickness, Paris Canyon.²Unweathered siltstone bed, Paris Canyon winze.³Unweathered phosphorite bed, Paris Canyon winze.⁴Unweathered shale bed, Paris Canyon winze.⁵Composite of lots 6-11, 6-12, and 6-13.

TABLE 9.—Partial chemical analyses (in wt percent) of vanadiferous beds in the Paris-Bloomington area, Idaho

[Analyses by the Anaconda Copper Mining Co.
No entry, not analyzed]

	Bed 1 ¹	Bed 2 ²	Bed 3 ³	Bed 4 ⁴
SiO	30.2			
Al ₂ O ₃	6.7			
FeO	2.7			
CaO	14.9			
P ₂ O ₅	9.2	11.0	16.6	22.0
S	1.0			
F85			
V ₂ O ₅87	1.10	1.14	1.40
Cr ₂ O ₃2			

¹Channel sample from full zone exposed in No. 2 Crosscut of Paris Canyon adit.²Calcined sample from bed 1.³Channel sample of shale and phosphorite beds 73 ft from portal in 16 South incline.⁴Calcined sample from bed 3.

vanadium in such rocks is held in the apatite lattice, it locally shows slight increases (Lotspeich and Marquard, 1963).

A period of deep chemical weathering preceded the deposition of the Tertiary Wasatch Formation in the Paris-Bloomington area and elsewhere in the region. Near the erosion surface on which the Wasatch sediments were deposited, the rocks of the Meade Peak are light gray, tan, and pink, in contrast to their dark brown or black color elsewhere, and are similar in

appearance to the burned rocks of the 14 South stockpiles. Weathering has removed calcium carbonate, organic matter, and vanadium, as well as part of the calcium from the apatite. This zone of leaching is exposed only in the trenches above the Consolidated mine in the Paris-Bloomington area and may extend to a depth of 150 to 175 ft below the surface.

Enrichment of vanadium is found at or near the base of the zone of weathering. The rocks there are soft to medium hard and dark brown to black, and bedding planes are well defined. Visible occurrences of red hewettite (CaO · 3V₂O₅ · 9H₂O), green sincosite (CaO · V₂O₄ · P₂O₅ · 5H₂O), and orange pascoite (2CaO · 3V₂O₅ · 11H₂O) are common. Locally, the hewettite forms tabular masses as much as a few inches thick and 2 ft in diameter.

The enrichment in some places is considerable. The enriched part of the zone in the Consolidated mine contains 1.75 percent V₂O₅, in comparison with 0.79 percent V₂O₅ for unenriched rock (table 12). The enriched part of the shale bed in the 16 South incline contains 1.66 percent V₂O₅ in comparison with 1.38 percent V₂O₅ in the shale below the enriched zone. Elsewhere, the obvious secondary concentrations of vanadium are spotty, and the increase in average vanadium content is slight. Large masses of hewettite are present in the 14 South stopes, for example, but they are so irregularly distributed that the average V₂O₅ content of the "enriched" rock is only 0.06 percent more than that of the unenriched rock.

The limits of the obviously enriched zone are irregular, but, in the 14 and 16 South inclines, where it is

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TABLE 10.—Analyses of samples from the vanadiferous zone at Bloomington Canyon, Idaho (from Gulbrandsen, 1975; written communication, 1985)

[Organic matter analyzed by Don Krier; Ti, Hg, and N (total) by E. Campbell; Se by J.S. Wahlberg, J.O. Johnson, and R.J. Young; As by E.J. Fennelly; Re for beds P-143, P-150, P-151, P-154, P-155, and P-156 by Rowe and Steinnes (1976); emission spectrographic analyses for all other elements by J.D. Fletcher. See McKelvey and others (1953) for description of beds. n.d., not detected]

Element	Bed P-142	Bed P-143	Bed P-146	Bed P-148	Bed P-150	Bed P-151	Bed P-153	Bed P-154	Bed P-155	Bed P-156
Amount, in wt percent										
Si	9.6	12	12	12	28	35	38	>34	33	30
Al	1.7	1.8	2.6	1.8	3.3	3.8	4.1	4.4	3.9	3.6
Fe	1.2	.61	2.4	.68	2.4	2.5	1.5	1.4	2.1	1.3
Mg	.17	.24	.21	.14	.24	.25	.37	.35	.35	.51
Ca	6.5	7.9	19.5	5.6	4.3	1.1	1.0	1.2	3.2	3.5
Na	.14	>.3	>.32	.09	>.32	>.32	.07	.08	.09	.08
K	.49	.55	.60	.39	1.2	1.4	1.7	1.4	1.4	1.4
Ti	.09	.11	.13	.08	.22	.26	.28	.28	.30	.24
P	7.0	>6.8	>6.8	6.2	4.0	1.4	1.2	1.6	2.9	2.1
Organic matter	n.d.	35.8	n.d.	n.d.	21.0	22.9	n.d.	24.2	24.4	18.1
N (total)	2.4	2.1	.41	1.0	1.0	1.3	1.1	1.2	1.5	.70
Amount, in parts per million										
Ag	22	22	14	16	14	12	14	14	16	16
As	50	20	40	25	50	50	20	20	25	12
Au	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
B	49	140	68	25	130	140	190	190	200	200
Ba	130	270	240	180	340	300	340	380	360	360
Be	1.9	2.9	3.3	2.4	3.7	2.3	2	2.7	3.3	2.9
Bi	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6
Cd	460	760	420	380	970	980	170	180	170	180
Ce	150	<63	<63	99	130	110	73	69	<63	130
Co	2.8	2.3	2.2	1.0	9.5	10	2.6	3.5	2.1	1.4
Cr	1,300	1,500	1,400	860	850	940	1,200	980	1,200	1,600
Cu	260	420	99	120	180	110	180	250	170	260
Dy	14	14	19	9.8	24	17	<6.8	8.7	14	7.8
Er	12	9.3	10	7.9	27	11	<4.6	6.6	8.7	<4.6
Eu	1.9	2.5	1.8	1.9	3.3	3.5	1.9	1.6	2.5	2.4
Ga	5.1	9.8	5.6	3.9	7.2	8.9	9.2	9.1	8.2	7.9
Gd	<4.6	23	<15	<4.6	18	26	19	23	16	<15
Ge	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	>3.2	<3.2	<3.2	<3.2
Hf	<22	<22	<22	<22	<22	<22	<22	<22	<22	<22
Hg	.91	.94	.60	1.3	.80	.78	.86	.80	1.6	1.1
Ho	4.4	3.7	<3.2	3.4	6.7	<3.2	<3.2	<3.2	3.8	<3.2
In	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6	<4.6
La	240	170	140	130	150	100	58	68	96	90
Lu	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
Mn	64	66	120	34	140	270	79	98	91	83
Mo	61	44	33	6.1	140	280	30	22	23	4.6
Nb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Nd	180	120	<68	<68	<68	<68	<68	<68	<68	<68
Ni	530	410	73	120	340	540	180	290	150	160
Pb	8.1	14	11	<6.8	10	14	19	11	14	13
Pr	<32	<32	22	25	33	26	<32	<32	<32	25
Re	<10	3.6	<10	<10	3.9	4.4	<10	4.9	5.8	.2
Sc	11	14	12	10	20	17	17	17	19	16
Se	420	820	21	430	440	590	480	1,200	940	420
Sm	7.4	6.7	<4.6	6.3	7.4	7.6	6.8	6.6	6.8	7.4
Sn	78	100	25	32	17	19	32	26	28	78
Sr	1,900	2,200	1,500	780	460	370	440	470	550	1,900
Tb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Tl	11	15	10	7.1	74	110	26	36	36	11
Tm	<3.2	<3.2	<3.2	<3.2	2.9	<3.2	<3.2	<3.2	<3.2	3.3
U	210	<150	<150	<150	<150	<150	<150	<150	<150	<150
V	4,700	>4,000	1,700	2,400	2,900	2,900	4,100	4,000	3,000	2,400
W	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Y	280	140	180	220	370	140	80	95	150	130
Yb	6.7	7.9	16	7.3	14	7.7	4.3	5.6	7.2	21
Zn	3,800	1,400	620	580	4,700	10,000	490	1,600	380	360
Zr	170	190	410	150	310	280	250	240	430	120

TABLE 11.—*Estimates of minor-element abundances in the vanadiferous zone at Bloomington Canyon, Idaho, in comparison with their average concentrations in continental crust (after Gulbrandsen, 1977)*

	Vanadiferous zone		Continental crust		Concentration factor ¹
	No. of Element	Average, samples	Maximum, in ppm	Average, in ppm	
As ²	10	30	50	1.8	17
B ³	10	130	200	10	13
Cd ³	10	470	980	.2	2,350
Cr ³	10	1,200	1,600	100	12
Hg ⁴	10	1	1.6	.08	12.5
Mo ³	10	60	280	1.5	40
Se ⁵	10	560	1,200	.05	11,000
Ag ³	10	16	20	.07	230
Tl ⁴	10	40	110	.45	89
Sn ³	10	40	100	2	20
V ⁶	10	4,600	17,000	135	34
Zn.....	10	2,400	10,000	70	34

¹Ratio of vanadiferous zone average to continental crust average.

²Spectrophotometric analysis by E.J. Fennelly.

³Semiquantitative spectrographic analysis by J. Fletcher.

⁴Analysis by E. Campbell.

⁵X-ray fluorescence analysis by J.S. Wahlberg, J.D. Johnson, and R.J. Young.

⁶Analysis by J. Fletcher and H.H. Lipp.

TABLE 12.—*Comparison of the thicknesses and V₂O₅ contents of partly leached, enriched, and unenriched rocks of the vanadiferous zone in the Paris-Bloomington area, Idaho*

[No entry, not analyzed]

	Partly leached rock		Enriched rock		Unenriched rock		Average	
	Thickness, in ft	V ₂ O ₅ , in percent	Thickness, in ft	V ₂ O ₅ , in percent	Thickness, in ft	V ₂ O ₅ , in percent	Thickness, in ft	V ₂ O ₅ , in percent
Consolidated mine								
Siltstone.....			3.5 ¹	1.50 ¹	4.7 ⁴	0.67 ⁴	4.4	0.94
Phosphorite.....			1.4 ¹	.74 ¹	2.8 ⁴	.49 ⁴	2.1	.57
Shale.....			2.9 ¹	1.89 ^{1,2}	3.4 ⁴	1.22 ⁴	3.3	1.45
Total.....			7.8	1.75 ³	10.9	.79 ³	9.8	1.03 ³
16 South incline								
Shale ⁵	3.3 ⁶	1.26 ⁶	5.2 ⁷	1.66 ⁷	4.1 ⁸	1.38 ⁸	4.1	1.40
14 South incline								
Shale.....	3.4	1.11	3.9	1.37	3.8	1.31	3.6	1.29

¹Sampled along 180 ft of drift.

²Includes siltstone bed below shale where enriched 45 to 140 ft north of No. 1 crosscut.

³Weighted average.

⁴Sampled along 283 ft of drift.

⁵Includes siltstone below shale 85 to 175 ft from portal.

⁶Sampled along 85 ft of incline.

⁷Sampled along 45 ft of incline.

⁸Sampled along 150 ft of incline.

defined by the presence of hewettite, the zone extends downdip for 40 to 50 ft. In the northern drift of the Consolidated mine, where the rocks are faulted and broken, enrichment extends to still greater depths. Differences in permeability of the individual beds also affect the depth of weathering and consequent enrichment. The phosphorite bed, for example, is commonly weathered to greater depths than the other beds are.

Enrichment in the Bloomington Canyon workings is almost entirely restricted to the shale bed and to the beds below it that are only weakly vanadiferous elsewhere. This restriction suggests that solutions migrating downward along the shale bed locally departed from it and moved downward into the underlying beds along steeply dipping fractures. In the northern drift of the Consolidated mine, where the rocks dip 50° to 60° W., all of the exposed beds are locally enriched, an indication that solutions there worked downward mainly along bedding planes but locally departed from them along fractures to enter either hanging-wall or footwall beds. Local lenses, particularly those between the phosphorite and siltstone beds, are strikingly enriched in places. Weathering apparently removed the calcite from these lenses and left a spongy mass favorable for the deposition of secondary minerals.

The rocks below the zone of enrichment are hard, black, and in places contain pyrite and white coatings on fractures and joints. Sincosite is found locally below the zone of enrichment in the Bloomington Canyon workings but is of no quantitative importance. The lenses and siltstone beds below the shale are calcareous in the Consolidated mine, but the beds of the vanadiferous zone there are only weakly calcareous. All the rocks in the bottom of the Paris Canyon winze, however, are calcareous, and the V_2O_5 content of the zone as a whole is only about 0.6 percent, in contrast to the average of 0.9 percent elsewhere in the mine.

Because the vanadium content of calcareous rocks from the bottom of the winze is lower than that of rocks elsewhere in the mine, samples from other workings may not be reliable indicators of the grade of the zone in deeper parts of the syncline, since the so-called unenriched rocks may in fact be somewhat enriched, even though they contain no visible signs of enrichment. Should this scenario prove true, the grade of the zone at depth might be more comparable to that near the base of the winze than to the higher values in the other workings.

VARIATIONS IN THICKNESS AND VANADIUM CONTENT OF THE VANADIFEROUS ZONE

The thicknesses and vanadium contents of the beds of the vanadiferous zone vary considerably in individual samples, although averages of groups of samples generally differ only slightly. However, some lateral variations, due chiefly to weathering, can be observed.

As table 13 shows, the beds on the normal limb of the syncline are about 20 percent thicker than those on the overturned limb. The siltstone and phosphorite beds on the normal limb are somewhat less vanadiferous.

The vanadiferous zone as a whole contains less than average amounts of vanadium in the apparently unaltered part of the Consolidated mine, owing to the presence of abundant, weakly vanadiferous calcareous lenses. These lenses also add to the thickness of the zone, making it somewhat thicker than it is elsewhere on the overturned limb (compare tables 13 and 14).

The most conspicuous differences in grade and thickness are between individual samples, as table 15 shows. Extreme differences in thickness occur on the overturned limb; differences in the vanadium contents of these rocks reflect the effects of leaching and enrichment.

TABLE 13.—Comparison of the thicknesses and vanadium contents of the vanadiferous beds on the normal and overturned limbs of the Paris syncline, Idaho

	Normal limb ¹		Overturned limb ¹		Average	
	V_2O_5 , in percent	Thickness, in ft	V_2O_5 , in percent	Thickness, in ft	V_2O_5 , in percent	Thickness, in ft
Siltstone	0.82	4.9	0.89	4.0	0.85	4.5
Phosphorite43	2.5	.61	2.1	.51	2.3
Shale ²	1.36	3.8	1.35	3.1	1.36	3.4
	.92	11.2	.98	9.2	.95	10.2

¹Based on samples obtained in underground workings only.

²Includes siltstone bed below shale where it is high grade in the Consolidated mine and 16 South incline.

TABLE 14.—*Effect of lenses on the unaltered vanadiferous zone in the Consolidated mine, Paris-Bloomington area, Idaho*

Bed	With lenses		Without lenses		Lenses only	
	Thickness, in ft	V ₂ O ₅ , in percent	Thickness, in ft	V ₂ O ₅ , in percent	Thickness, in ft	V ₂ O ₅ , in percent
Siltstone	4.8	0.67	4.5	0.68	1.1	0.48
Phosphorite	2.8	.49	2.2	.55	1.4	.26
Shale	3.3	1.22	2.7	1.40	2.4	.30
All beds	10.9	.86	9.4	1.22	4.9	.33

TABLE 15.—*Range in thickness and grade of the vanadiferous zone in the Paris-Bloomington area, Idaho*

	Range of local averages ¹		Extreme ranges ²	
	Thickness, in ft	V ₂ O ₅ content, in percent	Thickness, in ft	V ₂ O ₅ content, in percent
Siltstone	3.7-5.2	0.72-0.98	1.1-6.9	0.06-2.43
Phosphorite	2.0-3.0	.39-.67	.5-4.7	.08-2.43
Shale	2.9-4.1	.84-1.05	.05-7.2	.06-5.73 ³
Full zone	8.8-11.8	.84-1.05	5.8-16.1	.07-1.80

¹Range in local average thickness and grade is the range in average V₂O₅ content determined at each of the underground workings; it applies to the full zone as well as to individual beds.

²Extreme range in thickness and grade is the range in individual samples of the bed. For the full zone, it is the range in complete sections of the three beds.

³Includes siltstone bed (0.6 ft thick) below the shale, which contains 23.00 percent V₂O₅ at this point.

The distribution of vanadium within each bed is generally uniform. Sections of the vanadiferous zone in which the thinnest recognizable units of each bed were sampled separately show that the vanadium content of the siltstone is remarkably constant from top to bottom, that the siltstone layers of the phosphorite bed contain more vanadium than the phosphatic ones, and that the upper phosphatic and lower blocky parts of the overlying shale bed contain slightly less vanadium than the central part of the bed.

RESOURCES

The tonnages, stratigraphic distributions, and vanadium contents of the vanadiferous beds—classed as measured, indicated, and inferred subeconomic resources—are summarized in table 16. If the tonnage were projected to the northern end of the area mapped, it would be approximately tripled.

Estimates were made of the shale bed separately because of its much higher grade; of the shale and the phosphorite, in case it should prove impractical to mine the full zone; and of the full zone. The Wyodak Coal and Manufacturing Co. did not undertake experimental mining of the shale bed alone, but it did

successfully complete experimental mining of the other two units in the 14 South workings on the normal limb of the syncline by the longwall mining method. Although no experimental mining was attempted on the overturned limb, operations manager J.D. Johnson believed that the top-slicing method of mining would be suitable for that part of the deposit.

Although some possible means of vanadium recovery have been identified (Ravitz and others, 1947; De Voto and Stevens, 1979), the commercial feasibility of production from the zone has not been demonstrated, and its resources are considered subeconomic for the present. They are classed as measured where the vanadiferous beds are known to be present, and their thicknesses and vanadium contents have been well established by taking closely spaced samples and measurements. The limits of error in these estimates are judged not to exceed 15 percent. Resources have been measured in the Paris Canyon area, where the zone was sampled in 725 ft of underground workings, four trenches, and one short crosscut; in the Consolidated mine area, where the zone was sampled in nearly 500 ft of underground workings; and in Bloomington Canyon, between the 12 South adit and 16 South incline, where the zone was sampled in

TABLE 16.—*Subeconomic vanadium resources in the Paris-Bloomington area, Idaho*

	Tons (short)	Average thickness, in ft	V ₂ O ₅ content, in percent
Measured			
Shale bed only ¹	180,000	3.6	1.35
Shale and phosphorite beds.	320,000	6.0	1.02
Shale, phosphorite, and siltstone beds.	600,000	10.8	.93
Indicated			
Shale bed only.....	1,200,000	3.0	1.4
Shale and phosphorite	2,300,000	5.5	1.0
Shale, phosphorite, and siltstone beds.	4,000,000	10.0	.9
Inferred²			
Shale bed only.....	15,000,000- 25,000,000	3.0	1.0-1.4
Shale and phosphorite	25,000,000- 40,000,000	5.5	.7-1.1
Shale, phosphorite, and siltstone beds.	50,000,000- 75,000,000	10.0	.6-1.0

¹Siltstone below shale included where it is enriched in Consolidated mine and 16 South incline.

²Inferred resources stated for area south of northernmost intersection of zone in Paris Canyon.

nearly 1,200 ft of underground workings. The measured resources lie above a depth of 200 ft below drainage level.

In areas between or adjacent to those containing measured resources, the cover is such that the structural continuity of the zone is not well established, and samples and measurements are few and widely spaced. Resources in these areas—estimated partly on the basis of samples and measurements and partly on the basis of geologic projection from adjacent areas—are classed as indicated.

Because the hard, calcareous rocks encountered in the bottom of the Paris Canyon winze may be typical of unaltered rock, the beds sampled in most of the workings may be slightly enriched and therefore not representative of the rocks at depth. Indicated resources are therefore limited only to the beds between the surface and the depth below the old Tertiary surface equivalent to the bottom of the winze. This elevation in Paris and Bloomington Canyons is about 6,000 ft, but, at the divide between the two, it is assumed to be about 6,250 ft.

Because the vanadiferous zone is faulted out at the surface north of trench 4 North (on the northern side of Paris Canyon), the existence of resources on the overturned limb is not certain enough to justify the estimation of any indicated resources there. There are no exposures east and north of the 16 South incline to

define the extent of the zone on the normal limb. Since no evidence contradicts the reasonable assumption that the zone extends for some distance in this direction, resources extending 500 ft east of the 16 South incline are arbitrarily classed as indicated.

The limits of inferred subeconomic resources are defined by the boundaries of the measured and indicated resources in the southern and southwestern parts of the area, by the supposed position of a possible fault along the eastern edge of the Paris syncline, and, arbitrarily, by the northernmost exposure of the zone in Paris Canyon. The Paris syncline is known to extend as far north as Liberty, about 7 mi north of Paris Canyon, and it seems likely that the zone extends over the entire structure. For the purpose of this report, however, it is assumed that its northern limit corresponds to the northern limit of the area mapped, about 3.5 mi north of Paris Canyon. As table 16 (footnote 2) states, if inferred resources were considered to extend to the latter limit, the estimates would be approximately triple those shown in the table. Most of the inferred resources lie above a depth of 3,500 ft below drainage level.

The vanadium content of the greater part of the inferred resources may more nearly approximate that of the zone in the bottom of the Paris Canyon winze (0.6 percent V₂O₅) than that of the zone sampled in other workings (0.9 percent V₂O₅). Even if this assumption

is correct, part of these resources—those on the overturned limb of the syncline above an elevation of about 6,000 ft and those northeast of the 16 South incline on the normal limb above an elevation of 5,800 to 6,000 ft—should be comparable in grade to those of the measured and indicated resources. To emphasize the uncertainties caused by these factors, the tonnages and grades of the inferred resources are expressed as ranges in table 16.

To prepare these estimates, samples were weighted according to their abundance as well as to their area of influence. Thus, in determining the grade and thickness in a given block, the average of many samples from an underground working was given more weight than samples from individual trenches, even though the area of influence of the latter may have been greater. Because samples in the underground workings were rather uniformly spaced (about 10 ft apart), averages were determined by weighting the samples by thickness but not by distance between them. Samples of part of a bed were not included. The beds differ in density, and, if units had been combined according to weight rather than volume alone, the average grade would differ by 0.02 to 0.03 percent V_2O_5 . Because the discrepancy thus produced would have been small, weight was disregarded in calculating the average grades of the shale-phosphorite combination and the full zone.

The beds range in density from 12.3 to 15.3 ft^3/t and 14 ft^3/t . The estimates of the full zone and of the shale-phosphorite combination were based on a density of 14 ft^3/t ; those of the shale bed alone were based on a density of 15.3 ft^3/t .

EXPERIMENTAL MINING AND PROCESSING

The Wyodak Coal and Manufacturing Co. demonstrated in 1943 the feasibility of mining both the shale and phosphorite together and the full zone. The USBM (Ravitz and others, 1947) undertook preliminary studies of recovery processes. In the mid-1970's, Earth Sciences, Inc., did experimental mining in Bloomington Canyon and developed a plan for extracting the shale bed by augur mining. Mine production of 211,000 tons/yr was planned to yield, after roasting and leaching, 3,000,000 lb of V_2O_5 as ferrovandium, 67,500 lb of selenium, 33,900 lb of U_3O_8 , and 59,100 tons of phosphate concentrate containing 32 percent P_2O_5 ; molybdenum was recoverable, too, but in amounts too small to market (De Vota and Stevens, 1979). Cost analysis projected a 9.5 percent rate of return on investment. Although this rate was thought to be minimally adequate then, development did not

follow; given the subsequent decline in commodity prices, it may be assumed that production is still not economically feasible.

ORIGIN

Many marine black shales contain concentrations of vanadium in the range of 0.2 to 0.35 percent V_2O_5 (for example, Davidson and Lakin, 1961; Vine, 1969; Vine and Tourtelot, 1970), and a few contain somewhat larger amounts (Krauskopf, 1955; Coveney and Martin, 1983; Poole and Desborough, 1985). They also commonly contain suites of trace metals similar to those of the vanadiferous zone of the Phosphoria Formation. None have been reported, however, in the range of 2.0 to 2.5 percent V_2O_5 found within the zone in western Wyoming or at the average of nearly 1 percent over an average thickness of about 10 ft found in the Paris-Bloomington area of Idaho. Exceptional also is the total vanadium content of the Meade Peak Member. The member averages 0.02 to 0.1 percent V_2O_5 in southeastern Idaho and western Wyoming (fig. 3) (Maughan, 1976, 1980). All of its beds at Coal Canyon except one contain vanadium in amounts greater than the average crustal abundance, and 10 beds outside the vanadiferous zone contain it in the range of 0.2 to 0.42 percent V_2O_5 (McKelvey and others, 1953; Gulbrandsen, 1960).

The Meade Peak Member in general and its vanadiferous zone in particular, then, have exceptional concentrations of vanadium, although they are otherwise similar in trace-metal content to many other black shales. Their origins very likely are similar, but the higher concentration of V_2O_5 in the Meade Peak Member requires explanation. The vanadiferous zone is clearly the product of primary deposition from upwelling water in an anoxic marine environment below wave base in a water depth of 100 to 300 m or so. The deposits formed on a large embayment on the outer continental shelf on the western side of the North American craton at low latitude, where deep, cold, nutrient-rich seawater welled up as a result of divergent upwelling in a tradewind belt. The carbonaceous mudstones, of which the vanadiferous zone is a part, are the outer shelf facies equivalents of nearer shore phosphorite, chert, carbonate rock, redbeds, and evaporites. The carbonaceous, phosphatic, and cherty sediments are direct or indirect manifestations of the high biologic productivity characteristic of the shelf environment. Concentration of the vanadium and associated metals took place at about the same time as deposition or burial of the associated sediment, which accumulated very slowly in an environment of circulating seawater.

The reasons for these conclusions are straightforward. The lateral continuity over thousands of square miles of thin beds of very fine grained sediment underlain and overlain by rocks containing marine fossils allows only syngenetic deposition in a marine environment. The abundant organic matter (part of which may be bituminous), pyrite, and other sulfides testify to accumulation under reducing conditions. The geographic setting of the Meade Peak Member, including its relation to upwelling, has been established by regional stratigraphic studies of the Phosphoria Formation (for example, McKelvey and others, 1959; Sheldon, 1964, 1981). The requisite slow deposition and circulating seawater are also necessary for phosphorite (McKelvey, 1946). The concentrations of vanadium in the zone are so high (locally, 150 times or more its crustal abundance of 150 g/t) (Rankama and Sahama, 1950) relative to its ordinary occurrence that they could have been attained only in the absence of the dilution that would have resulted from sedimentation at ordinary rates. Furthermore, the vanadium content of seawater (2.5 ppb (Brewer, 1975)) is so low that even the total extraction of the vanadium in a standing column of seawater several times the probable depth of the Meade Peak sea would not begin to equal the amount of vanadium found in the vanadiferous zone.²

Beyond these observations, the origin of the vanadiferous zone can be addressed only with questions and speculations. For example, how are vanadium and other metals held? What led to their precipitation from seawater? What factors are responsible for their exceptionally high concentration in both the vanadiferous zone and in the Meade Peak Member as a whole? What was the specific environment in which the high concentrations were localized?

As McKelvey (1946) discussed, the vanadium in the vanadiferous zone may occur as sulfide, as adsorbed ions on clay minerals, or contained in organic matter. Vanadium has been found in each of these forms in some sedimentary rocks (Rankama and Sahama, 1950). Some support for its presence in a clay or other silicate mineral came from R.A. Gulbrandsen (written communication, 1985), who tested a sample of the Coal Canyon vanadiferous zone in hydrochloric and hydrofluoric acids. He found that essentially no vanadium was dissolved by hydrochloric acid but that vanadium was dissolved by hydrofluoric acid. Since hydrofluoric acid dissolves silicate minerals, this result suggests

²For example, a water column 1 m² and 1,000 m deep—10 times the probable depth of the Meade Peak sea—containing 2.5 ppb V (see table 16) would contain only 2.5 g V. One square meter of the upper part of the vanadiferous zone in Sublette Ridge, averaging 0.686 m thick and 0.594 percent V, contains 8,521 g V, the equivalent of the vanadium in about 3,400 such water columns.

that vanadium occurs in one or more silicate minerals. Desborough's (1977) subsequent electron microprobe studies showed that vanadium is held in organic matter. The recent work of E.C.T. Chao, J.A. Minkin, and J.M. Back (written communication, 1986) confirmed both observations—that vanadium is within semifusinite but that some of it is attached to illite.³ According to George Breit (written communication, 1986), "...there seems to be a general progression in the form of vanadium in black shales. Soon after deposition the vanadium is tightly associated with organic fragments. In older units, especially those past the point of oil generation, the vanadium is tied up in clays and occasionally sulfides."

In what chemical form is the vanadium held by the organic matter? The richest bed of the vanadiferous zone in western Wyoming has a V₂O₅ content of 2 percent or more and an organic matter content of about 25 percent; thus, its V₂O₅ content would be 8 percent or more. Carbonaceous matter is known to be a good chemical adsorbent for metals, and bituminous shales that are high in vanadium and some other metals are relatively high in organic carbon (Desborough, 1977; Maughan, 1980; Holland, 1984). But many shales rich in organic carbon, including some in the Phosphoria Formation, have low trace-metal contents, so the correlation is not necessarily direct.

Bader (1937, cited by Rankama and Sahama, 1950, p. 599) believed that the vanadium in vanadiferous crude oils and bituminous shales is held in porphyrin complexes. A Persian crude oil has been reported to contain 2.82 percent V (5.03 percent V₂O₅), but the maximum vanadium content in most vanadiferous crudes, including the heavy crudes from which vanadium is recovered commercially, is of the order of 1,000 ppm (Hunt, 1979). Bader's average vanadium content for asphalt is 5,400 ppm, although Fischer (1973) reported that many asphaltites contain about 1 percent. Recently, a vanadyl deoxyphylloerythroetioporphyrin was extracted from an oil shale at Julia Creek in Queensland, Australia (Ekstrom and others, 1983; Miller and others, 1984). This oil shale, which contains as much as 0.5 percent V, is in a mica-montmorillonite clay; that part of the vanadium in organic matter is in kerogen (Riley and Saxby, 1982). Saoiabi and others (1983) also reported vanadyl and

³Semifusinite, which consists of carbonized woody tissue, is characteristically of terrestrial origin, but, because the environment of deposition of the vanadiferous zone was more than 125 mi from the nearest land, where an arid climate probably prevailed, a terrestrial origin for it here seems dubious. The point of its origin is not important, however. As Chao recognized, its environment of deposition was marine, and it is clear that the living plants could not have acquired such large quantities of vanadium.

nickel porphyrins from Moroccan oil shales. The vanadium content of these porphyrins is not known to us, but, if they were the vanadium analogue of the nickel porphyrin abelsonite ($C_{31}H_{32}N_4Ni$) (Milton and others, 1978), they would contain 17.85 percent V_2O_5 —just about the amount needed if half the organic matter in the highly vanadiferous beds were in that form.

Premovic and others (1986) also found VO_2^+ porphyrins in the Triassic Serpiano marl of Switzerland and the Cretaceous La Luna shaly limestone of Venezuela, which contain about 2,700 and 1,100 ppm V, respectively. About half of the total vanadium in both formations is in kerogen, and the remainder is in the extractable organic, HCL-soluble, and HF-soluble fractions. The VO_2^+ porphyrins are in the extractable organic and kerogen fractions. In view of these occurrences and others reported by Premovic and others, it seems likely that at least some of the vanadium in the Meade Peak Member is in the form of porphyrins.

In addition to the phosphorite in the vanadiferous zone in the Paris-Bloomington area, several other phosphorites in the Meade Peak Member contain vanadium, generally in the range of 0.2 to 0.4 percent V_2O_5 . In fact, vanadium is currently being recovered as a byproduct of the manufacture of elemental phosphorus in southeastern Idaho. Some of the vanadium in phosphorite probably occurs in carbonate fluorapatite in substitution for phosphorus (Rankama and Sahama, 1950; McConnell, 1953). Some of it, however, may also be held by organic matter (Krauskopf, 1955; Gulbrandsen, 1966).

Phosphorites also contain moderately high concentrations of the other metals found in the vanadiferous zone. Southeastern Idaho phosphorites, for example, average 90 ppm Cd, 800 ppm Cr, 85 ppm Cu, 30 ppm Mo, 100 ppm Ni, 30 ppm Se, 5 ppm Ag, 3 ppm Th, and 250 ppm Zn (Gulbrandsen, 1977). These concentrations, for the most part, are much higher than those of the average phosphorite reported by Altschuler (1980)—namely, 18 ppm Cd, 125 ppm Cr, 7 ppm Cu, 9 ppm Mo, 53 ppm Ni, 4.6 ppm Se, 2 ppm Ag, and 195 ppm Zn. No gold determinations have been made for phosphorite in the Sublette Ridge or Paris-Bloomington areas, but 0.4 ppm Au has been found farther north in western Wyoming (Love, 1984).

According to Rankama and Sahama (1950), vanadium in upper oxygenated seawater is in the quinquevalent state. Reduction in oxygen-deficient bottom waters would lead to its precipitation in some form. Holland (1979) found that the concentrations of Ag, Cu, Ni, V, and Zn at the highest median value reported for 20 sets of black shales by Vine and Tourtelot (1970) represent a surprisingly narrow range of enrichment

factors over their concentrations in seawater of 2.5 to 8×10^5 (table 17). Even at the highest 95th percentile in the same 20 sets of samples, the enrichment factor for these metals ranged only from 5 to 23×10^5 . Noting the reported removal of such metals by precipitation from the anoxic part of the water column in the Black Sea (Brewer and Spencer, 1974), Holland (1979, p. 1679) concluded that, although "...many metals participate actively in biochemical cycles...the available data (see, for instance, Brewer, 1975) suggest that the concentration of trace metals in living organisms is not large enough to account for the observed enrichment of trace metals in black shales. Apparently, the concentration of metals in organic-rich sediments owes more to chemical precipitation and to reactions with dead organic remains than to their incorporation in living organisms" (see also Holland, 1984).

The common occurrence of these metals in bituminous shales deposited in the upwelling environment led Brongersma-Sanders (1969) to suggest that they are transported from surface to deeper water layers by organisms and concentrated there by resolution after death. Precipitation of the metals may take place if the decay of organic matter leads to deoxygenation of the bottom waters and the formation of H_2S . She cited data given by Schutz and Turekian (1965) on Ag, Ni, and Co showing "...high concentrations in areas of high organic productivity (upwelling water) accompanied by an increase of concentration with depth" (Brongersma-Sanders, 1969, p. 234).

Thus, upwelling water itself may be important as a source of the metals. Bruland (1980) reported a marked increase in the content of Zn, Cd, Ni, and Cu with depth in the central North Pacific; the increase for Zn, Cd, and Ni between the surface and a depth of 1.0 to 1.5 km is severalfold, a pattern almost identical to that long known for phosphate and nitrate (fig. 4). Cutter (1982) found that selenium also increases with depth and that it changes from selenate and selenite forms in the oxic zone to an organic selenide form in the anoxic zone. If, as seems likely, vanadium and the other characteristic trace metals of black shales follow the same pattern, upwelling would move metal-rich materials into the environment of deposition, just as it does for phosphate and the other major nutrient elements.⁴ Baturin (1982) confirmed the effectiveness

⁴Hite (1978) also considered a high metal source important, but he envisioned that source as a warm brine, enriched in phosphate as well as metals, refluxed to the sea from an evaporite basin and reacting with cold seawater. Perhaps the most problematic aspect of this novel hypothesis is the idea that the brine (presumably) retains its coherence as a sheet extending a few hundred miles seaward from its source, across bottoms where the fossil record shows sessile organisms lived, to the black shale environment.

TABLE 17.—Some trace metals in seawater in comparison with their concentrations in black shales (Holland, 1979)

	Seawater, in ppb	Highest median of 20 sets of black shale samples, in ppm ¹	Enrichment factor over seawater, ×10 ⁵	Highest 95th percentile of 20 sets of black shale samples, in ppm ¹	Enrichment factor over seawater, ×10 ⁵
Ag.....	0.04 ²	10	2.5	20	5
Cr.....	3 ²	1,000	30	3,000	90
Cu.....	.25 ³	200	8	500	20
Mo.....	10.0 ²	300	.3	700	.7
Ni.....	.05 ⁴	500	8	1,000	16
Pb.....	.03 ¹	50	17	100	34
V.....	2.5	1,000	4	2,000	8
Zn.....	-3.0 ¹	1,500	5	7,000	23

¹Vine and Tourtelot (1970).²Brewer (1975).³Boyle and others (1977).⁴Sclater and others (1976).

of upwelling in helping to concentrate the metals when he reported that diatomaceous ooze in the area of strong upwelling off southwestern Africa contains 455 ppm Ni, 337 ppm Zn, 129 ppm Cu, 500 ppm Mo, and 360 ppm V, all fixed mainly in organic matter.

Although the metal content of organisms is generally very small, Z.A. Vinogradova and V.V. Koval'skiy (see Calvert, 1976) reported 200 ppm Cu and 2,600 ppm Zn in Black Sea plankton. Remarkable concentrations of vanadium occur in the blood of ascidians and holothurians. Rankama and Sahama (1950) reported an astonishing 10.4 percent V (18.6 percent V₂O₅) in holothurian blood (dry weight)—again, just about the right concentration needed if roughly half of the organic matter in the richly vanadiferous beds were in such a form. The idea that a significant part of the organic matter in the vanadiferous zone might be derived from holothurian blood is too bizarre to discuss further, but it does seem possible (even likely) that organisms played some part in extracting vanadium and other metals from seawater, similar to the role that has long been postulated for them in concentrating phosphate (see Gulbrandsen's (1969) review). Addressing the similar assemblage of metals found in phosphorites, Prevot and Lucas (1980) suggested that organisms bring these elements together and that the first trap for these elements is biologic. Subsequent steps in their concentration are accomplished by both biochemical and inorganic chemical processes.

As we indicated previously, it is possible that vanadium and some other metals are in the form of a porphyrin. Determination of the crystal structure of the vanadyl porphyrin from Australia is regarded as confirmation of the hypothesis that this porphyrin is a

degradation product of chlorophyll (Ekstrom and others, 1983). But, although this hypothesis in turn may be taken as proof of the biologic origin of crude oil, it is also proof that the vanadium, replacing the magnesium of chlorophyll, was not sited in the porphyrin by a primary biologic process. Premovic and others (1986) reached a similar conclusion with respect to the Serpiano marl and the La Luna shaly limestone.

Are organisms the common denominator that brings the black shale metals (here taken to be Ag, Cd, Cr, Mo, Ni, Se, Ti, U, V, and Zn) together, as Prevot and Lucas suggested? According to Bowen (1966), only Mo, Se, V, and Zn are essential to the life of some or all organisms. Cr and Ni may have an essential role, and Cd is known to be involved in a special biologic process. No biologic role has been reported for Ag, Ti, or U. Three other metals that are also essential to life (Co, Cu, and Mn) are present in black shales in low concentrations only. All of the black shale metals are known to be moderately to highly toxic to organisms in more than trace amounts. It thus seems unlikely that biologic necessity brings all of these metals together, particularly in the high concentrations in which they are found in the black shales. However, even though a biologic role is unknown for Ag and is limited or uncertain for Cd, Cr, and Ni, all four elements are known to occur in both marine plants and animals, and all the black shale metals are known to occur in seawater. It is possible, therefore, that, even though some metals do not play a biologic role, they might be carried to the bottom in small concentrations in living or dead organic tissue.

Organic matter has been shown to be effective in adsorbing metals from seawater (Krauskopf, 1955).

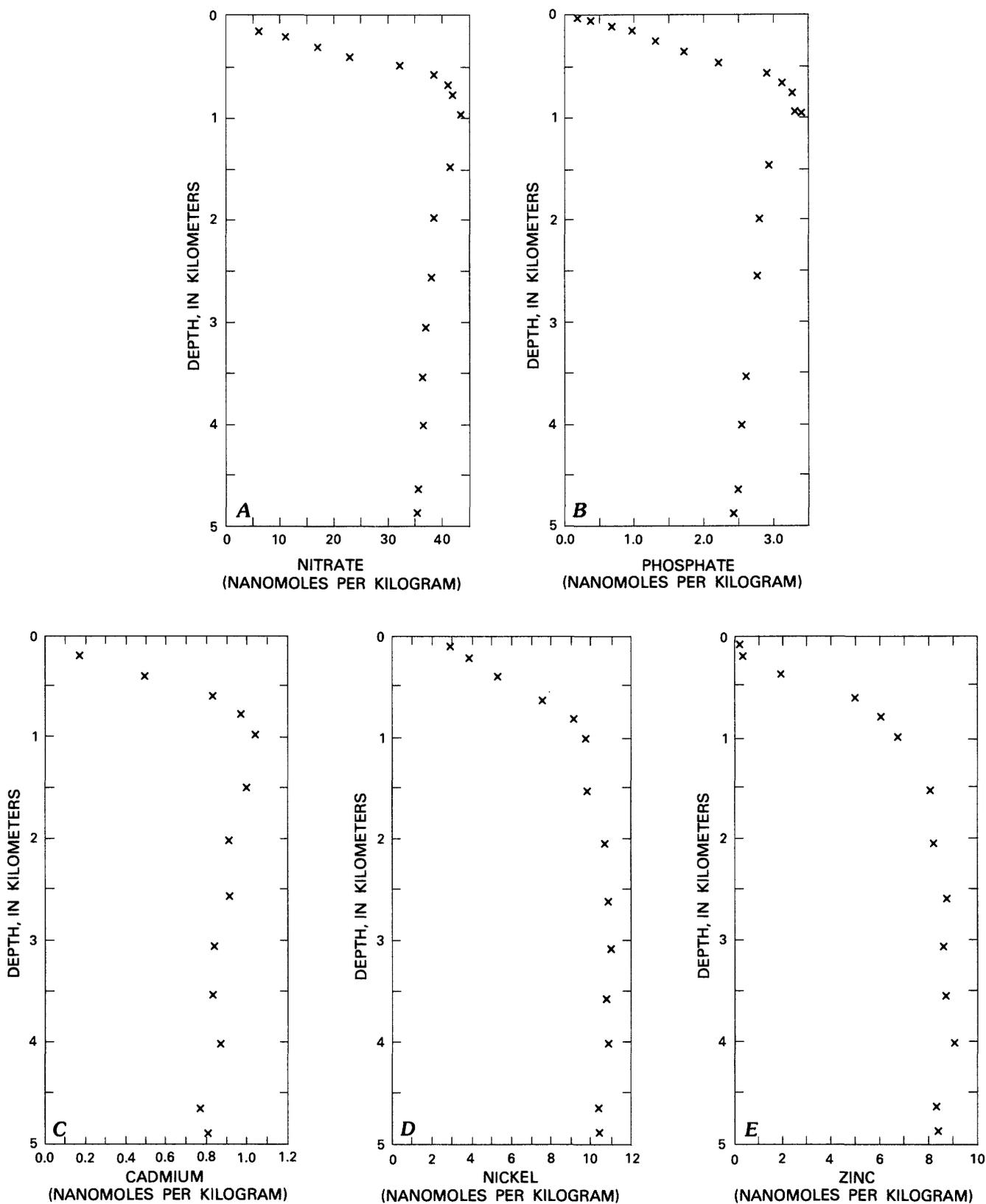


FIGURE 4.—Variation of (A) nitrate, (B) phosphate, (C) Cd, (D) Ni, and (E) Zn in seawater with depth in the North Pacific Ocean at 32°41.0' N., 144°59.5' W. (drawn from Bruland, 1980).

All things considered, the rough correlation between metal content and amount of organic carbon noted by other authors (for example, Maughan, 1976, 1980, 1984; Desborough, 1977) for metalliferous black shales does not seem to indicate that a biologic process is directly responsible for the deposition of the metals but rather shows the importance of organic matter in progressively concentrating the metals. Organisms withdraw small quantities of them, perhaps using them as nutrients, and these metals are then carried in dead tissue to the bottom, where they may be dissolved to add to their concentrations in bottom or interstitial water. Decaying organic matter creates the reducing conditions necessary for the fixation of vanadium and other metals and forms a site favorable for the fixation of some. As time passes, vanadium may move from organic matter to illite or other minerals (George Breit, written communication, 1986). The importance of an anoxic environment to the precipitation of the metals is worth stressing, since one thing that they all have in common is that their precipitation is favored by reducing conditions.

In summary, it seems reasonable to assume that the concatenation of such processes, combined with the slow accumulation of sediment, may account for the occurrence of vanadium and several other metals in the Meade Peak Member and in some other black shales. But the extraordinary concentrations of vanadium in the richest part of the vanadiferous zone (an order of magnitude higher than the ordinary black shale highs) seem to require conditions or processes not yet identified. The increase and subsequent decrease in the vanadium content from the base to the top of the zone over an area of several hundreds of square miles in western Wyoming (see, for example, pl. 2) imply a gradual buildup and then decline in one or more favorable environmental conditions, which cannot be defined with certainty. One possibility is that the principal variable was sediment accumulation rate, which increased and then decreased the time available for the resolution of vanadium from decaying organic tissue and for its withdrawal from circulating seawater. That variable alone, of course, would not account for the variation in the distribution of high concentrations of other metals within the vanadiferous zone.

Although the specifics of the environment in which the high concentrations of vanadium and other metals were deposited cannot yet be identified, the factors controlling the deposition of vanadium are independent of those controlling the deposition of phosphate, uranium, and carbonate, which increase westward from Wyoming to southeastern Idaho without appreciable change in the vanadium content of the zone. Such

an increase would be expected if the redox potential (Eh) were the controlling factor in the deposition of vanadium and if hydrogen ion concentration (pH), temperature, and CO₂ content controlled the precipitation of apatite (which hosts the uranium) or carbonate, for those factors do not necessarily vary in concert. Although the deposition of V, P, U, and carbonate may take place simultaneously, the maximum concentration of vanadium and most other metals is favored by a pH and temperature low enough to prevent or retard accumulation of diluting phosphate or carbonate. Apatite, for example, is unstable below a pH of about 7.0, and carbonate is unstable below a pH of about 7.5 (Gulbrandsen, 1969; Bendor, 1980). Apatite in modern sediments precipitates where the dissolved oxygen in bottom waters is lowest, probably owing to increased preservation of organic phosphorus rather than to an Eh control over the precipitation of apatite (Burnett and others, 1980).

Although other metals have been treated here as a group along with vanadium, their distribution within the zone does not conform exactly to that of vanadium, nor does it in other black shales. For example, in a group of 18 samples of black shales from the Pennsylvanian Mecca Quarry and Logan Quarry of Illinois and Indiana, analyzed by Coveney and Martin (1983), only the high value of zinc (14,300 ppm) and total organic matter (46.5 percent) corresponded with the high vanadium value (10,100 ppm). High U (240 ppm) and Mo (1,600 ppm) values were in another sample, and high values of Pb, Se, Cu, and Ni (500, 400, 500, and 1,300 ppm, respectively) were each in other samples. According to Disnar (1981), the capacity for organic matter to fix U, Cu, Pb, Zn, and Ni increases with increasing pH, but, for Mo and V, it increases with decreasing pH; both groups of metals might be fixed coevally in the intermediate pH range. The divergence in the metal concentrations expected from these relations is not seen in either the Meade Peak or the Mecca-Logan samples, but it seems likely that the differences in the distribution of the metals do reflect differences in their behavior under varying Eh, pH, temperature, and perhaps other chemical conditions.

The exceptionally high concentrations of vanadium and other metals throughout the Meade Peak Member also deserve explanation. Perhaps these concentrations are merely the result of a long continued strong upwelling environment. An enriching factor, however, might have been volcanic ash, the presence of which is shown by the occurrence of buddingtonite (the ammonium feldspar) in most of the Meade Peak mudstones. According to Gulbrandsen (1974, p. 697), its "...distribution and concentrations...seem to show that great airfalls did not occur, but that small falls were

frequent for a long period of time...." Buddingtonite is formed by the alteration of volcanic glass in an ammonia-rich environment, probably beneath the sediment-seawater interface. Its alteration conceivably might have released metals, which added to the amounts derived from seawater. Premovic and others (1986) favored volcanic ash as the source of vanadium in the Serpiano and La Luna rocks.

CONCLUSIONS

The vanadiferous zone of the Meade Peak Member in the Sublette Ridge area of Wyoming and the Paris-Bloomington area of Idaho contains about 5.9 million tons of indicated subeconomic resources averaging about 0.9 percent V_2O_5 . Indicated resources in the Afton area of Wyoming area above drainage level total about 35 million tons of the same quality (Love, 1961). Inferred resources in western Wyoming and southeastern Idaho of about the same tenor are many times larger. The zone also contains Cd, Cr, Mo, Ni, Se, Ag, Th, Zn, and (in the Paris-Bloomington area) U in amounts many times their average crustal abundance.

Although the feasibility of mining these deposits has been shown by the Wyodak Coal and Manufacturing Co. and Earth Sciences, Inc., the feasibility of recovering vanadium commercially remains to be demonstrated. When the need for vanadium is reflected in increased prices, however, processes for its extraction will be explored again, under the justifiable expectation that economic production will be possible one day. The initial output probably will not be large—the production planned by Earth Sciences, Inc., would have supplied only 8.5 percent of national vanadium demand—but Meade Peak resources could eventually be a more important source of vanadium and several other metals.

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