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Metals in Devonian kerogenous marine strata at  
Gibellini and Bisoni properties in southern Fish  
Creek Range, Eureka County, Nevada

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## ABSTRACT

A kerogen-rich sequence of siliceous mudstone, siltstone, and chert as much as 60 m thick on ridge 7129 in the southern Fish Creek Range, referred to as Gibellini facies of the Woodruff Formation, has been evaluated on the surface and in drill holes principally for its potential resources of vanadium, zinc, selenium, molybdenum, and syncrude oil content. The strata are part of a strongly deformed allochthonous mass of eugeosynclinal Devonian marine rocks that overlies deformed allochthonous Mississippian siliceous rocks and relatively undeformed autochthonous Mississippian Antler flysch at this locality.

The vanadium in fresh black rocks obtained from drill holes and fresh exposures in trenches and roadcuts occurs chiefly in organic matter. Concentrations of vanadium oxide ( $V_2O_5$ ) in unoxidized samples range from 3,000 to 7,000 ppm. In oxidized and bleached rock that is prevalent at the surface, concentrations of vanadium oxide range from 6,000 to 8,000 ppm, suggesting a tendency toward enrichment due to surficial weathering and ground-water movement. Zinc occurs in sphalerite, and selenium occurs in organic matter; molybdenum appears to occur both in molybdenite and in organic matter. Concentrations of zinc in unoxidized rock range from 4,000 to 18,000 ppm, whereas in oxidized rock they range from 30 to 100 ppm, showing strong depletion due to weathering. Concentrations of selenium in unoxidized rock range from 30 to 200 ppm, whereas in oxidized rock they range from 200 to 400 ppm, indicating some enrichment upon weathering. Concentrations of molybdenum in unoxidized rock range from 70 to 960 ppm, whereas in

oxidized rock they range from 30 to 80 ppm, indicating strong depletion upon weathering. Most fresh black rock is low-grade oil shale, and yields as much as 12 gallons/short ton of syncrude oil.

Metaheuwettite is the principal vanadium mineral in the oxidized zone, but it also occurs sparsely as small nodules and fillings of microfractures in unweathered strata. In fresh rock, bluish-white opaline-like silica (chalcedonic quartz) fills microfractures, and is believed to have originated by diagenetic mobilization of opaline silica from radiolarian tests and sponge spicules.

As revealed by microscopic study, the Gibellini facies originally consisted of siliceous muds, slimes, and ooze high in organic constituents. The organic matter is amorphous flaky and stringy sapropel, and probably includes remains of bacteria, phytoplankton, zooplankton, and minor higher plants. Recognizable organic remnants include radiolarian tests, sponge spicules, conodonts, brachiopod shells, algae, and humic debris. Diagnostic radiolarians indicate a Late Devonian age for the Gibellini facies of the Woodruff Formation. Some pyrite is disseminated through the rock and may be primary (syngenetic) but significant pyrite and marcasite occur in chalcedonic quartz veinlets and appear to be diagenetic.

In fresh rock, black solid bitumen and liquid oil fill voids and microfractures. These early phase hydrocarbons probably were released during diagenesis from complex nonhydrocarbon molecular structures originating from living organisms, and formed without any major thermal degradation of the kerogen. Gas chromatographic analysis of the saturated hydrocarbon fraction indicates a very complex mixture

dominated by branched and cyclic compounds. Conodont and palynomorph color alteration, vitrinite reflectance, and other organic geochemical data suggest that the organic matter in the rock is thermally immature and has not been subjected to temperatures greater than 60°C since deposition in Devonian time. All of these characteristics are consistent with the interpretation of a relatively low temperature and a shallow-burial history for the Gibellini facies on ridge 7129.

## INTRODUCTION

Vanadium, zinc, selenium, and molybdenum occur in anomalously high concentrations in Devonian kerogenous marine strata at the Gibellini and Bisoni properties on ridge 7129 in the Cockalorum Wash 15-minute quadrangle, southern Fish Creek Range, Eureka County, Nevada (fig. 1). The ridge is located 0.5 km west of the Gibellini manganese mine and about 4 km northwest of Eightmile Well.

The area was extensively drilled by Noranda Exploration Inc., and subsequent detailed laboratory and field studies by the U.S. Geological Survey integrated laboratory, surface, and subsurface data. The metalliferous and kerogenous marine strata are considered to be a large low-grade metal and shale oil resource whose mineralogical and chemical characteristics were imprinted during deposition, diagenesis, and tectonism. Our evaluation of the economic potential of the deposit considers its size, grade, configuration, and the processes of extraction that will be required to recover valuable products.

Vanadium has been known in high concentrations in this Devonian sequence in the southern Fish Creek Range for many years; analyses of drill cuttings and fresh surface samples in U.S. Geological Survey and other laboratories have revealed, in addition, anomalously high concentrations of zinc and selenium (table 1), as well as molybdenum and other metals.



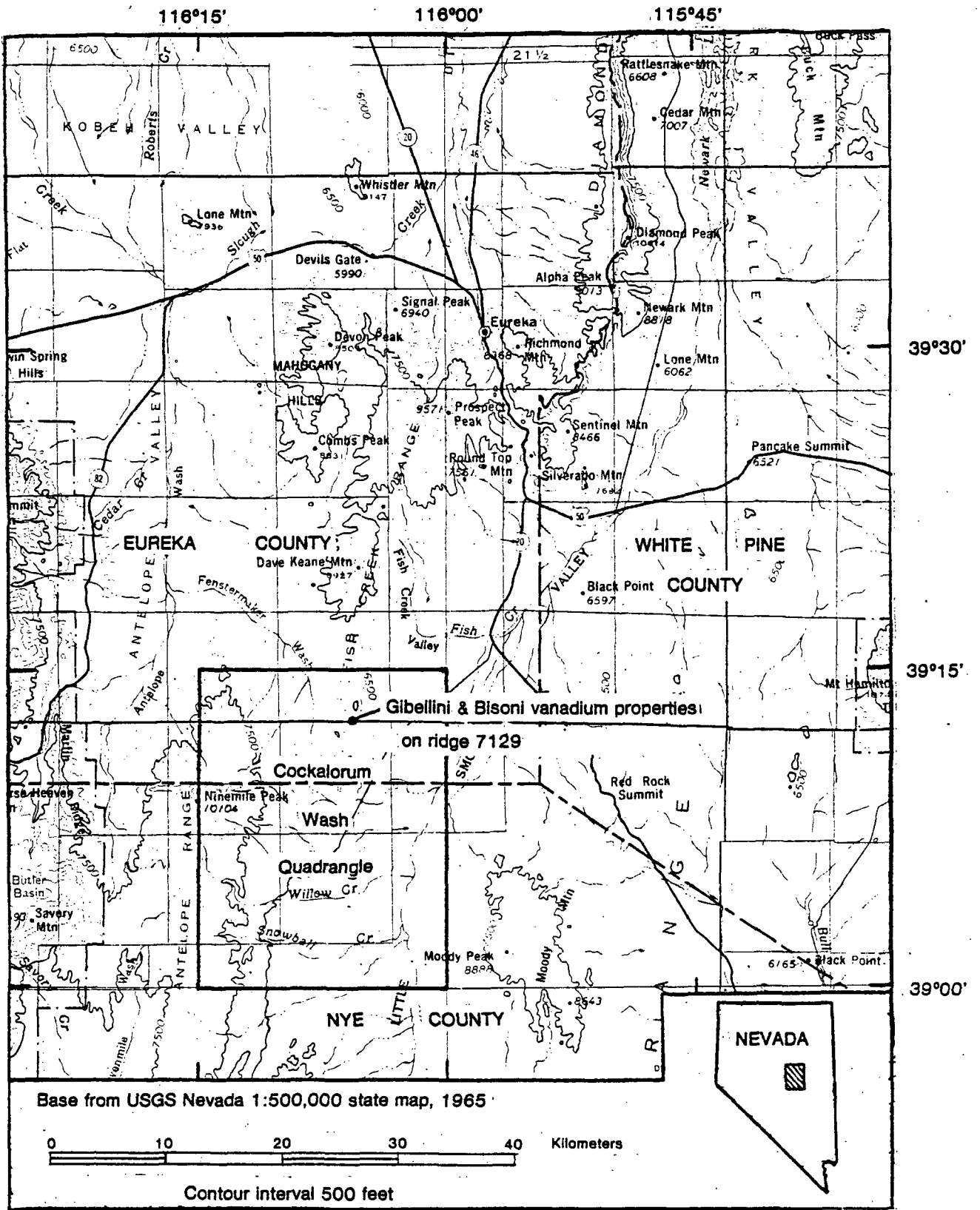


Figure 1.--Map of east-central Nevada showing Gibellini and Bisoni vanadium properties on ridge 7129 in the southern Fish Creek Range, Eureka County.

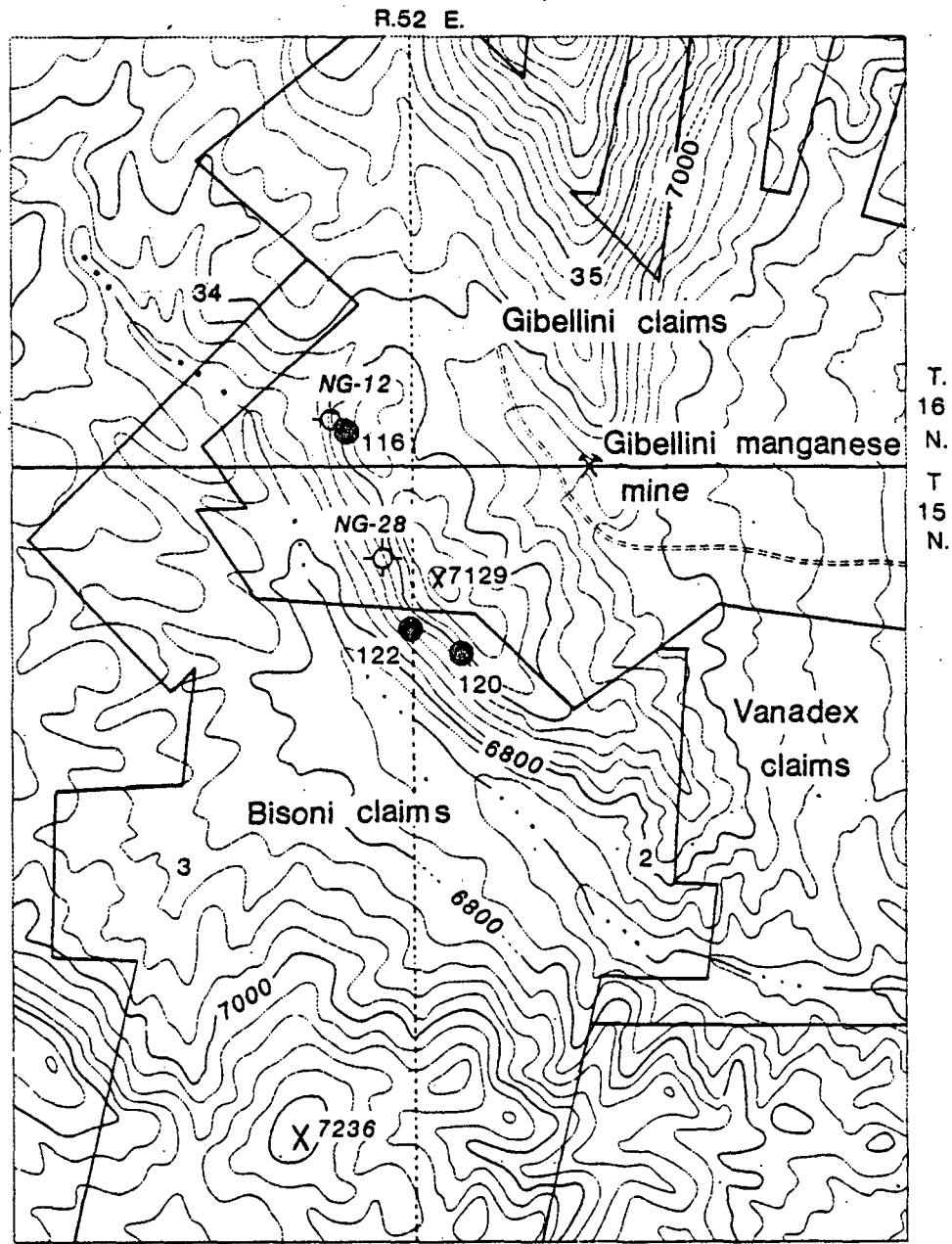
The metalliferous black mudstone occurs as a strongly deformed allochthonous rock mass that forms the upper part of a N. 35° W.-trending topographic ridge whose top is about 7,100 feet (2,164 m) in altitude. Maximum relief of the ridge is about 300 feet (91 m). Estimated dimensions of the metalliferous mudstone body, based on surface mapping and drill-hole information, are about 600 m long, 300 m wide, and at least 60 m thick. Maximum thickness of the mudstone is not known because the stratigraphic base has not been penetrated. Surface geologic relations indicate that locally the thickness may be as much as 100 m.

#### METHODS OF STUDY

The metalliferous black mudstone of the southern Fish Creek Range was studied both in the field and in the laboratory. Most samples were taken from drill cuttings and from fresh surface exposures. Extensive drilling and sampling by Noranda Exploration Inc. provided the subsurface samples and Dr. Geoffrey Snow of Noranda generously provided analytical data for vanadium. Splits of samples from two drill holes, NG-28 and NG-12 (figs. 2, 3, 4), have been quantitatively analyzed for oil, zinc, selenium, and molybdenum, and the bulk mineralogy of these samples has been determined by X-ray diffraction studies (table 1). Fischer oil-assay data for the same samples are given in table 2. Rock chips from subsurface samples have been polished and studied by reflected light microscopy and electron microprobe methods. Unoxidized or fresh samples on the surface were obtained from rocks exposed by blasting and bulldozing (locality 122, figs. 2, 3, 4). Incipiently oxidized samples on the surface were obtained from rock outcrops

(localities 116 and 120, figs. 2, 3, 4). These surface samples provided fragments large enough to evaluate gross texture and mineralogy, as well as material sufficient for organic geochemical, microprobe, X-ray diffraction, palynologic, micropaleontologic, vitrinite reflectance, fluorescence microscopic, pyrolysis, oil yield, and maturation studies.

Owing to the small-grain size and microfabric of the siliceous sapropelic mudstones, siltstones, and cherts, most megascopic methods of mineral and organic matter identifications are inadequate. The small-grain size also limits the use of standard petrographic thin sections in identifying mineral and organic matter. Most of the organic material is amorphous and cannot be identified even with high magnification.



Base from USGS Cockalorum Wash  
1:62,500 quadrangle, 1956.

Claim boundaries approximately located and drawn from  
information furnished by Noranda Exploration Inc.

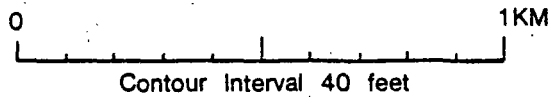


Figure 2.—Topographic map of ridge 7129 and vicinity showing location of samples and Gibellini and Bisoni vanadium properties.

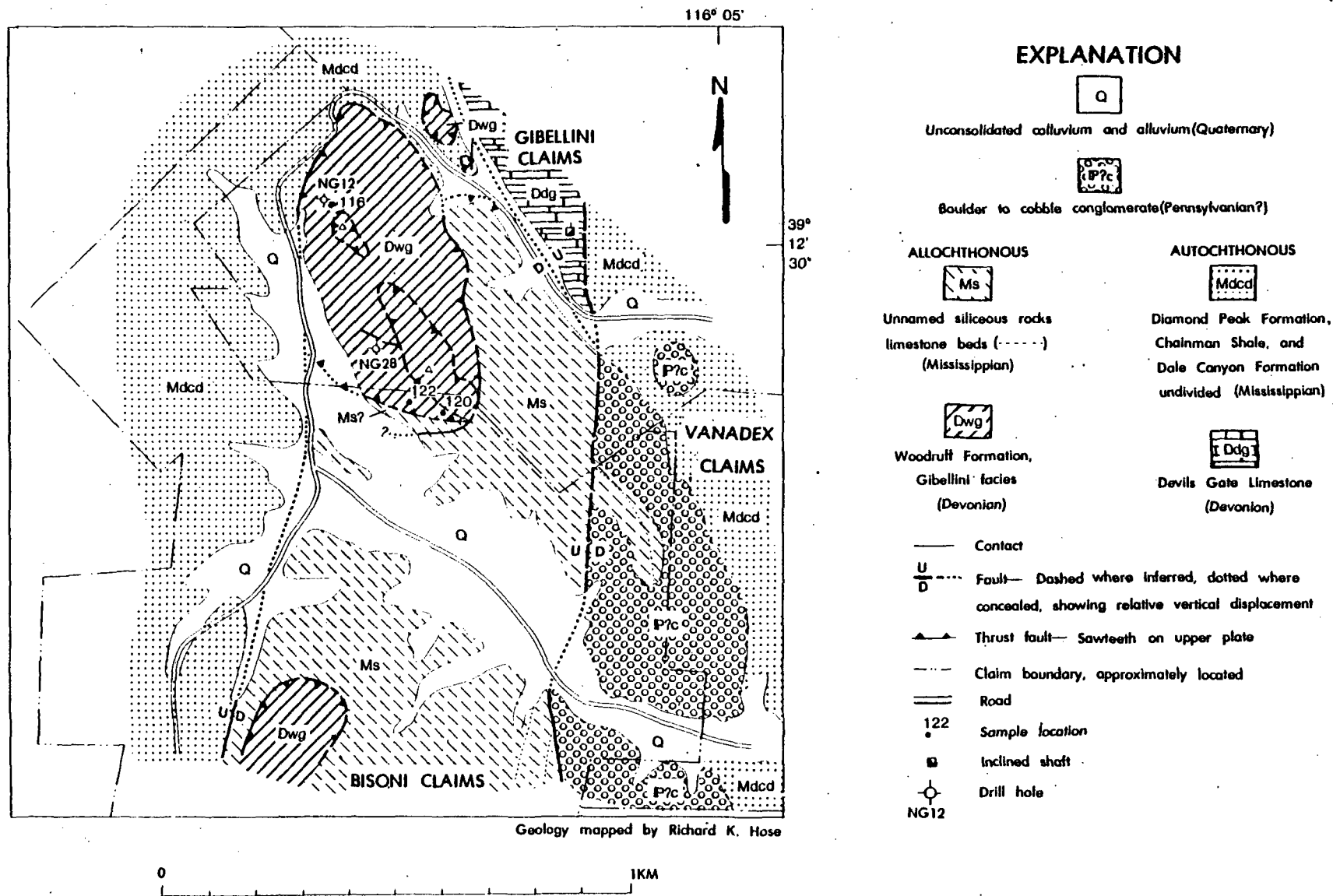


Figure 3. -- Preliminary geologic map of Gibellini and Bisoni properties and vicinity, southern Fish Creek Range, Eureka County, Nevada.

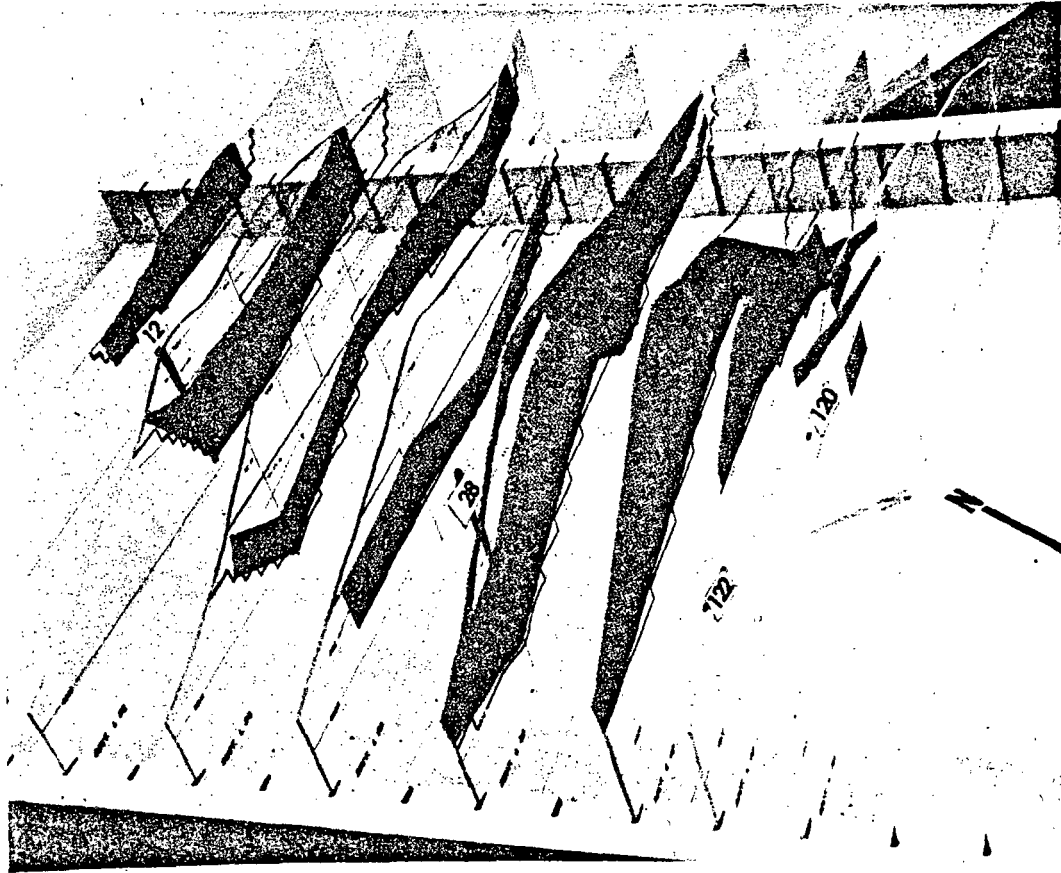


Figure 4.--Panel diagram of Gibellini and Bisoni vanadium and zinc deposit on ridge 7129 in the southern Fish Creek Range, Eureka County. Courtesy of Noranda Exploration Inc. Gray pattern represents rock containing vanadium-oxide values greater than 0.3 weight percent. Dark line near base of gray pattern is approximate lower limit of rock with 0.3 weight percent  $V_2O_5$ , and marks the floor of proposed open-pit mine.

## LITHOLOGIC CHARACTERISTICS AND ROCK PROPERTIES

The bedded siliceous sediments in the Gibellini facies of the Woodruff Formation on ridge 7129 consist largely of siliceous mudstone, siliceous siltstone, and banded chert. Unaltered strata are olive black, olive gray, brownish black, and brownish gray, whereas altered (weathered) strata are generally lighter shades of gray and brown and locally, where intensely oxidized, yellow and red owing to the presence of secondary vanadium, selenium, and iron minerals.

The bedded siliceous mudstones, siltstones, and cherts are irregularly laminated and color banded. Pyrite, marcasite, and sapropel are common constituents. Most fresh rock is fractured and veined with bluish-white chalcedonic quartz and sparse black solid bitumen. Some of the beds contain very thin layers of healed diagenetic breccia. Dark-colored laminae contain amorphous organic material. Sparse poorly preserved radiolarians and sponge spicules are the characteristic fossils in these siliceous rocks. The silica in these rocks occurs as flattened blebs and clots of chalcedonic quartz that interlock with one another to form a very hard rock. Grain boundaries commonly are coated with solid bitumen. The Gibellini facies contains no calcareous fossils and very little carbonate of any type except minor carbonate-fluorapatite (table 1). The siliceous mudstones and siltstones are transitional into cherts by increase of silica and decrease in clay and sapropelic material. Most chert beds have wavy layering and locally are nodular.

In addition to chalcedonic quartz, the major authigenic minerals in the siliceous sediments are sphalerite, apatite, authigenic potassium

Table 1.--Concentration of vanadium, zinc, selenium, molybdenum, and oil, and bulk mineralogy for composite samples from  
drill-holes NG-28 and NG-12, Gibellini vanadium property, Eureka County, Nevada

Depth interval (ft)	V <sub>2</sub> O <sub>5</sub> (wt.%)	Zn (wt.%)	Se (wt.%)	Mo (wt.%)	Oil (wt.%)	Minerals in addition to quartz (X-ray diffraction)
Drill-hole NG-28						
75-85	0.35	0.073	0.008	0.015	2.8	10A clay, K-feldspar, apatite, Fe-chlorite
85-95	.42	.390	.005	.015	3.0	sphalerite, K-feldspar, Fe-chlorite, 10A clay
95-105	.39	.740	.006	.013	3.6	sphalerite, K-feldspar, pyrite, apatite, Fe-chlorite, 10A clay
105-115	.43	.910	.006	.016	3.3	sphalerite, K-feldspar, pyrite, apatite, 10A clay, Fe-chlorite
115-125	.41	.530	.005	.018	3.2	sphalerite, K-feldspar, pyrite, apatite, 10A clay
125-135	.44	.450	.005	.015	3.1	sphalerite, K-feldspar, 10A clay, pyrite, apatite, Fe-chlorite
135-145	.33	.820	.004	.010	2.1	10A clay, sphalerite, K-feldspar, pyrite, apatite, calcite, Fe-chlorite
145-155	.40	.520	.003	.014	2.4	sphalerite, 10A clay, pyrite, K-feldspar, apatite, Fe-chlorite
155-165	.42	.790	.004	.016	2.8	sphalerite, apatite, pyrite, Fe-chlorite, 10A clay, calcite
165-175	.27	.390	.003	.007	1.3	10A clay, sphalerite, K-feldspar, Fe-chlorite, marcasite
Drill-hole NG-12						
100-110	0.75	0.004	0.024	0.003	<0.5	apatite, 10A clay
110-120	.69	.003	.042	.003	<.5	apatite, 10A clay, calcite(?)
120-130	.79	.004	.021	.008	<.5	10A clay
130-140	.58	.013	.037	.005	1.6	apatite, 10A clay, fluorite(?)
140-150	.66	.190	.032	.011	3.5	apatite, 10A clay, sphalerite, albite(?)
150-160	.60	.420	.018	.020	2.3	10A clay, Fe-chlorite, sphalerite, pyrite, calcite
160-170	.41	1.800	.006	.096	1.6	K-feldspar, sphalerite, 10A clay, pyrite, Fe-chlorite
170-180	.29	.900	.005	.023	3.1	apatite, sphalerite, 10A clay, Fe-chlorite, pyrite
180-190	.38	1.410	.006	.053	2.4	sphalerite, 10A clay, Fe-chlorite, pyrite, K-feldspar, apatite
190-200	.34	.890	.006	.023	2.5	sphalerite, pyrite, K-feldspar, 10A clay, Fe-chlorite, apatite



feldspar, 10A clay (illite), pyrite, and iron-chlorite (table 1). Marcasite and molybdenite are also present but, where in small amounts, were not detected by the X-ray diffraction method. With the exception of illite, argillaceous impurities are sparse in the Gibellini facies.

#### Organic constituents and fossils

The dark color of the siliceous mudstone, siltstone, and chert results from black sapropelic organic material. In fresh rock the organic matter is dominantly very fine grained kerogen consisting of flaky and stringy organism fragments less than 15 microns in size preferentially oriented parallel to bedding. Most of the organic matter examined microscopically is translucent and yellowish brown. Most of the kerogen is amorphous, probably owing to microbial alteration during sedimentation, and only sparse organic remains can be recognized. Organic matter is generally abundant and comprises as much as 12 weight percent of the rock. Solid bitumen coats many silica clots as well as filling open spaces and microfractures. Liquid oil was seen on some fracture surfaces in freshly broken unoxidized rock.

Surface sample 122 (figs. 2, 3, 4) contains 11.5 weight percent organic carbon; 0.7 percent of the rock consists of chloroform extractable bitumen (7,300 ppm) and 10.8 percent consists of kerogen. Less than 10 percent of the total organic matter consists of vitrinite, liptinite (mostly sporinites), and inertinite. The vegetal components are generally less than 15 microns in size. The bitumen in sample 122 is 59 percent hydrocarbon with the balance nonhydrocarbon asphaltic material. The sample contains 1,690 ppm saturated hydrocarbons and 2,620 ppm aromatic hydrocarbons with a saturated-to-aromatic ratio of

0.65 and a hydrocarbon-to-organic carbon ratio (HC/C) of 3.8. The saturated-to-aromatic hydrocarbon ratio of 0.65 is consistent with the dominantly asphaltic content of the extract. Generally, HC/C values greater than 1 percent suggest either thermochemical conversion of solid organic matter to hydrocarbons, or the presence of nonindigenous hydrocarbons. According to G. E. Claypool (written commun., 1978), gas chromatographic analysis of the saturated hydrocarbon fraction indicates a very complex mixture dominated by branched and cyclic compounds, with the bulk of the material obtained by solvent elution in the range of n-C<sub>15</sub> to n-C<sub>25</sub>. The bulk rock yielded 12.4 gallons/short ton (51.7 liters/metric ton) of syncrude oil by Fischer assay. Total sulfur in sample 122 is 2.2 weight percent. Bar-type conodonts in the sample are pale yellow in color (CAI=1) which suggests less than 60 percent fixed carbon and a maximum rock temperature of less than 60°C since deposition. The vitrinite reflectance mean value of 0.43 (n=23) for sample 122 is compatible with the conodont and palynomorph color alteration and other organic geochemical data, and indicates that the organic matter in the rock is immature and has not reached the postdiagenetic stage of catagenesis. Claypool noted that highly pigmented (red) components of the hydrocarbon extract from sample 122 were retained on a silica-gel column during elution with n-heptane, but were partially removed during benzene elution. The red material is probably a vanadium and/or a selenium organic complex.

A composite sample of cuttings from drill-hole NG-12 (figs. 2, 3, 4) taken 117 to 190 feet (35 to 58 m) below the surface averages 7.9 weight percent organic carbon and 1.5 weight percent sulfur. The

composite sample contains 5,000 to 5,600 ppm extractable hydrocarbons (saturated and aromatic phases). The oil content for composite samples of 10-foot (3-m) intervals from drill-holes NG-28 and NG-12 is listed in table 2, and from these data, the rock is estimated to yield as much as 8 gallons/short ton (33 liters/metric ton) of syncrude oil. The organic matter seen microscopically in cuttings is very fine grained, averaging 2-6 microns in maximum dimensions. The organic material occurs principally as pervasively disseminated amorphous debris that is intimately admixed with the minor minerals listed in table 1. Unoxidized mudstone yields 1.6-3.6 weight percent (about 4-9 gallons/short ton or about 17-37 liters/metric ton) of oil by Fischer-assay analysis as shown in tables 1 and 2. The relatively high content of water obtained during Fischer-assay pyrolysis (table 2) is from both dehydration of "opaline" silica and kerogen. Silica dehydration is verified by electron microprobe studies during which the electron beam leaves a decomposition hole in the  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  phase, which does not happen with quartz. This phenomenon is the reason for using the term silica, although the X-ray diffraction pattern is that of quartz.

Surface sample 120 (figs. 2, 3, 4) is oxidized and the organic material largely has been removed. The sample is olive-gray chert or silicified mudstone that weathers yellowish to pinkish gray and light brownish gray. The rock contains both marcasite and pyrite, and is strongly fractured with most of the fractures healed with silica. In reflected light examination under crossed nicols, round to subhedral grains of marcasite and pyrite can be seen that range in size from about 50 to 500 microns. Also unoriented bluish-white veinlets of opaline-

Table 2.--Fischer oil-assay data for composite samples from drill-  
holes NG-28 and NG-12, Gibellini vanadium property,

Eureka County, Nevada

[Analyst: John D. Mensik, Organic Fuels Laboratory, Geolabs, Inc.]

Depth interval (ft)	Oil (wt.%)	Oil (gal/ton**)	H <sub>2</sub> O (gal/ton**)	Specific gravity	Spent (wt.%)	Gas + Loss (wt.%)
Drill-hole NG-28						
75-85	2.76	6.99	7.1	0.948	92.4	1.86
85-95	3.03	7.65	6.3	.949	92.6	1.78
95-105	3.62	9.16	4.5	.949	92.7	1.79
105-115	3.29	8.28	6.1	.951	92.0	2.15
115-125	3.18	8.02	4.7	.951	93.3	1.58
125-135	3.06	7.70	4.5	.953	93.6	1.48
135-145	2.13	5.39	5.9	.949	93.7	1.65
145-155	2.41	6.08	5.1	.950	93.4	2.09
155-165	2.78	7.05	5.1	.946	93.6	1.49
165-175	1.34	3.49	6.1	*	95.1	1.02
Drill-hole NG-12						
100-110	<.5	<.5	4.3	*	98.0	0.25
110-120	<.5	<.5	5.4	*	97.5	.22
120-130	<.5	<.5	7.2	*	96.1	.89
130-140	1.55	4.03	7.2	*	93.8	1.66
140-150	3.54	8.84	5.4	.959	92.8	1.47
150-160	2.32	5.84	5.6	.954	94.2	1.13
160-170	1.60	4.17	5.9	*	94.6	1.32
170-180	3.13	7.81	2.9	.960	93.9	1.77
180-190	2.36	5.99	3.9	.945	93.8	2.19
190-200	2.46	6.25	3.7	.945	94.2	1.84

\* Assumed specific gravity 0.920

\*\* Gallons-per-short ton = 4.17 liters-per-metric ton

like silica (chalcedonic quartz) transect the rock. Red and yellow grains of metaheawettite as large as 50 microns are scattered through the chert. Metaheawettite also occurs in a veinlet 25 microns wide.

Recognizable organic remnants in fresh samples include radiolarian tests, sponge spicules, conodonts, brachiopod shells, algae, and humic debris. Radiolarian tests and sponge spicules are locally abundant in the siliceous rocks. Sparse bar-type conodonts, phosphatic linguloid brachiopods, algal spores, and small pieces of plant material were seen in some specimens. The radiolarian capsules are largely recrystallized into clear spherical bodies of cryptocrystalline silica, and most sponge spicules are obscure and appear to have been partially or marginally resorbed. Some beds, however, contain well-preserved radiolarians and sponge spicules; an example is silicified siltstone surface sample

77FP-116F collected near drill-hole NG-12 (figs. 2, 3). The sample yielded radiolarians of Late Devonian age according to D. L. Jones (oral commun., 1978). Another sample (GIB) collected from a chert bed near sample locality 122 (figs. 2, 3) also yielded radiolarians of Late Devonian age according to Brian Holdsworth of the Univ. of Keele, England (oral commun., 1978). The marine algal spore *Tasmanites* sp. was identified by J. M. Schopf (written commun., 1960) in a sample collected by C. W. Merriam from the southwest side of ridge 7129. The middle Paleozoic range of *Tasmanites* is compatible with the radiolarian age determinations.

Distribution and concentration of vanadium, zinc,  
selenium, and molybdenum

The gray pattern shown in the panel diagram (fig. 4) represents rock containing concentrations of vanadium oxide greater than 0.3 weight percent. The vanadiferous rocks extend southward into the two panels that contain samples 120 and 122. This area is outside the Gibellini property, and was not evaluated by Noranda Exploration Inc.

The vanadium in fresh black rocks occurs chiefly in organic material; we interpret the vanadium and associated metals to be syngenetic. Concentrations of vanadium oxide ( $V_2O_5$ ) in unoxidized rock range from 3,000 to 7,000 ppm (table 1). In oxidized and bleached rock, concentrations of vanadium oxide range from 6,000 to 8,000 ppm, suggesting a tendency toward enrichment due to surficial weathering and ground-water movement. Zinc occurs in sphalerite, and selenium occurs in organic matter; molybdenum appears to occur both in molybdenite and in organic matter. Concentrations of zinc in unoxidized rock range from 4,000 to 18,000 ppm (table 1), whereas in oxidized rock they range from 30 to 100 ppm, showing strong depletion due to weathering. Concentrations of selenium in unoxidized rock range from 30 to 200 ppm (table 1), whereas in the oxidized rock it ranges from 200 to 400 ppm, indicating some enrichment upon weathering. Concentrations of molybdenum in unoxidized rock range from 70 to 960 ppm (table 1), whereas in oxidized rock they range from 30 to 80 ppm, indicating strong depletion upon weathering. Unoxidized surface sample 122 contains 2,200 ppm zinc, 68 ppm selenium, and 430 ppm molybdenum.

Fresh rocks in excavations oxidize rapidly as a result of surficial weathering, and a pink-tinted coating of metaheuwettite forms at the surface and usually persists for several years. Rocks which have been exposed for longer periods lose this coating as the vanadium is dissolved and carried away. Zinc occurs in fine-grained sphalerite which is abundant in the unoxidized rock, but zinc has been dissolved and removed from the oxidized zone. Selenium occurs in the organic matter in the unoxidized rock, and is enriched in the oxidized zone. Molybdenum occurs in fine-grained molybdenite and possibly in organic matter in the unoxidized rock, but is depleted in the oxidized zone.

Sparse microcrystalline red metaheuwettite in microfractures in subsurface samples and in nodules of fresh surface samples of the unoxidized zone has been identified by X-ray diffraction methods. Electron microprobe analysis for all elements heavier than oxygen revealed that calcium and vanadium were the only major constituents in the metaheuwettite.

Microscopic, electron microprobe, and X-ray diffraction studies of unoxidized drill cuttings and of the unoxidized samples obtained from excavations show that vanadium minerals are sparse. Most of the vanadium in unoxidized mudstone occurs in the organic matter, according to electron microprobe studies using both wavelength and energy dispersive spectrometers simultaneously. The  $VK_{\beta}$  peak was used for both qualitative and quantitative electron microprobe analyses because of the serious interference of the  $TiK_{\beta}$  and  $VK_{\alpha}$  peaks.

Concentration of vanadium in kerogen is in the range of about 0.3-3.0 weight percent. The exact amount cannot be determined by electron

microprobe analysis because even under lowest-intensity-beam conditions, the kerogen volatilizes immediately. Vanadium and sulfur are the chief components (heavier than oxygen) in the kerogen. Thus, virtually all of the vanadium in the unoxidized mudstone is dispersed in kerogen at relatively low concentrations.

Zinc occurs in widely dispersed grains of sphalerite that are generally less than about 40 microns in size. Microprobe analysis shows that all sphalerite grains contain less than 0.1 weight percent of manganese and iron, but that cadmium is present locally. Cadmium constitutes as much as 6.0 weight percent of some grains, but generally constitutes 0.2 weight percent or less of the sphalerite. Pyrite and marcasite are also present as small, widely dispersed grains in the unoxidized mudstone; these grains are distributed completely independently of the sphalerite grains. Although volumetrically insignificant, the pyrite and marcasite are conspicuous microscopically owing to their high reflectance in comparison with other minerals in the rock.

Concentrations of selenium in kerogen are probably greater than 0.04 weight percent, but accurate determinations cannot be made because of decomposition of kerogen in the microprobe beam. The selenium dispersed in kerogen is concentrated during oxidation, and is enriched in the weathered zone where concentrations range from 0.02 to 0.04 weight percent (table 1).

Molybdenum occurs in widely dispersed grains of molybdenite less than 5 microns in size. It appears that most of the molybdenite grains may have been plucked from the polished sections during preparation.



Molybdenum probably constitutes more than 0.01 weight percent of the kerogen, but like selenium, accurate determination cannot be made owing to decomposition of kerogen in the microprobe beam.

## INTERPRETATION

### Potential resources

Many Paleozoic dark-colored marine mudstones and siltstones contain significant syngenetic metal concentrations as well as sufficient syncrude oil to qualify as low-grade oil shales. In addition, they commonly host epigenetic metal deposits, and serve as significant source rocks for petroleum. As they commonly form thick and laterally persistent rock masses, they potentially could serve as vast low-grade metal resources. Additionally, they are either low-grade oil shales or have already generated and expelled petroleum that has migrated elsewhere. For these reasons, it is important to identify the mineralogical, chemical, depositional, diagenetic, and tectonic factors which collectively govern the size, grade, and distribution of the deposits, and which will influence the choice of extractive process(es) necessary to exploit these resources.

The economic potential of marine "black shales" in the Western United States is very difficult to evaluate for a number of reasons:

- (1) The strata commonly are in allochthonous blocks above regional thrust faults, and generally are intensely deformed and broken. Both vertical and lateral continuity are virtually unpredictable without subsurface data, and reliable resource projections are generally limited to very small areas. Tectonic fracturing promotes accelerated weathering and erosion so that the shales are generally poorly exposed;

in addition, the broken rocks are extensively leached by ground water and tend to be severely altered to substantial depths.

(2) The rocks are generally fine to very fine grained, and megascopic field methods generally are ineffective in mineral or chemical identification. Even petrographic examination of standard thin sections is of limited value.

(3) The sapropelic organic matter in these sediments is widely dispersed, and appears virtually opaque in standard thin sections.

(4) The residence of elements is so extensively dispersed that chemical and mineralogical studies must be conducted on a micro-scale.

#### Depositional setting and tectonics

Siliceous marine sediments that contain abundant sapropel dominate the Gibellini facies of the Woodruff Formation. These deposits originally consisted of siliceous muds, slimes, and oozes with a high organic content derived from microscopic phytoplanktonic organisms. Radiolarians and sponge spicules are common to abundant in many beds, but conodonts, linguloid brachiopods, and plant spores are sparse. Radiolarian tests and sponge spicules show little or no compaction and the peripheries of the fossils are sharply defined in some beds. In many beds, however, outlines of the siliceous fossils tend to be blurred and obscure, indicating in part marginal resorption and in part masking by kerogen or bitumen. During diagenesis, silica probably dissolved, reached saturation, and reprecipitated; at the same time, authigenic sulfide minerals of iron, zinc, molybdenum, and other metals formed. Pyrite and marcasite occur both in the matrix and in opaline-like silica veinlets which indicates that their principal time of formation was

during diagenesis.

Within the siliceous sediments, abundant amorphous flaky and stringy organic matter is present, and probably includes remains of bacteria, phytoplankton (algae), zooplankton, and minor higher plants. The organic matter (kerogen and bitumen) includes, and is the source of, additional hydrocarbons produced by heating. The early phase hydrocarbons (liquid oil and solid bitumen) present in the rock probably formed without any major thermal degradation of the kerogen. They were probably released during diagenesis from complex nonhydrocarbon molecular structures originating from living organisms.

These kerogen-rich sediments were deposited in an area receiving organic debris from large volumes of near-surface marine waters that contained abundant phytoplankton. Fine-grained mineral particles of terrigenous origin were sparse, and organic sediments were not effectively diluted by hemipelagic sediments. Abundant kerogen of marine origin indicates anoxic bottom conditions.

The Gibellini facies of the Woodruff Formation appears to have been deposited in a continental-rise setting on the east side of a Devonian inner-arc basin (Poole and others, 1977) that periodically was anoxic which allowed deposition and preservation of organic-rich sapropelic sediments. Anoxic bottom water (that is, minimal mixing with near-surface water) probably accounts for the preservation of the organic matter. Water depth was well below wave-base influence, and may have exceeded 100 m. Although most of the organic matter is kerogen of marine origin, traces of vegetal macerals derived from land plants have been recognized.

The characteristics of the kerogen indicate that a relatively low temperature regime has persisted since deposition of the original predominantly marine aquatic plant material. A low-temperature shallow-burial history prevented catagenesis and generation of significant amounts of petroleum.

The Devonian Gibellini facies on ridge 7129 is strongly folded, fractured, and imbricated, and is part of an allochthonous block that has been emplaced over deformed allochthonous Mississippian siliceous rocks (unnamed formation) and relatively undeformed autochthonous Mississippian flysch (Diamond Peak Formation, Chainman Shale, and Dale Canyon Formation undivided). Structural relations are shown on figure 3. Although the Gibellini facies was probably part of the Roberts Mountains allochthon emplaced in latest Devonian and earliest Mississippian time (Poole and Sandberg, 1977), it now rests on rocks as young as Late Mississippian. During thrusting, the Gibellini facies apparently was located near the leading edge of the Roberts Mountains allochthon, and sometime after emplacement, it was detached from the allochthon and slid eastward across upper Paleozoic strata. This event probably occurred during Mesozoic time.

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#### REFERENCES CITED

- Poole, F. G., Sandberg, C. A., and Boucot, A. J., 1977, Silurian and Devonian paleogeography of the Western United States, *in* Stewart, J. H., Stevens, C. H., and Fritsche, A. E., eds., Paleozoic Paleogeography of the Western United States: Society of Economic Paleontologists and Mineralogists, Pacific Sec., Pacific Coast Paleogeography Symposium 1, p. 39-65.
- Poole, F. G., and Sandberg, C. A., 1977, Mississippian paleogeography and tectonics of the Western United States, *in* Stewart, J. H., Stevens, C. H., and Fritsche, A. E., eds., Paleozoic Paleogeography of the Western United States: Society of Economic Paleontologists and Mineralogists, Pacific Sec., Pacific Coast Paleogeography Symposium 1, p. 67-85.

## APPENDIX

### Factors affecting extraction of vanadium and associated metals

#### Extraction of vanadium

Attempts to apply the conventional vanadium extraction method of salt roasting to unoxidized samples from the southern Fish Creek Range low-grade vanadium deposit have been relatively uneconomic.

Metaheuttite is amenable to vanadium recovery by salt roasting, but the proportion of metaheuttite in the unoxidized rock to organic-bound vanadium is very low.

Recovery of vanadium from the organic-rich rock by relatively inexpensive extraction methods requires that the rock be oxidized, possibly by explosive fracturing, and induced in situ combustion of kerogen. The combustion method might follow the general scheme of mining oil shale in situ for recovery of syncrude oil. Following combustion, leaching of fractured and oxidized rock with water should extract vanadium in the oxidized state. Zinc also should be mobilized if the water is acidic. The leach water should become slightly acidic immediately because of high concentration of sulfur relative to low concentration of carbonates. In sediments where carbonates are more abundant than sulfides, the carbonates would act as a buffer.

The method of in situ extraction just described would be environmentally compatible because the leach water would be recovered, processed for extraction of vanadium and other metals, and then recycled through fractured and oxidized rock.

Desirable requirements for this extractive process include:

- (1) Relatively homogeneous vanadium, zinc, selenium, molybdenum,

and kerogen distribution through a thick section of strata to allow consistent results.

(2) Brittle nature of the host to allow ready fracturing.

(3) Location of the deposit on a hill to allow easy recovery of leach fluid.

(4) Simple mineralogy of the bulk rock; presence of chalcedonic quartz which is relatively inert to combustion and leaching.

(5) Syncrude oil that is required for in situ combustion and that might be recovered incidentally during combustion and before water leaching.

(6) Four to seven gallons of auto-generated water/short ton (17-29 liters of water/metric ton), produced during combustion, to eliminate the need for ground water which is inadequate in this area.

A method of extraction with greater energy requirements might be used in which the rock is treated as described in a patent by Earth Sciences Inc. (U.S. Patent No. 4115110) titled "Vanadium Recovery Process" by Roman Z. Pyrih and Robert S. Rickard. This complex process involves oxidation at a temperature less than about 600°C to remove organic matter, then roasting in an oxygen atmosphere at about 800°C, followed by acid leaching to recover vanadium. Several other commodities, such as selenium, uranium, and molybdenum, are recoverable by this process.



## Extraction of zinc

George A. Desborough<sup>1</sup> and Ronald L. Keil<sup>2</sup>

Organic-rich rock samples were subjected to two types of heat treatment during preparation for analyses made in this study. The spent-shale residues from Fischer oil-assay analysis were slowly heated in an atmosphere of very low partial pressure of oxygen to 500°C and held at that temperature for 20 minutes to obtain oil. Splits from the spent-shale residues were then ashed in ambient atmosphere at 700°C for 1 hour.

Sets of samples of the spent-shale residues and of the ashed shales both were then treated by identical digestion methods and by identical analytical methods. All values were then converted to a raw-shale basis (that is, weight fraction of spent shale multiplied by the zinc concentration) and only these data are reported in table 3, along with the calculated relative percent of zinc lost. Loss of zinc ranges from 8 to 18 percent for samples which initially were naturally unoxidized. Samples which were originally oxidized show higher relative losses ranging from 15 to 50 percent, although the initial concentrations of zinc in these samples are much lower than they are in unoxidized samples. Organic-rich samples, which contain the highest concentrations of zinc, showed the highest absolute losses of zinc.

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<sup>1</sup> U.S. Geological Survey

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Table 3.--Loss of zinc by air-roasting treatment of samples. Concentrations,  
in weight percent, on a raw-shale basis. Percent of zinc loss referenced  
in Fischer-assayed spent-shale values

[Analyst: Ronald L. Keil, Geolabs]

Fischer-assayed spent shale wt.% Zn	Fischer-assayed spent shale, 700°C air roasted wt.% Zn	Percent of zinc lost
0.004	0.003	25
.003	.002	33
.004	.002	50
.013	.011	15
.190	.140	26
.420	.386	8
1.800	1.610	11
.900	.800	11
1.410	1.220	13
.890	.810	9
.073	.056	23
.390	.324	17
.740	.650	12
.910	.782	14
.530	.450	15
.450	.400	11
.820	.700	15
.520	.450	13
.790	.690	13
.390	.342	12

These data illustrate that sample preparation methods, such as high-temperature ashing, may volatilize certain elements. Optimistically, further research may show that volatilization of zinc in the presence of organic matter has potential for commercial recovery of zinc. It is conceivable that a metastable zinc metal-organic compound is formed by reaction of sphalerite (ZnS) with the organic material. Sphalerite alone is a relatively refractory mineral which transforms to wurtzite (ZnS) at temperatures about 1,000°C; wurtzite sublimates at 1,185°C.

Further studies are planned on zinc loss at higher temperatures to determine the feasibility of application to extraction methods.