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SPECTROSCOPIC GEOCHEMICAL STUDY OF  
VANADIFEROUS MARINE SEDIMENTS OF THE GIBELLINI CLAIMS,  
SOUTHERN FISH CREEK RANGE, EUREKA COUNTY, NEVADA

By

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ABSTRACT

Samples of cuttings from three drill holes in the Gibellini claims were analyzed by emission spectroscopic techniques for a large suite of major and trace elements. Unoxidized siliceous "black shale" from drill hole NG47 is strongly enriched in Cd, Mo, Sb, Se, V, and Zn, and also contains relatively high concentrations of As, Ba, Cu, Ni, and Tl compared with nonmetalliferous shales. Analyses of 103 samples plotted against depth in drill holes NG4, NG31, and NG47, and selected XRD data, show the following:

1. Groups of elements with distinct distribution patterns define most of the major mineralogic components of the rocks. The "normal shale" component, which includes several detrital and authigenic phases, is indicated by covariations among Ti, Al, Fe, Na, Mg, K, B, Be, Co, Cr, Ga, La, Sc, Sr, and Zr. The shale component is diluted by varying amounts of the following minerals (and associated elements): silica (Si); dolomite (Mg, Ca, Mn, Sr); apatite (Ca, Be, Cr, La, Sr, Y); barite (Ba, Sr); sphalerite (Zn, Cd, Fe?); smithsonite (Cd, Co, Mn, Ni, Zn); bianchite (Cd, Ni, Zn); and bokite (V). Pyrite, gypsum, and jarosite were also identified.

2. The highly siliceous kerogenous metalliferous Gibellini facies is underlain by argillaceous and (or) dolomitic rocks. The transition zone deduced from the chemical data is not well defined in all instances, but probably represents the bottom of the black shale deposit.

3. Oxidation has reached to variable depths up to at least 150 ft, and has caused profound changes in the distributions of the enriched metals. Molybdenum, Se, and V have been partially removed from the upper parts of the sections and are concentrated near or slightly above the base of the Gibellini facies. Cadmium, Ni, and Zn have been strongly leached and now occur at or below the base of the Gibellini facies.

The variable depth of oxidation, the redistribution and separation of the metals, and the complex mineralogy of the deposit may make development of the claim complicated.

## INTRODUCTION

Sedimentary rocks rich in organic matter in the western United States are increasingly interesting as potential sources of both petroleum and strategic metals. Rocks underlying the Gibellini claims in Eureka County, Nev., are currently being evaluated as a source of vanadium, which reaches concentrations on the order of 1 to 2 percent ( $V_2O_5$ ). These rocks contain as much as 10 percent organic carbon, and are also significantly enriched in Ag, As, Cd, Mo, Ni, Sb, Se, Tl, and Zn.

In this paper we report a detailed geochemical analysis of samples from three drill holes at the Gibellini claims in the Fish Creek Range, Eureka County, Nev. A large number of samples has been analyzed by a combination of photographic and automatic direct-reading semiquantitative spectroscopic techniques in order to follow variations of major- and trace-element contents with depth in the section. The main objectives in reporting these data are:

1. To record the range and variability in the concentrations of many elements in an organic-rich, V-rich sedimentary deposit, for comparison with other similar deposits.
2. To correlate the occurrences of the elements and speculate on the mineralogical controls of their distribution.
3. To determine the general geologic, stratigraphic, and alteration features in the chemical section.

The spectroscopic methods used in this investigation may not provide accurate assays of some of the important metals of the deposit; however, the significant features of element distribution with depth are readily determined from closely spaced, internally precise, semiquantitative data. Work is currently being done to quantify some of these results and to correlate the metal distribution patterns with carbon and sulfur data.

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## PREVIOUS WORK

The need for systematic study of the metal contents of sedimentary rocks was pointed out by Krauskopf (1955). Silver, Cr, Mo, Nb, Ni, Pb, V, and Zn are among the elements that Krauskopf suggested might be found in economic quantities in organic-rich (black) shales. Subsequent studies have proven that a number of elements are present in very high concentrations in black shales. Davidson and Lakin (1961, 1962) compiled semiquantitative analyses of several different Paleozoic black shales in the United States, and showed that

the Cr, Cu, Mo, Ni, V, and Zn contents of these shales are as high or higher than those indicated by Krauskopf (1955).

Tourtelot, Schultz, and Gill (1960) analyzed 69 samples of bentonite, shale, claystone, and marlstone from the Pierre Shale in the western United States. They found that shale and claystone samples rich in organic carbon (>1.0 percent) have the highest mean contents of As, Cu, Mo, Se, U, and V. Boron, Cr, and Zn also tend to be concentrated in organic-rich samples.

In a series of papers, Vine and coworkers showed that many of the major and trace elements in black shales could be assigned statistically to one or more of three main components of the rocks in which they occurred (Vine, 1966, 1969; Vine and others, 1969). The rock components are (1) detrital sediments, (2) chemical or biological precipitates, and (3) organic matter. A summary of statistical studies of 20 sample sets of black shales in the United States indicates that the elements are distributed roughly as follows: Ti, Al, Ga, Sc, and Zr (+, Fe, Mg, Na, K, B, Ba, Be) in the detrital fraction; Mg, Ca, Mn, and Sr in carbonates; Ag, Cr, Cu, Mo, Ni, V, and Zn (+ Co, La, Pb, Se, Tl, U, Y) with organic matter (Vine and Tourtelot, 1970).

Many of these associations differ from place to place or are statistically rather poorly defined. Vine and Tourtelot (1970) suggest that the metal-enrichment patterns in black shales are dependent on the availability of metals in the various solutions which interact with the shales during deposition, diagenesis, and later events. Late element remobilization and rock alteration (including oxidation) could well mask or change the distribution patterns established during earlier events. Effects such as these may be difficult to sort out using statistical correlations.

A few analyses have been published of black shale samples from the Fish Creek Range itself. Partial semiquantitative analyses of 26 samples are summarized by Davidson and Lakin (1961). Their ranges for 11 elements are roughly similar to those reported here, except that we have found higher concentrations of Ni, V, Mo, and Se in a number of samples. Of six black shale deposits in the western United States studied by Davidson and Lakin (1961), the Fish Creek Range materials seems to have a relatively low Ag content.

Desborough and others (1979) report V, Zn, Se, Mo, and oil analyses of 20 samples from two drill holes in the Gibellini claims. Vanadium and Se concentrations appear to be related, as are Zn and Mo, but the oil content does not follow closely with either of these pairs. The most significant variations in metal content occur with depth, and are presumably related to recent oxidation of the upper part of the section. Oxidized (bleached) samples from deep in the holes are relatively depleted in Zn and Mo, and enriched in V and Se. In unoxidized (black) samples these metals are distributed among syngenetic phases as follows: V and Se in organic matter (kerogen), Mo in both organic matter and molybdenite, and Zn in sphalerite (Desborough and others, 1979). It is the purpose of the present study to refine and extend these results using more complete sampling and analyzing for a larger suite of elements.

## GEOLOGIC SETTING

The general geology in the area of the Gibellini vanadium claims is described by Roberts, Montgomery, and Lehner (1967), Hose (1978), and Desborough and others (1979), and the pertinent regional stratigraphy is summarized in Poole and Sandberg (1977) and Poole, Sandberg, and Boucot (1977). The vanadium-rich rocks of the Gibellini claims were deposited offshore in a north-south-trending (back-arc?) basin. They were thrust eastward, perhaps as a reactivated part of the Roberts Mountains thrust system, and emplaced above rocks deposited nearer the eastern margin of the basin.

Earlier interpretations placed the kerogenous, metalliferous section in the Gibellini facies of the Devonian Woodruff Formation, which was thrust over allochthonous and parautochthonous Mississippian rocks (Hose, 1978; Desborough and others, 1979). Recent work suggests that the Gibellini facies may actually be a part of the underlying allochthonous Mississippian section, now called the Bisoni Formation (R. K. Hose, oral commun., 1980). The interpretation of ages and contact relations of rocks within the Gibellini claims is subject to change, owing to the extreme structural complexity of the area. A tentative geologic map of the area near the Gibellini claims, based on recent interpretations by R. K. Hose, is given in figure 1.

The drill holes sampled for this study are from a small north-south trending hill (Ridge 7129) in the southern Fish Creek Range which consists almost entirely of highly deformed kerogenous Gibellini facies rocks. Ridge 7129 appears in figure 1 as an isolated mass of Gibellini facies, overlying nonmetalliferous siliceous and calcareous facies of the Bisoni Formation, and in thrust contact with the parautochthonous Antelope Range Formation. Three vertical sections are drawn in figure 2 to illustrate relationships between the drill holes and surface geology. The Gibellini facies consists of siliceous mudstone, siltstone, and chert containing abundant amorphous sapropelic material when fresh. The rocks are strongly folded, fractured, and imbricated; however, kerogen analysis indicates a fairly low temperature, shallow-burial history since deposition (Desborough and others, 1979). G. A. Desborough (oral commun., 1979) believes that the entire section of Gibellini facies in Ridge 7129 was originally enriched in metals and organic matter, though much of it has since been oxidized.

## ANALYTICAL METHODS

A total of 103 samples from three drill holes in the Gibellini vanadium claims in the Fish Creek Range, Nev., were analyzed spectroscopically by a combination of photographic and automated direct-reading techniques. In addition, X-ray diffraction patterns were obtained from smear slides of several whole-rock samples which most nearly represent the chemical end members.

The samples consist of drill cuttings collected in 5 ft increments. Each sample therefore represents 5 ft of vertical section. The cuttings were subsampled, crushed in a steel mortar and ground by hand in an alumina mortar to approximately -200 mesh.

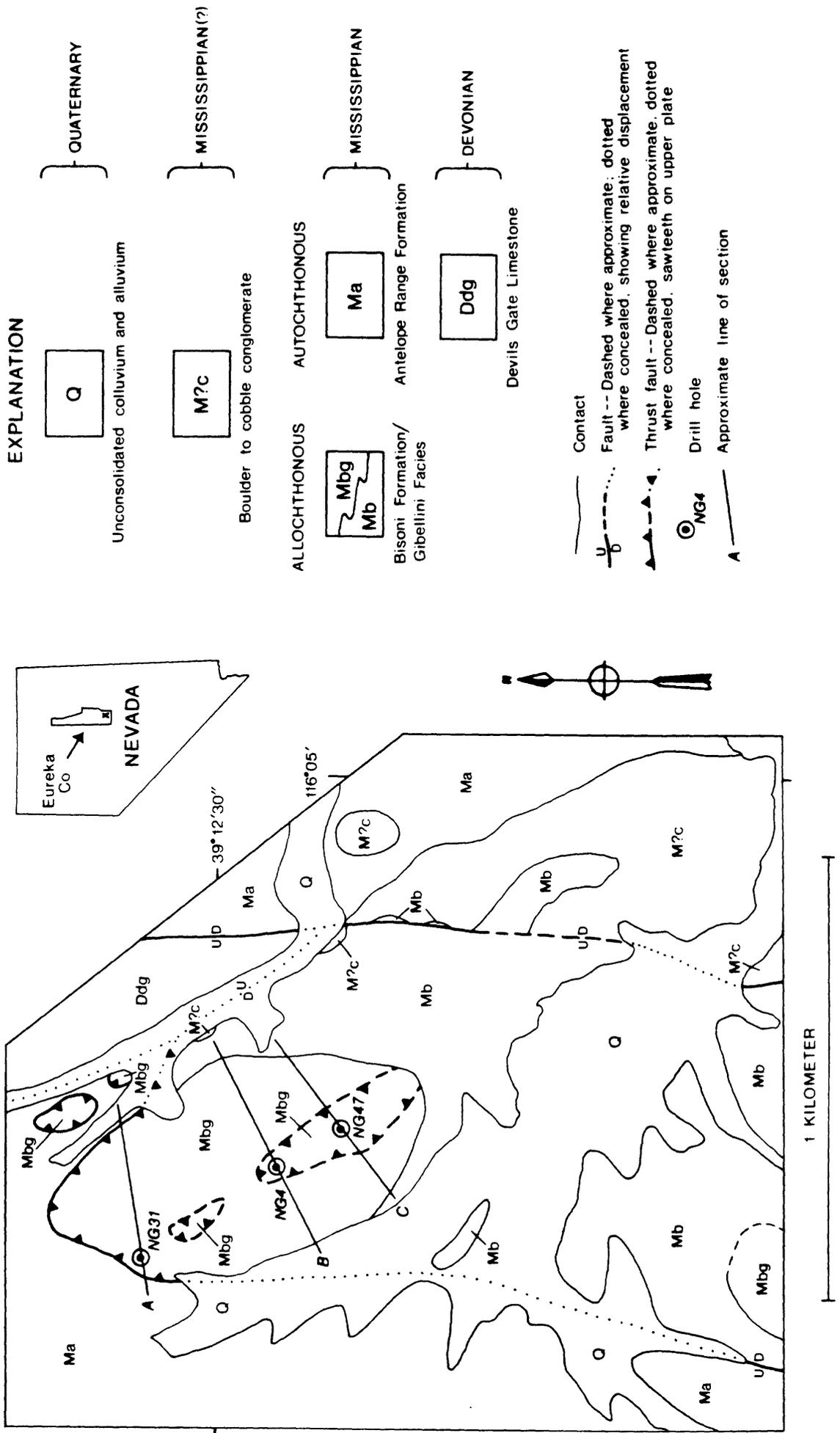


Figure 1. Geologic sketch map of the vicinity of the Gibellini vanadium claims and location of drillholes. (Geology by R.K. Hose)

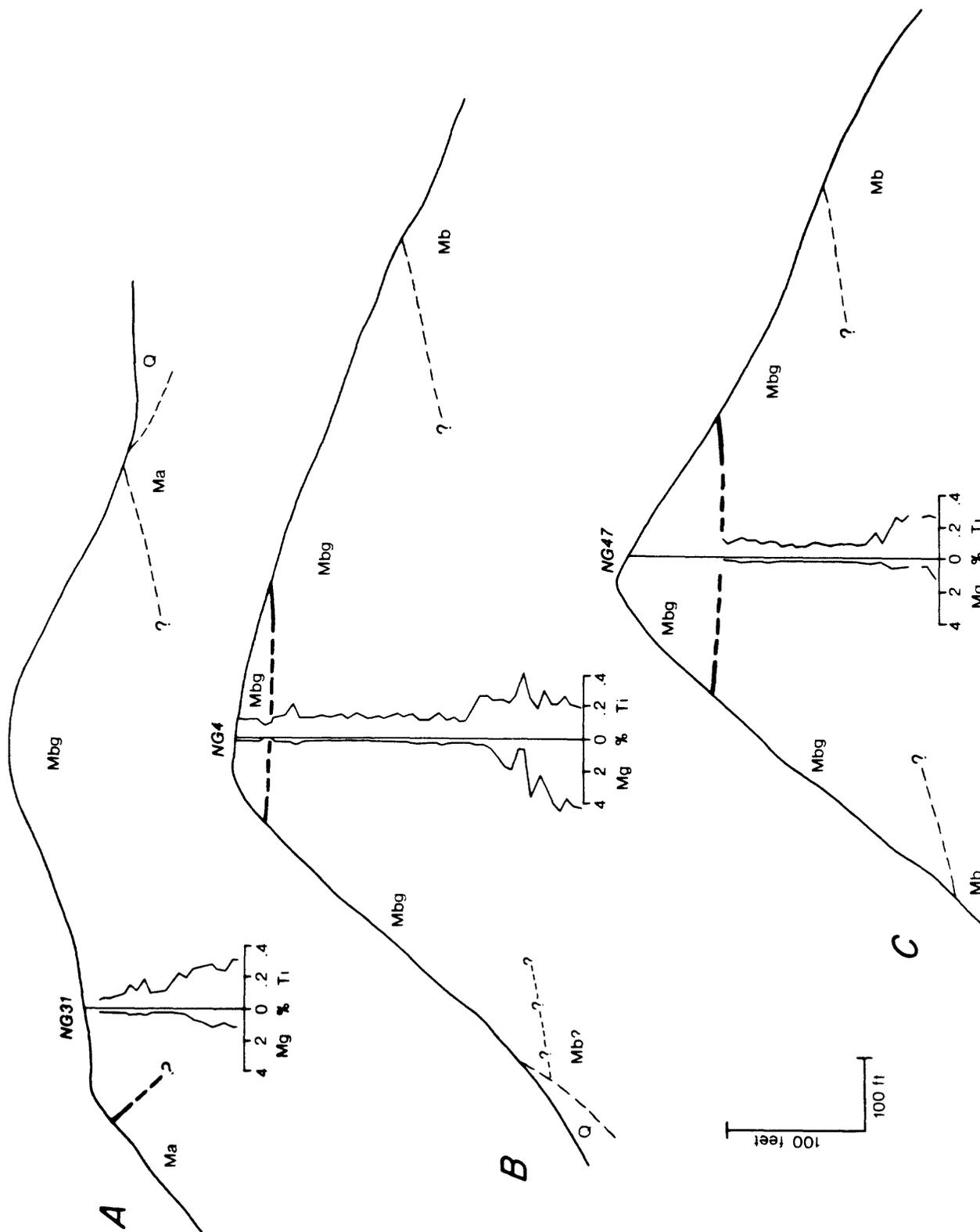


Figure 2. Schematic southwest-northeast sections through Ridge 7129 including drill holes NG4, NC31, and NG47. Symbols as in figure 1.

Forty-one elements were analyzed simultaneously using a Jarrel-Ash 1.5 m direct reading emission spectrometer (D. R.) equipped with a d.c. arc excitation source. In the D. R., exit slits are placed at preselected positions on the focal curve of the instrument so that only light of chosen wavelengths can pass through to photomultiplier tubes (table 1). Computer controlled readout electronics permit integrated light yields to be recorded for up to 60 lines after a single 90 second exposure.

All materials, i.e. standards, samples or buffer were ground to -200 mesh before mixing. Charges were prepared by mixing sample, RbCl buffer, and graphite in a ratio of 4:1:7.5 respectively, and then pack loading a 40 mg charge into a 3/8 inch undercut electrode. Pd and Ge were added to the graphite for use as internal standards. All charges were preheated overnight at 110°C before excitation. Samples and standards were burned in duplicate by arcing each charge for 90 seconds in a 70 percent Ar/30 percent O<sub>2</sub> atmosphere using a stepped-current program (3 seconds at 3 amps, 10 seconds at 8 amps, then 77 seconds at 15 amps).

Standard curves for each element were prepared by using International standard rocks, U.S. Geological Survey standard rocks, and serial dilutions of synthetic standards made from specpure compounds. The matrix used for dilutions of both standards and samples is a synthetic pegmatite (SPB) made by mixing 60 parts of spectroscopically clean quartz with 40 parts of synthetic microcline. The synthetic microcline is made by fusing for 4 hours at 1,000°C a mixture of 1 part SK (as K<sub>2</sub>CO<sub>3</sub>), 1 part Al (as Al<sub>2</sub>O<sub>3</sub>) and 3 parts Si (as SiO<sub>2</sub>).

The volatile elements (As, Au, Bi, Cd, Hg, Pb, Sb, Se, Tl, Zn) were analyzed both semiquantitative and quantitatively using short wavelength radiation (SWR) photographic techniques, between 190 and 310 nm wavelength. For all SWR analyses, 80 mg charges were prepared from 40 mg sample (either diluted or undiluted) and 40 mg graphite (containing 20 percent CsCl). The charges were arced at 30 amps in an argon atmosphere.

For semiquantitative analyses each sample was arced for 90 seconds. Concentrations were determined by visual comparison of sample spectra with standard spectra obtained using identical conditions. The standard U.S. Geological Survey system of dividing each decade of concentration into six equal logarithmic steps was used.

For quantitative analyses, each sample was arced twice for 145 seconds, once undiluted and once diluted with an equal amount of SPB. One-hundred parts per million (ppm) Te was added to the graphite (containing 20 percent CsCl) as an internal standard.

Replicate analyses of a small group of samples by all of the above methods and by the standard emulsion (III-0) semiquantitative photographic technique indicate that for most elements the agreement among the different spectroscopic methods is within the accepted precision of the semiquantitative techniques. The main advantage of the D. R. method, aside from its speed and convenience, is the fine relative precision of analyses obtained from a sequence of samples. This relative precision allows visual correlation of element distribution patterns.

The data reported in table 1 were obtained by what we believe to be the "best method" among those employed for each element. The chosen techniques are listed in the caption with the limits of detection. Discrepancies among absolute concentrations determined by different methods for Ag, Cd, Cr, and Zn, and Zr are discussed briefly in the appendix but generally have little effect on the distribution patterns of these elements with depth.

#### DESCRIPTION OF DRILLED SECTIONS

The photographed sections which appear in figure 3 were constructed from alcohol smear slides of the sample powders that were used for analysis. The color of each sampled interval was taken from the dried surface of the smear slide using the Munsell Soil Color Charts (1975 ed.) as a guide.

The colors of the sample powders range from very pale brown (mostly in the upper parts of the holes) to very dark grayish brown. Fresh dark organic-rich rock is found throughout a fairly large portion of NG47, but is absent or rare in NG4 and NG31. The lighter intervals are presumed to have been bleached by oxidation of the organic matter. This bleaching has occurred to considerable but variable depths from the surface. There is also a deep narrow bleached zone in NG31, which may indicate a second zone of oxidation, perhaps related to a zone of major weakness (or high permeability) in the rock.

The last few samples in the bottom of each drill hole are almost neutral gray. Though they are fairly dark, these deepest rocks do not appear to contain abundant organic matter.

Core loggers' descriptions, along with surface samples, drill cuttings, and descriptions by Desborough and others (1979), indicate that the Gibellini facies consists of sapropelic siltstone, mudstone, and chert with very little carbonate. The stratigraphy of the deposit is disrupted by intense fracturing and faulting. In the following discussions, the originally organic-rich metalliferous Gibellini facies rocks are termed "black shale," following the nonrestrictive use of this term by Vine and Tourtelot (1970).

The Mississippian section beneath the Gibellini facies consists of siliceous and calcareous rocks (Hose, 1978).

#### X-RAY MINERALOGY

Interpretations of the X-ray diffraction patterns obtained from selected whole sample powders are summarized in table 2. Quartz and illite are dominant, and most samples contain lesser amounts of potassium feldspar, pyrite, and a 7A clay mineral. A component of the 7A phase is tentatively identified as Fe-chlorite because very weak 14A peaks were obtained from two fine-grained samples which had been separated by suspension in distilled water; however, kaolinite may also be present.

Apatite, dolomite, barite, gypsum, jarosite, sphalerite, smithsonite, bianchite, and bokite were each detected in a few samples. Bokite is tentatively identified on the basis of small diffraction peaks at 10.5 and 3.5A whose intensity varies with the V content of rocks in part of NG31. Bokite was also tentatively identified in fracture coatings of surface samples

Table 2. Summary of whole-rock X-ray diffraction data

Sample	Minerals other than quartz <sup>1</sup>	Unidentified peaks
NG4: (40-45)	<u>illite</u> , pyrite, (7A clay), (apatite?)	5.7, 3.5, 2.99, 2.87
(45-50)	<u>illite</u> , (potassium-feldspar)	3.5, 2.99
(175-180)	<u>illite</u> , potassium-feldspar, bianchite, 7A clay, pyrite, jarosite	3.5, 2.99
(180-185)	<u>illite</u> , potassium-feldspar, bianchite, pyrite, jarosite, gypsum, 7A clay, (apatite?), (dolomite?)	5.7, 3.5, 2.99
(185-190)	<u>illite</u> , dolomite, gypsum, potassium-feldspar, 7A clay, pyrite, barite?, (apatite?)	3.5, 3.00
(205-210)	<u>illite</u> , potassium-feldspar, 7A clay, pyrite, gypsum, jarosite, (sphalerite?)	3.5, 2.99
(210-215)	<u>dolomite</u> , <u>illite</u> , pyrite, potassium-feldspar, gypsum, 7A clay, (apatite?)	3.5, 2.99
(230-235)	<u>dolomite</u> , <u>illite</u> , potassium-feldspar, 7A clay, pyrite, (apatite?)	3.5, 3.0
NG31: (5-10)	<u>apatite</u> , <u>illite</u>	--
(50-55)	<u>illite</u> , bokite?, apatite	(3.89), (2.16)
(60-65)	potassium-feldspar, <u>illite</u> , barite, 7A clay	--
(80-85)	<u>illite</u> , potassium feldspar, 7A clay, smithsonite, pyrite	3.78, 2.99, 1.90, 2.16
NG47: (95-100)	<u>illite</u> , (apatite), (gypsum?)	--
(100-105)	<u>apatite</u> , <u>illite</u> , dolomite?, gypsum?	(1.90), 1.61
(155-160)	<u>illite</u> , sphalerite, pyrite	1.61
(180-195)	<u>illite</u> , potassium-feldspar, (sphalerite?)	--

<sup>1</sup>Underlined minerals are abundant, those in parentheses are barely detectable

by Zientek, Radtke, and Oscarson (1979). Likewise, bianchite and smithsonite were each identified by a limited number of X-ray peaks which vary in intensity with Zn content in parts of NG4 and NG31, respectively. In the interval NG4 (175-190), the apparent abundances of bianchite and jarosite are inversely proportional to those of dolomite and gypsum.

#### MAJOR- AND MINOR-ELEMENT CHEMISTRY

Variations in element concentrations with depth in each drill hole are shown graphically in figure 3. Most of the following conclusions are derived from visual analysis of figure 3. Combined statistical analysis of the data is precluded largely by the effects of oxidation, but also by primary lithologic changes. Several elements have been mobilized and re-concentrated, resulting in a high degree of variability of concentrations. Also, the mobilized elements and some others (such as Ca, Mg) reside in different phases in different places.

Details of the distribution of each element are described in the appendix. The following section is a summary and discussion of the major observations.

#### DISCUSSION

##### Rock components

Visual analysis of element concentration vs depth patterns in each of three drill holes (fig. 3) generally provides a clear distinction among the major components of the rocks. A rock component is defined by an element or group of elements that has a distinctive depth profile. For example, Ti, Al, K, B, Zr, and despite limited data, Na, Ga, and Sc, follow almost identical variation trends through most of the drilled intervals. These elements constitute the "shale" component of the rocks, which is similar to Vine and Tourtelot's (1970) "detrital component". Their term is not used here because the distinction between detrital (e.g. illite) and authigenic or diagenetic (e.g. feldspar, pyrite) contributions for certain elements is not always clear, though variations in ratios such as K:Ti and Fe:Ti probably indicate that such a distinction could be made. Portions of Mg, Fe, Be, Co, Cr, La, and Sr are also assigned to the "shale" component. In many instances the distributions of the minor elements can be definitely correlated with the occurrence of identified minerals, though they may be associated with different minerals in different places. In some instances, such correlation is ambiguous. For example, a given minor-element anomaly may correspond to a peak in the distribution of an identified mineral, but peaks in the same mineral elsewhere may not correlate with anomalies in the same element. Either the correlation is fortuitous, or some of the minerals have widely varying trace-element compositions. Finally, several elements appear to occur more or less independently (e.g. Cu, Pb, As). These elements may be present as major components of minor minerals, or in some instances, may be tied up to varying degrees with organic materials. The main identifiable mineral components (underlined), together with their associated elements (parentheses indicate questionable associations), are given below.

The distribution of free silica is indicated by the pattern of Si concentrations in excess of those required by the silicate minerals of the "shale" fraction. Silica is dominant as an independent phase in the Gibellini facies, but is less abundant toward the bottom of the drilled section. According to Desborough and others (1979) silica occurs both in primary concentrations (e.g. chert beds) and as secondary deposits (e.g. opaline veins) in the Gibellini facies.

Dolomite is a major constituent near the bottom of NG4. Dolomite apparently contains the bulk of the Ca, Mg, Mn, and Sr in this section.

Apatite is probably present in small amounts through much of the section, but it is anomalously abundant in several samples from within the Gibellini facies. Apatite-rich samples, indicated by certain peaks in Ca content, are sometimes accompanied by anomalies in (Ag), Be, Cr, (Cu), La, Sr, and Y. The irregular association of these trace elements with "apatite"-Ca could indicate that the "apatite" phase has a variable composition. Alternatively, diagenesis, faulting, or other conditions which may ultimately have caused apatite to be locally concentrated, could have also favored local concentrations of trace elements.

Narrow zones rich in barite occur toward the bottoms of all three drill holes. Barite is not associated with significant quantities of the other trace elements except Sr, which is apparently enriched in only one of the barite-rich samples. As with apatite, it may be either that barite has variable Sr content or that a separate Sr-phase was concentrated in the one sample along with the barite.

Most of the significantly enriched metals of the deposit are clearly not related with any of the above components. Desborough and others (1979) found Cd and Zn in sphalerite, Mo in molybdenite, and Mo, Se, and V in organic matter in unoxidized samples. Sphalerite has been detected in NG47 in two deep samples that have very high Zn and Cd concentrations. In the unoxidized interval from about 125 to 190 ft in NG47, the distributions of Cd, Mo, Ni, Se, V, and Zn have vague similarities which may reflect sympathetic "primary" stratigraphic or structural zoning of these metals in the black shale.

The highest concentrations of enriched metals do not appear to be primary occurrences, but rather are found in secondary phases, some of which clearly indicate that oxidation has taken place.

Bianchite ( $ZnSO_4 \cdot 6H_2O$ ) is the major Zn phase in the Zn-rich zone deep in NG4. The highly similar distribution patterns of Cd, Ni, and Zn in this hole suggest that Cd and Ni are present in either bianchite or chemically similar sulfate phases, such as nickel hexahydrate ( $NiSO_4 \cdot 6H_2O$ ). Likewise, Cd, Co, Mn, and Ni apparently occur in smithsonite or independent carbonates in the Zn-rich zone deep in NG31.

Bokite ( $KAl_3Fe_6V_{26}O_{76} \cdot 30H_2O$ ) is tentatively identified as the principal V phase in the highly enriched zone in NG31. Molybdenum, Se, and V do not appear to be related mineralogically, though all tend to be highly concentrated at comparable depths.

### Lower boundary of the deposit

The Gibellini facies is described by Desborough and others (1979) as consisting of organic-rich bedded siliceous mudstones, siltstones, and cherts. These rocks are highly fractured and altered, and are bounded, at least in the north, by faulting. Element distribution patterns (fig. 3) strongly suggest that the base of the metalliferous Gibellini facies was penetrated by drilling. The following features are observed at depth: (1) a marked change in lithology is indicated by increase in the "shale" and (or) dolomite components at the expense of silica; (2) the concentrations of several enriched elements such as As, Sb, Tl, and V fall more or less abruptly to low concentrations; and (3) the colors of sample powders change from light or dark brown or almost black to neutral gray. Preliminary analyses of samples from the bottom of NG4 and NG31 indicate that the neutral gray rocks contain about 1 percent organic C. These changes occur at depths which are compatible with fairly simple projection of the surface map boundaries through the drill holes in figure 2. In NG31, a conspicuous deep zone of strongly bleached rock (fig. 3) may mark the location of a fault. This could be the projection of the high-angle bounding fault at the surface in section A. Unfortunately the changes in lithology, selected-element concentrations, and rock color are not precisely coincident. In NG47, the lowermost interval is dolomitic, but other evidence for a contact is obscure. In part, the indefinite nature of the contact in all three holes is probably the result of imbricate faulting or other structural disturbances accompanied or followed by downward movement of chemical constituents of the black shale into the rocks below.

Dolomite is known from Devonian rocks of the Woodruff and Davis Springs Formations, but has not been found in surface exposures of Mississippian rocks in the vicinity of the Gibellini claims (R. K. Hose, oral commun., 1980). If the Gibellini facies is considered to be part of the Mississippian Bisoni Formation, then the occurrence of dolomitic rocks near the bottom of holes NG4 and NG47 is anomalous. If the Gibellini facies and the dolomite are part of the Devonian Woodruff Formation, then the fault separating these rocks from the underlying Mississippian rocks was not penetrated by the drill holes, except perhaps in NG31.

In either case, the chemical data indicate that the dolomitic rocks beneath parts of the south end of Ridge 7129 were originally nonmetalliferous. The major element distributions in figure 3 suggest that argillaceous rocks occur just above the dolomitic section in NG4 and NG47. It is not clear whether this transition zone between the upper siliceous zone and the lower dolomitic zone was part of the metal-rich "black shale." Much of the metal content of the argillaceous and carbonate-rich rocks near the bottom of all three drill holes was apparently derived from above during oxidation of the deposit (see below).

It is concluded that the drill holes bottomed in rocks which were originally nonmetalliferous, but which have received secondary deposits of metals that were leached from above by oxidation. Based on the distributions of metals in NG4 and NG31, it is considered unlikely that these secondary enrichment zones extend much deeper than has been drilled. Because of uncertainty about the geology under the deposit, however, it is not known whether other "black shale" horizons might be encountered at greater depths.

## Composition and origin of the black shale

Because of the effects of oxidative alteration on the element distribution patterns in the drill holes, some selection is required to obtain a representative analysis of black shale from the Gibellini facies. For the following discussion, an average composition has been calculated from the interval of NG47 between 130 and 175 ft, where the effects of oxidation and leaching are believed to be minimal, and where the primary lithology (as deduced from the chemical data) appears to be uniform.

The possibility that certain of the spectroscopic determinations are systematically in error (such as Ag, Cd, Co, Cr, Zn, and Zr--see app.) may alter this average composition somewhat. With the possible exception of Cr, these errors should not change the general conclusions reached with regard to metal enrichment. The further possibility that some elements (such as Zn, Cd) may be enriched by secondary deposition in this section after being leached from above is potentially more serious. However, the very rough covariation among Cd, Mo, Ni, Se, V, and Zn in the unoxidized interval is suggestive of a primary enrichment pattern.

Compared with normal shale (table 3, cols. 1, 2), the Gibellini facies is strongly depleted in the "shale" component (e.g. Ti, Al, Fe, K, Zr). These elements are fairly uniformly diluted by free silica. Potassium and Al contents are slightly high, relative to Ti, Fe, and Zr possibly because the Gibellini facies contains an unusually high proportion of authigenic potassium feldspar. It is interesting that B, which correlates well with the "shale" component graphically, shows no depletion relative to the average shale. Degens, Williams, and Keith (1957) found that the B content of carboniferous shales in the eastern United States is roughly proportional to the salinity of the depositional environment (marine, brackish, or fresh water). The relatively high B content of the Gibellini facies "shale" may indicate that it was deposited in highly saline conditions, though there is no substantiating evidence for this. The Gibellini rocks are especially poor in Mg, Ca, and Na.

The dark-colored segment of NG47 is highly enriched (by greater than one order of magnitude) in Cd, Mo, Sb, Se, V, and Zn compared with "normal shale." It is enriched by about 2 to 5 times in As, Ba, Cu, Ni, and Tl. Silver is probably also highly enriched as it was detected in several samples at levels of greater than 1 ppm (see also discussion of Silver in app.). Compared with Vine and Tourtelot's (1970) definition of "metal-rich black shale," the selected interval is noteworthy only for its Ba, V, and Zn contents. None of these enriched elements are associated with the silica, "shale," carbonate, or apatite components of the rocks. Several are known to occur in organic matter (Mo, Se, V) or associated sulfides (Cd, Zn) in unoxidized samples (Desborough and others, 1979). It is not known how or when the enrichment in these elements took place, but it is likely that highly reducing conditions and (or) abundant organic material are related to the cause. Vine and Tourtelot (1970) concluded that large numbers of statistical geochemical studies of black shales were not helpful in differentiating environments of deposition of the shales. This failure was attributed to diagenetic and later alterations of the shale compositions, which obscured the syngenetic chemical patterns.

Table 3. Comparison of unoxidized Gibellini facies black shale with "normal shale" and seawater

Element	NG47 (130-175)	"Normal shale" (Wedepohl, 1968)	Enrichment Factor <sup>1</sup>	Modern seawater (Holland, 1979)	Enrichment factor <sup>2</sup>
	(percent)	(percent)			
Si -----	>40.	27.4	>1.5	--	--
Ti -----	.09	.46	.20	--	--
Al -----	2.1	8.8	.24	--	--
Fe -----	.77	4.82	.16	--	--
Mg -----	.17	1.57	.11	--	--
Ca -----	.20	1.58	.13	--	--
Na -----	<.15	1.56	<.10	--	--
K -----	.70	3.0	.23	--	--
	(ppm)	(ppm)			
Ag -----	≤1.	.07	≤14.	.04 (x10 <sup>-3</sup> )	≤.25 (x10 <sup>5</sup> )
As -----	46.	10.	4.6	--	--
B -----	97.	100.	.97	--	--
Ba -----	1448.	580.	2.5	--	--
Be -----	2.4	3.	.80	--	--
Cd -----	≥135	.8	≥169.	--	--
Co -----	6.2	19.	.33	--	--
Cr -----	37.	90.	.41	.3 (x10 <sup>-3</sup> )	1.2 (x10 <sup>5</sup> )
Cu -----	81.	45.	1.8	.25 (x10 <sup>-3</sup> )	3.2 (x10 <sup>5</sup> )
Ga -----	<10.	19.	<.53	--	--
Hg -----	<1.	.4	<2.5	--	--
La -----	≤21.	49.	≤.43	--	--
Mo -----	97.	2.6	37.	10. (x10 <sup>-3</sup> )	.10 (x10 <sup>5</sup> )
Mn -----	<200.	850.	<.24	--	--
Ni -----	190.	68.	2.8	.6 (x10 <sup>-3</sup> )	3.2 (x10 <sup>5</sup> )
Pb -----	9.	20.	.45	.03 (x10 <sup>-3</sup> )	3.0 (x10 <sup>5</sup> )
Sb -----	34.	1.5	23.	--	--
Sc -----	<10.	13.	<.77	--	--
Se -----	54.	.6	90.	--	--
Sr -----	103.	300.	.34	--	--
Tl -----	3.0	1.4	2.1	--	--
V -----	2399.	130.	18.	2.5 (x10 <sup>-3</sup> )	9.6 (x10 <sup>5</sup> )
Y -----	26.	41.	.63	--	--
Zn -----	<sup>3</sup> 1382.	95.	13.	3. or .4 (x10 <sup>-3</sup> )	4.6 or 35. (x10 <sup>5</sup> )
Zr -----	32.	160.	.20	--	--

<sup>1</sup>Column 1/Column 2.

<sup>2</sup>Column 1/Column 4.

<sup>3</sup>Atomic absorption values are 50 to 100 percent higher.

Holland (1979) selected the highest median concentrations of metals from among Vine and Tourtelot's (1970) data sets for black shales from several different environments, and found that the enrichment factors

$$\frac{\text{concentration of } x \text{ in deposit } z}{\text{concentration of } x \text{ in modern seawater}}$$
 for Ag, Cu, Ni, V, and Zn were similar

(roughly  $2.5-8.0 \times 10^5$ ). Although the individual concentration values used in the calculations came from different deposits, Holland suggested that the enrichment factors could indicate a simple common mechanism for the incorporation of the metals into black shales. Similar calculations performed for the unoxidized section of the Gibellini facies in NG47, give much the same numerical result (table 3, col. 5) in that Cr, Cu, Ni, Pb, V, and Zn are about  $10^5-10^6$  times more concentrated in the rocks than in modern seawater. The corresponding enrichment of Mo is much smaller, as Holland (1979) noted in other black shale deposits and in Black Sea sediments. As Holland pointed out, there is little information with which to judge these coincidences. However, it is noted that Pb and Cr, which are actually depleted in the Gibellini facies relative to normal shale and may be in part related with the "shale" (or detrital?) fraction, have seawater enrichment factors only slightly less than that of V, which is strongly enriched and believed to be mostly associated with organic matter.

Comparable concentrations of some metals occur in several recent organic-rich sediments, but the metal ratios differ from place to place. Some diatomaceous organic-rich clay sediments in an area of upwelling on the southwest African shelf contain higher concentrations of Cu, Ni, and Pb than the unoxidized segment of NG47, but have much lower Zn contents (Calvert and Price, 1970). Recent Black Sea sediments attain roughly similar Cu, Mo, and Ni contents, but have much less V and Zn than the Gibellini rocks (Volkov and Fomina, 1974; Hirst, 1974). Incorporation of some of the metals in the Gibellini facies could therefore have occurred syngenetically by processes that have been operative in certain recent nonoxidizing sedimentary environments; however, V and probably Zn appear to be anomalously enriched in the Gibellini facies, as is also indicated by comparison with Vine and Tourtelot's (1970) compilation of black shale deposits.

#### Oxidation and metal redistribution

The colors of the sample powders range from very pale brown to very dark grayish brown (fig. 3). Lighter colors in the upper parts of all three drill holes reflect oxidation, which has apparently occurred to depths well in excess of 100 ft in some parts of the deposit (e.g. NG4), while in other areas black (unoxidized) material can be found just below the surface. The highly variable distribution of oxidized rocks can perhaps be explained as a result of the highly fractured nature of the allochthonous mass. In NG31, a deep zone of light-colored rock occurs near the inferred projection of a high-angle surface fault indicating that oxidation may have been facilitated along this boundary.

The distributions and mineral occurrences of Cd, Mo, Ni, Se, V, and Zn suggest that these metals have been mobilized by oxidation and reconcentrated at deep levels in the deposit by secondary deposition. They are generally present at lower concentrations in the zone of oxidation than in the unoxidized part of NG47. They tend to be highly enriched in relatively narrow zones near or below the base of the zone of oxidation (bleaching). Unpublished information supplied by Noranda Exploration, Inc., suggests that V is generally most concentrated throughout the deposit in a zone located near the lower end of the transition from bleached (oxidized) to dark (unoxidized) rock. The highly enriched zones for different metals generally do not coincide, as one might expect if they represented primary metal-rich sedimentary horizons. Vanadium, Se, Mo, and Cd-Ni-Zn zones occur more or less independently at different depths. In NG31, Cd, Ni, and Zn are concentrated together well below the inferred base of the Gibellini facies in otherwise nonmetalliferous rocks. The mineralogy of the metal-rich zones themselves indicates that they are within the oxidized zone, and not in their primary unoxidized forms. Gypsum, barite, and jarosite are common in the vicinity of the major accumulations of metals, which themselves occur as sulfates, carbonates, and vanadates.

If the maximum concentrations of Cd, Mo, Ni, Se, V, and Zn were caused by secondary enrichment, as suggested, then a crude hierarchy of relative mobility is indicated by the depths of the metal-rich zones. Cd, Ni, and Zn were carried deepest before being precipitated, Se is concentrated at the shallowest level, and Mo and V are at intermediate depth. Thus the relative mobilities are:  $Se < Mo, V < Cd, Ni, Zn$ . The conspicuous Ba-rich horizons deep in all three drillholes may be related with the oxidation of the deposit.

The possible economic implications of oxidation and metal redistribution for development of the Gibellini V claim involve both the present location of the metals and their mineralogy. The richest vanadium ore occurs at considerable depth throughout much of the deposit. Possible byproduct metals are concentrated at different levels, more or less predictably located with respect to V. In some instances, certain metals such as Cd, Ni, and Zn may actually be concentrated below the base of the black shale. Extraction of the metals, either by surface processing or by in situ leaching will be complicated by the variety of minerals and (or) organic phase which hold the metals in different parts of the deposit.

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## APPENDIX

### Element distributions

The distributions of elements in the three drill holes (NG4, NG31, and NG47) are discussed individually in this section. These element descriptions are derived from observations of patterns in figure 3 and from the interpretations offered in previous discussions.

Silicon is present in the upper parts of all three drill holes at concentrations greater than 40 percent (>85 percent SiO<sub>2</sub>), reflecting the highly siliceous nature of the "black shale" sequence. Chalcedonic quartz is abundant in the rocks in the form of veins, nodules, and layers (Desborough and others, 1979). Silicon concentration decreases rapidly below the siliceous "black shale" facies, where it is diluted by detrital and (or) carbonate components.

Titanium and aluminum concentrations correlate well. The ratio Ti:Al+Ti ranges from 0.03 to 0.06, with an average of 0.045. This is close to the ratio for average shale (0.05) taken from the compilation of Wedepohl (1968), suggesting that these elements reflect mainly the detrital component of the sediments. If this is true, then the range of Al contents (about 2-6 percent) implies that "shale" makes up on the order of 20 to 70 percent of the analyzed samples. The relative contributions of authigenic feldspars and clay minerals to the "shale" component is not known, but may account for variations in the element ratios.

The Ti and Al contents are generally low through most of the primary metalliferous section,, changing abruptly to higher and more variable values in the lower parts of the holes. The change in lithology to greater dilution by clastic sediments could be the depositional base of the siliceous Gibellini facies, though a fault contact is also possible.

Iron correlates in a general way with the "shale" component. Noticeable but minor departures from the "shale" pattern may be caused by local concentrations of authigenic or later phases, such as pyrite and (or) Fe-chlorite, both of which were detected by X-ray diffraction. Iron is not greatly enriched in the black shale.

Magnesium concentrations are low (about 0.1-0.3 percent) and vary with the "shale" component through the Gibellini facies, though this relationship does not appear clearly at the scale used in constructing figure 3. In the lower part of NG4 and possibly in the last interval of NG47, the close correlation of Ca and Mg reflects the abundance of dolomite in the Mississippian(?) section below the siliceous black shale. The molar ratio Mg:Mg+Ca in the lower section of NG4 ranges from 0.41 to 0.50, which is close to the stoichiometric ratio in well-ordered dolomite, such as that detected by X-ray. The mutual dilution of dolomite, free silica, and "shale" is readily apparent in the lower section of NG4.

Calcium occurs mainly in dolomite (see Mg) or apatite. Apatite is highly concentrated in several samples in the upper parts of all three cores, i.e. within the Gibellini facies.

Sodium is present at less than 0.15 percent (limit of detection) in most samples. The few samples which contain between 0.15 and 0.22 percent Na also have relatively high "shale" content, suggesting that Na occurs largely in the "shale" component.

Potassium concentrations correlate well with Ti and Al concentrations, indicating that K resides mainly in the "shale" fraction. Much of this K is probably held in illite, though potassium feldspar is also common in X-ray traces.

Silver distribution patterns (fig. 3) suggest vaguely that Ag might be associated with apatite (NG4, NG31), with V (NG31, NG47) or with Zn (NG47); however, all concentrations are near or below the limit of detection of the spectroscopic methods (1 ppm). G. A. Desborough (oral commun., 1980) has found that Ag concentrations determined by other methods are several times higher than those obtained by optical emission in Gibellini facies rocks, so the values given here may be too low.

Arsenic content varies between 6 and 95 ppm in the Gibellini facies and is generally low (<20 ppm) near the bottom of NG4 and NG31. It therefore appears to be significantly enriched in the black shale. Arsenic distributions in NG4 and NG31 do not give clear evidence of mobilization during oxidation, though the higher concentrations (50-100 ppm) occur in several distinct zones. These As-rich zones may reflect stratigraphic or structural zonation, or they may be a result of local mobilization and redeposition caused by oxidation. There is an apparent correlation of As with Fe in the intervals NG4 (65-110) and NG31 (5-40). The As content of NG47 is more uniform, it increases gradually with depth.

Boron follows closely the distributions of Ti and Al, indicating that it is part of the "shale" component. It reaches its highest concentrations (to >200 ppm) in the lower sections of the holes, and is not enriched in the Gibellini facies.

Barium concentrations vary between roughly 1,000 and 3,000 ppm in all parts of the holes with the exception of a few rich narrow zones. Barite was detected in X-ray diffractograms from two of these zones. These Ba-rich zones occur in all three holes below the V-rich zones and at or just below the inferred lower boundary of the Gibellini facies.

Beryllium concentrations are generally 1.5 to 2.5 ppm, but approach 5 ppm in several zones. Beryllium varies through most of the cores roughly with the constituents of the "shale" component. Anomalous Be peaks in all three holes appear to correlate with Ca peaks which are interpreted as representing apatite, though the samples with the most apatite (near the top of NG31) do not contain much Be.

Cadmium determinations by the different spectroscopic methods are rather variable. The values used here (from Quantitative SWR) are generally the highest. Cadmium ranges from less than 1 ppm in the leached zone of NG4 to greater than 150 ppm in parts of all three holes. Desborough and others (1979) found up to 6 percent Cd in sphalerite from unoxidized samples by microprobe. In most instances in figure 3 cadmium appears to follow Zn, whether Zn occurs as sulfide, sulfate, or carbonate (see Zn).

Cadmium has been largely removed from the oxidized zone and is highly enriched by secondary precipitation deep in the section. In the case of NG31, the deep zone of enrichment may be beneath the base of the Gibellini facies, in otherwise nonmetalliferous rocks. It is not known whether the Cd occurs in the same secondary phases as Zn, or if it forms discreet phases.

The notable exception to the Cd-Zn correlation occurs just above the base of the Gibellini facies in NG31, where Se, Tl, and V reach exceptionally high concentrations. This may also be a zone of secondary enrichment, where Cd has been precipitated with other phases than the secondary Zn phases.

Cobalt concentrations determined spectroscopically are low by roughly 50 percent, compared with atomic absorption analyses. With few notable exceptions, the distribution patterns of Co are roughly the same as those of Ti and Al, indicating that Co occurs mainly as part of the "shale" component. The major departure from this behavior occurs in the narrow Zn-carbonate zone below the Gibellini facies in NG31. Though there is no evidence that this concentration of Co was derived from above, its strong association with the secondary Zn-Ni-Cd component suggests that some Co may have been present in the black shale in leachable (sulfide?) form.

Chromium reaches high concentrations in several samples that are rich in apatite. Otherwise, Cr appears as though it may constitute a part of the "shale" component, as it follows B roughly. From the spectroscopic data, therefore, it appears that Cr is not significantly enriched in the black shale.

Chromium values obtained by atomic absorption analysis are in some instances higher by about 50 to 100 percent than those reported in table 1. G. A. Desborough (written commun., 1980) has found Cr concentrations up to several times higher than any reported here, in other Gibellini facies rocks. If the spectroscopic determinations are indeed low, then it may be that the deposit is enriched in Cr.

Copper content is variable but tends to low values in the lower parts of NG4 and NG31, indicating that Cu may be somewhat enriched in the black shale. Copper distribution does not suggest that it is a component of any of the identified phases, nor does it correlate with any other element patterns. The highest Cu concentration (245 ppm) occurs in an isolated sample in the Gibellini facies in NG31, where it is associated with Ca, Be, Cd, and Y anomalies. Copper does not appear to have been mobilized significantly during oxidation.

Gallium is present at levels below the detection limit (10 ppm) in most samples. In NG4 and near the bottom of NG31, Ga goes with the "shale" component, though all reported concentrations are close to the analytical limit.

Mercury is generally near or below the detection limit (1 ppm). Its scattered distribution in measurable quantities in NG4 and NG31 suggests that mercury was slightly enriched in the black shale deposit, but may have required reconcentration during alteration to be detectable. However, all Hg values reported should be viewed as qualitative only.

Lanthanum appears to correlate rather well with Be. The distribution of La is similar to that of the "shale" component except in several apatite-rich samples, which contain anomalously high La concentrations.

Molybdenum concentrations range from below the detection limit (10 ppm) to several hundred parts per million. Desborough and others (1979) reported finding molybdenite in unoxidized samples from the Gibellini facies, but suggested also that some Mo might reside in organic matter. Molybdenum is highly concentrated near the base of the Gibellini facies in NG4, along with Cd, Ni, V, Y, and Zn. This metal-rich zone is near the bottom of the strongly leached section in the hole, and appears to be a zone of secondary enrichment. Molybdenum correlates roughly with Ni and perhaps with Zn in the relatively unoxidized interval of NG47.

Manganese is present at less than 200 ppm in most samples. It is not enriched in the black shale, but occurs mainly in carbonate rocks below. Manganese occurs in the dolomite component in the lower part of NG4. It reaches its highest concentration (700 ppm) in the smithsonite-rich zone below the Gibellini facies in NG31, where Mn apparently follows Cd, Co, Ni, and Zn.

Nickel is distributed almost precisely as Zn in NG4 and NG31. In these holes, therefore, it is inferred that Ni has been strongly leached from the oxidized intervals and concentrated near or below the base of the black shale sequence by secondary deposition. The striking similarity of the Ni and Zn patterns suggests that Ni occurs in the same or chemically comparable phases as Zn (as a sulfide in unoxidized black shale, and as carbonate or sulfate-hexahydrate in the secondary enrichment zones). In the dark relatively unoxidized interval of NG47, Ni correlates roughly with Mo and Zn.

Lead is present in almost uniformly low concentrations of around 10 ppm in all three holes. The major Pb anomaly occurs within the Gibellini facies in NG31, where it reaches 38 ppm, suggesting that Pb may be somewhat enriched locally in the black shale. The Pb-rich zone of NG31 is brown (oxidized) and also contains high concentrations of Cd, Se, Tl, and V.

Antimony appears to be enriched in the Gibellini facies, as its concentration ranges from 11 to 61 ppm in the upper parts of NG4 and NG31, but falls to less than 10 ppm near the bottoms of the holes. The highest Sb content is in a zone in NG31 which also contains anomalously high concentrations of Cd, Pb, Se, Tl, and V. In general, Sb is distributed in a similar way as As, but the small variations in Sb content are not readily correlated with those of any other element.

Scandium was detected in only a few samples at greater than 10 ppm (the limit of detection); however, these few data are sufficient to assign Sc to the "shale" component of the rocks.

Selenium concentrations determined semiquantitatively using the SWR technique range from less than 10 ppm to well over 1,000 ppm. Lowest concentrations are encountered near the bottoms of the holes, indicating that Se is strongly enriched in the Gibellini facies. Desborough and others (1979) stated that Se is located largely in the organic matter (kerogen) in unoxidized samples, and that it is relatively enriched in the oxidized zone. Distribution patterns of figure 3 show that Se is highly concentrated near the

base of the bleached (oxidized) section, suggesting that Se may be redeposited at depth after being partially leached from rocks higher in the oxidized section. This inferred behavior is similar to that of V, but minor relative displacements of the V- and Se-rich zones indicate that they were redeposited as separate phases, perhaps with slightly different depositional controls. Zientek, Radtke, and Oscarson (1979) report the possible existence of an Fe-V-Se phase in fractures in oxidized surface samples from the Gibellini claim. The Se-rich zones are in all instances within the leached zone of Zn.

Strontium concentration is relatively high in most of the apatite-rich samples, and in one of the barite-rich samples. Strontium varies with dolomite content near the bottom of NG43. Strontium therefore may substitute for Ca or Ba in these phases, but does not always (e.g. the two samples with the highest Ba contents do not have high Sr concentrations). Other variations in the distribution of Sr, including the largest anomaly in NG4, are not easily explained. There appears to be a correlation between Sr and the "shale" indicators Ti and Al through much of the midsection of NG4.

Thallium, like As and Sb, tends to its lowest concentrations in the lower parts of NG4 and NG31, suggesting that Tl is enriched in the Gibellini facies. The most conspicuous Tl anomaly is in NG31, and coincides roughly with the large Cd, Pb, Sb, Se, and V anomalies near the base of the Gibellini facies. In NG4, Tl content tends to higher values downward in the oxidized black shale section. This tendency may be caused by partial leaching and redeposition, or it may be related with original Tl variations in the black shale.

Vanadium content is variable, though it is clearly enriched in the Gibellini facies. Unpublished analyses supplied to Noranda Exploration, Inc., show V concentration up to 15,500 ppm in the V-rich zone of NG31. Desborough and others (1979) state that V-minerals are sparse in unoxidized samples, but metaheawettite has been detected in microfractures. Most of the V in the unoxidized rocks is thought to reside in kerogen, which contains about 0.3-3.0 percent V. In oxidized rocks, metaheawettite  $[\text{CaV}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}]$ , bokite  $[\text{KAl}_3\text{Fe}_6\text{V}_{26}\text{O}_{76} \cdot 30\text{H}_2\text{O}]$ , schoderite and metaschoderite  $[\text{Al}_2(\text{PO}_4)(\text{VO}_4) \cdot 6-8\text{H}_2\text{O}]$ , and unidentified Fe-V and Fe-P-V minerals have been found deposited in fractures (Zientek and others, 1979).

The apparent concentration of V near the bottom of the strongly bleached (oxidized) zone in all three holes (fig. 3) suggests the possibility of secondary enrichment of V leached from above as a result of oxidation. This interpretation is supported by the tentative identification of bokite, which correlates with V abundance in the highly enriched zone of NG31, and therefore probably contains the bulk of the V in this zone.

The zones of V enrichment in NG31 and NG47, are well above the zones of secondary Zn enrichment, while in NG4, the two anomalies roughly coincide. The inferred removal of V from the leached zones in all three holes has been far from complete, owing to the stability of the above-mentioned secondary V minerals. These observations reflect the relatively greater mobility of Zn compared with V in the oxidized environment of the deposit.

Yttrium correlates fairly well with Ca in NG31, and may be moderately concentrated in several apatite-rich samples. The highest concentrations in NG4 and NG47 occur roughly with the major V-rich zones. The Y distribution pattern of NG4, in particular, suggests that Y, like V and Zn, may have been partially leached during oxidation and redeposited at depth. It may be, therefore, that Y was at least moderately enriched in the Gibellini facies.

Zinc concentrations determined by all three spectroscopic techniques are consistently low by about 50 percent compared with values obtained by atomic absorption. Desborough and others (1979) determined that Zn occurs in sphalerite in unoxidized rocks, and is leached as a result of oxidation. Zinc-rich zones are well defined in figure 3, and in all instances fall at or below the distinct V-rich zones. In NG4, Zn is highly concentrated in the form of hydrous sulfate (bianchite) near the base of the "leached zone," where Cd, Mo, Ni, and V also reach their highest values. In NG31, Zn occurs as smithsonite in a Cd, Co, Mn, and Ni-rich zone well below the inferred base of the "black shale." There is an apparent tendency for these metal-rich carbonate and sulfate zones to be bounded more abruptly toward the top, more gradually downward.

Sphalerite occurs in the Zn-rich very dark organic-rich lower section of NG47. It is not known whether all of the several thousand parts per million Zn in most of this section is original, or if some secondary sulfide enrichment (as sulfide, sulfate, or carbonate?) has taken place. Vague similarities in the distributions of Cd, Mo, Ni, Se, V, and Zn in this unoxidized interval way indicate "primary" zoning of these metals.

Zirconium concentrations may be somewhat high because the correction factor for D.R. emission is not well known for this element. Zirconium follows the distribution patterns of Ti and Al, indicating that it is present mainly in the "shale" (or detrital) component. There is no clear evidence of unusual enrichment of Zr in the deposit.

Table 1. Spectroscopic analyses of drill cuttings from holes NG4, NG31, and NG47

[Si, Ti, Al, Fe, Mg, Ca, Na, and K are reported in percent; all other elements in parts per million; B = no analysis; L = less than lower limit of detection (see below); G = greater than upper limit of measurement (see below). The following elements were not detected in any sample at the detection limits given below: Au <1 ppm; Nb <25 ppm; Bi <1 ppm; Re <50 ppm; Ce <100 ppm; Sn <10 ppm; Li <50 ppm; Te <1 ppm]

Element	L	G	Selected Method	(A)
Si -----	10	40	D.R. (St.)	3905
Ti -----	.025	--	do.	4533
Al -----	.25	--	do.	2652
Fe -----	.05	--	do.	3758
Mg -----	.10	--	do.	2779
Ca -----	.05	--	do.	4454
Na -----	.15	--	do.	3302
K -----	.08	--	do.	4044
Ag -----	1	--	do.	3382
As -----	5	--	SWR	2349
B -----	10	200	D.R. (St.)	2497
Ba -----	20	26,000	D.R. (1:10)	4554
Be -----	1	--	D.R. (St.)	2348
Cd -----	1	170	SWR	2265
Co -----	1	--	D.R. (St.)	3453
Cr -----	10	--	do.	4254
Cu -----	1	--	do.	3274
Ga -----	10	--	do.	2943
Hg -----	1	--	SWR	2536
La -----	20	--	D.R. (St.)-	4086
Mo -----	10	--	D.R. (St.+1:10)	3170
Mn -----	200	--	D.R. (St.)	3823
Ni -----	1	600	do.	3414
Pb -----	1	--	SWR	2833
Sb -----	2	--	do.	2311
Sc -----	10	--	D.R. (St.)	3613
Se -----	10	1,000	SWR-SQ	1960
Sr -----	10	--	do.	4215
Tl -----	1	--	SWR	2767
V -----	10	5,500	D.R. (1:10+St.)	4379
Y -----	10	--	do.	3600
Zn -----	50	10,000	D.R. (St.+1:10)	3345
Zr -----	20	--	D.R. (St.)	3496

Table 1. (continued)

## NC4 CHEMICAL DATA-continued

SAMPLE	AG	AS	B	BA	BE	CD	CO	CR	CU	GA
0-5	0.0L	30.	82.	1960.	2.2	13.0	1.4	41.	64.	0.1
5-10	0.0L	33.	68.	1550.	2.2	5.5	0.0L	34.	61.	0.1
10-15	0.0L	63.	78.	2100.	2.9	9.6	11.0	39.	106.	0.1
15-20	0.0L	61.	88.	1660.	2.9	6.1	5.1	41.	98.	0.1
20-25	1.9	74.	52.	2400.	3.6	52.0	1.7	136.	113.	0.1
25-30	0.0L	65.	82.	1870.	3.2	7.1	0.0L	37.	91.	0.1
30-35	0.0L	42.	88.	2410.	3.3	6.1	0.0L	45.	64.	0.1
35-40	0.0L	18.	106.	3550.	3.4	3.1	0.0L	49.	78.	0.1
40-45	0.0L	25.	173.	3810.	4.9	4.3	1.9	93.	124.	12.
45-50	0.0L	10.	100.	1600.	3.1	3.5	0.0L	61.	152.	0.1
50-55	0.0L	9.	86.	2850.	2.9	3.6	0.0L	45.	166.	0.1
55-60	0.0L	6.	84.	2600.	2.6	2.4	0.0L	42.	119.	0.1
60-65	0.0L	9.	83.	2280.	2.4	3.6	0.0L	43.	127.	0.1
65-70	0.0L	21.	90.	2370.	2.3	3.4	0.0L	44.	139.	0.1
70-75	0.0L	21.	87.	2520.	1.7	2.5	0.0L	40.	104.	0.1
75-80	0.0L	32.	95.	2380.	2.0	1.8	0.0L	44.	122.	0.1
80-85	0.0L	45.	89.	2250.	1.8	2.7	0.0L	39.	110.	0.1
85-90	0.0L	26.	96.	2560.	1.8	1.0	0.0L	40.	115.	0.1
90-95	1.0	51.	88.	2190.	2.0	0.0L	0.0L	46.	129.	0.1
95-100	0.0L	71.	91.	2130.	1.7	0.0L	0.0L	42.	116.	0.1
100-105	0.0L	26.	90.	2410.	1.7	2.5	0.0L	42.	106.	0.1
105-110	0.0L	14.	81.	2270.	1.5	0.0L	0.0L	33.	81.	0.1
110-115	0.0L	16.	79.	2520.	1.7	1.7	0.0L	37.	116.	0.1
115-120	0.0L	19.	81.	2590.	1.7	0.0L	0.0L	38.	120.	0.1
120-125	0.0L	31.	85.	2400.	1.6	0.0L	0.0L	37.	114.	0.1
125-130	0.0L	24.	95.	2650.	1.8	0.0L	0.0L	55.	133.	0.1
130-135	0.0L	45.	73.	2600.	1.5	0.0L	0.0L	41.	110.	0.1
135-140	0.0L	35.	71.	2270.	1.5	1.1	0.0L	47.	122.	0.1
140-145	0.0L	58.	70.	1680.	1.5	2.6	0.0L	46.	123.	0.1
145-150	0.0L	60.	97.	3000.	2.2	4.8	0.0L	48.	99.	0.1
150-155	0.0L	85.	88.	2210.	1.9	4.7	1.3	40.	93.	0.1
155-160	0.0L	49.	91.	2920.	2.0	9.2	0.0L	37.	100.	0.1
160-165	0.0L	47.	91.	2260.	2.2	85.0	6.7	40.	109.	0.1
165-170	0.0L	89.	110.	2780.	2.6	0.0G	12.0	41.	67.	0.1
170-175	0.0L	95.	148.	3580.	3.0	0.0G	16.0	71.	48.	11.
175-180	0.0L	81.	161.	2660.	2.9	0.0G	22.0	56.	51.	12.
180-185	1.1	79.	197.	4090.	3.9	0.0G	21.0	98.	88.	14.
185-190	0.0L	39.	173.	9160.	4.5	59.0	14.0	80.	79.	0.1
190-195	0.0L	33.	135.	1790.	3.0	58.0	14.0	63.	60.	0.1
195-200	0.0L	31.	122.	1370.	2.4	26.0	9.1	48.	67.	0.1
200-205	1.0	30.	191.	1520.	3.6	28.0	21.0	67.	43.	11.
205-210	0.0L	19.	0.6	1040.	4.5	3.3	18.0	68.	30.	15.
210-215	0.0L	28.	150.	1790.	4.9	14.0	18.0	55.	28.	10.
215-220	0.0L	49.	117.	1880.	3.8	70.0	17.0	49.	55.	0.1
220-225	0.0L	28.	157.	1100.	3.2	4.7	17.0	49.	23.	0.1
225-230	0.0L	17.	113.	1070.	1.8	3.7	10.0	42.	16.	0.1
230-235	0.0L	17.	104.	1720.	1.7	4.3	13.0	42.	14.	0.1
235-240	0.0L	17.	143.	2120.	1.7	6.7	20.0	44.	27.	0.1
240-245	0.0L	15.	90.	2260.	1.5	4.5	12.0	42.	14.	0.1
245-250	0.0L	11.	91.	1850.	1.4	2.5	9.2	37.	12.	0.1

Table 1. (continued)

## NG4 CHEMICAL DATA

SAMPLE	ELEV	DEPTH	SI	TI	AL	FE	MG	CA	MA	K
0-5	7072.5	2.5	0.6	0.11	2.7	0.70	0.22	0.19	0.00L	0.79
5-10	7067.5	7.5	0.6	0.10	2.6	0.63	0.20	0.17	0.00L	0.72
10-15	7062.5	12.5	0.6	0.11	3.0	1.30	0.22	0.14	0.00L	0.74
15-20	7057.5	17.5	0.6	0.11	2.9	1.70	0.21	0.25	0.00L	0.81
20-25	7052.5	22.5	0.6	0.07	1.9	1.30	0.00L	3.10	0.00L	0.44
25-30	7047.5	27.5	0.6	0.11	2.8	1.70	0.20	0.88	0.00L	0.76
30-35	7042.5	32.5	0.6	0.12	2.9	1.20	0.21	0.88	0.00L	0.82
35-40	7037.5	37.5	0.6	0.14	3.5	0.79	0.25	0.69	0.00L	0.95
40-45	7032.5	42.5	0.6	0.21	4.8	1.60	0.38	0.83	0.18	1.40
45-50	7027.5	47.5	0.6	0.12	3.0	0.47	0.24	0.39	0.00L	0.87
50-55	7022.5	52.5	0.6	0.12	2.9	0.36	0.21	0.18	0.00L	0.77
55-60	7017.5	57.5	0.6	0.12	2.8	0.17	0.20	0.33	0.00L	0.81
60-65	7012.5	62.5	0.6	0.13	2.8	0.21	0.20	0.33	0.00L	0.82
65-70	7007.5	67.5	0.6	0.13	2.9	0.68	0.20	0.24	0.00L	0.76
70-75	7002.5	72.5	0.6	0.12	2.5	1.20	0.16	0.12	0.00L	0.78
75-80	6997.5	77.5	0.6	0.14	2.8	1.20	0.19	0.12	0.00L	0.96
80-85	6992.5	82.5	0.6	0.11	2.4	1.00	0.16	0.15	0.00L	0.75
85-90	6987.5	87.5	0.6	0.14	2.8	0.73	0.19	0.13	0.00L	0.90
90-95	6982.5	92.5	0.6	0.12	2.5	1.20	0.17	0.13	0.00L	0.84
95-100	6977.5	97.5	0.6	0.11	2.2	1.50	0.16	0.13	0.00L	0.79
100-105	6972.5	102.5	0.6	0.12	2.3	0.46	0.16	0.12	0.00L	0.74
105-110	6967.5	107.5	0.6	0.11	2.1	0.17	0.14	0.11	0.00L	0.62
110-115	6962.5	112.5	0.6	0.12	2.5	0.24	0.18	0.11	0.00L	0.70
115-120	6957.5	117.5	0.6	0.14	2.7	0.42	0.20	0.13	0.00L	0.77
120-125	6952.5	122.5	0.6	0.12	2.4	0.65	0.18	0.13	0.00L	0.73
125-130	6947.5	127.5	0.6	0.14	3.0	0.53	0.22	0.15	0.00L	0.86
130-135	6942.5	132.5	0.6	0.11	2.4	0.51	0.17	0.13	0.00L	0.70
135-140	6937.5	137.5	0.6	0.11	2.3	0.45	0.16	0.13	0.00L	0.62
140-145	6932.5	142.5	0.6	0.11	2.3	0.66	0.17	0.15	0.00L	0.65
145-150	6927.5	147.5	0.6	0.15	3.4	1.10	0.31	0.31	0.00L	0.96
150-155	6922.5	152.5	0.6	0.10	2.6	1.40	0.16	0.14	0.00L	0.67
155-160	6917.5	157.5	0.6	0.12	2.8	1.30	0.18	0.10	0.00L	0.81
160-165	6912.5	162.5	0.6	0.09	2.2	1.20	0.15	0.39	0.00L	0.69
165-170	6907.5	167.5	39.	0.11	3.5	1.90	0.18	0.19	0.00L	0.83
170-175	6902.5	172.5	36.	0.20	5.3	2.00	0.32	0.16	0.00L	1.60
175-180	6897.5	177.5	33.	0.27	6.2	2.90	0.31	0.13	0.00L	1.90
180-185	6892.5	182.5	31.	0.26	6.2	2.80	0.48	0.39	0.19	2.10
185-190	6887.5	187.5	32.	0.23	4.6	2.30	1.10	1.80	0.00L	1.90
190-195	6882.5	192.5	36.	0.23	4.1	1.70	1.60	2.80	0.15	1.80
195-200	6877.5	197.5	32.	0.21	3.7	1.50	1.80	3.30	0.00L	1.50
200-205	6872.5	202.5	34.	0.28	4.9	2.20	0.66	0.48	0.00L	2.20
205-210	6867.5	207.5	34.	0.40	6.8	2.40	0.53	0.15	0.19	3.10
210-215	6862.5	212.5	27.	0.24	5.0	2.20	3.50	8.30	0.18	2.40
215-220	6857.5	217.5	31.	0.18	3.4	1.60	2.00	4.60	0.16	1.40
220-225	6852.5	222.5	27.	0.30	5.3	1.90	2.90	4.80	0.00L	2.00
225-230	6847.5	227.5	22.	0.21	3.8	1.90	3.90	8.20	0.00L	1.70
230-235	6842.5	232.5	22.	0.21	3.7	1.70	4.40	9.30	0.00L	1.80
235-240	6837.5	237.5	24.	0.26	4.7	2.00	3.50	6.70	0.00L	1.70
240-245	6832.5	242.5	22.	0.21	3.2	1.60	4.00	8.90	0.00L	1.60
245-250	6827.5	247.5	21.	0.19	3.1	1.50	4.10	8.60	0.00L	1.50

Table 1. (continued)

## NG4 CHEMICAL DATA-continued

SAMPLE	MG	LA	MO	MN	NI	PB	SB	SC	SE	SR
0-5	0.0L	0.0L	27.	0.0L	87.	11.	24.	0.0L	0.0L	201.
5-10	0.0L	0.0L	16.	0.0L	81.	10.	23.	0.0L	0.0L	144.
10-15	0.0L	23.	19.	0.0L	137.	14.	32.	0.0L	0.0L	250.
15-20	0.0L	0.0L	34.	0.0L	136.	9.	34.	0.0L	0.0L	170.
20-25	0.0L	0.0L	69.	0.0L	128.	6.	11.	0.0L	150.	478.
25-30	0.0L	0.0L	22.	0.0L	93.	9.	47.	0.0L	10.	238.
30-35	0.0L	24.	14.	0.0L	66.	12.	38.	0.0L	0.0L	325.
35-40	0.0L	27.	13.	0.0L	59.	10.	22.	0.0L	20.	530.
40-45	0.0L	44.	20.	0.0L	102.	11.	30.	0.0L	70.	740.
45-50	0.0L	0.0L	0.0L	0.0L	43.	13.	36.	0.0L	30.	142.
50-55	0.0L	22.	0.0L	0.0L	27.	11.	25.	0.0L	100.	263.
55-60	0.0L	21.	0.0L	0.0L	28.	12.	12.	0.0L	30.	309.
60-65	0.0L	21.	11.	0.0L	25.	12.	11.	0.0L	30.	274.
65-70	0.0L	23.	11.	0.0L	28.	15.	14.	0.0L	150.	282.
70-75	0.0L	23.	22.	0.0L	19.	14.	28.	0.0L	100.	300.
75-80	0.0L	29.	53.	0.0L	24.	13.	41.	0.0L	50.	352.
80-85	0.0L	21.	43.	0.0L	28.	13.	34.	0.0L	70.	241.
85-90	1.6	25.	41.	0.0L	23.	16.	40.	0.0L	70.	306.
90-95	0.0L	0.0L	23.	0.0L	23.	14.	28.	0.0L	100.	207.
95-100	0.0L	0.0L	31.	0.0L	22.	11.	34.	0.0L	200.	167.
100-105	1.2	0.0L	35.	0.0L	21.	12.	22.	0.0L	70.	201.
105-110	2.4	0.0L	26.	0.0L	15.	11.	14.	0.0L	15.	215.
110-115	2.8	23.	33.	0.0L	19.	11.	21.	0.0L	30.	219.
115-120	1.4	25.	43.	0.0L	18.	12.	26.	0.0L	100.	253.
120-125	1.7	21.	36.	0.0L	19.	16.	33.	0.0L	300.	176.
125-130	0.0L	25.	36.	0.0L	23.	18.	39.	0.0L	700.	276.
130-135	0.0L	0.0L	23.	0.0L	19.	14.	31.	0.0L	1000.	256.
135-140	0.0L	23.	54.	0.0L	19.	14.	54.	0.0L	700.	214.
140-145	1.5	23.	50.	0.0L	24.	17.	53.	0.0L	150.	150.
145-150	1.4	38.	67.	0.0L	33.	15.	40.	0.0L	300.	328.
150-155	1.4	0.0L	148.	0.0L	28.	14.	36.	0.0L	100.	188.
155-160	1.5	31.	149.	0.0L	25.	14.	40.	0.0L	300.	270.
160-165	1.4	0.0L	156.	0.0L	146.	11.	28.	0.0L	200.	164.
165-170	0.0L	25.	360.	0.0L	365.	7.	26.	0.0L	30.	261.
170-175	0.0L	37.	450.	0.0L	499.	10.	32.	10.	20.	348.
175-180	0.0L	45.	400.	0.0L	0.6	6.	17.	10.	15.	150.
180-185	0.0L	47.	170.	0.0L	510.	11.	22.	13.	15.	267.
185-190	0.0L	40.	65.	219.	323.	11.	16.	10.	15.	199.
190-195	0.0L	37.	71.	257.	300.	12.	15.	0.0L	15.	138.
195-200	0.0L	34.	62.	276.	214.	10.	15.	0.0L	15.	116.
200-205	2.1	43.	33.	0.0L	424.	8.	9.	11.	10.	91.
205-210	0.0L	54.	17.	0.0L	303.	12.	4.	14.	0.0L	96.
210-215	0.0L	60.	18.	553.	254.	10.	9.	12.	0.0L	184.
215-220	0.0L	41.	60.	336.	415.	12.	24.	0.0L	20.	152.
220-225	0.0L	43.	12.	392.	276.	10.	7.	11.	0.0L	86.
225-230	0.0L	50.	0.0L	507.	136.	11.	4.	0.0L	0.0L	154.
230-235	0.0L	56.	0.0L	601.	183.	9.	4.	0.0L	0.0L	207.
235-240	0.0L	51.	0.0L	484.	100.	16.	5.	10.	0.0L	135.
240-245	0.0L	55.	12.	549.	206.	10.	4.	0.0L	0.0L	238.
245-250	0.0L	52.	0.0L	508.	145.	10.	3.	0.0L	0.0L	228.

Table 1. (continued)

## NG4 CHEMICAL DATA-continued

SAMPLE	TL	V	Y	ZN	ZR
0-5	1.6	1450.	25.	321.	42.
5-10	1.3	1290.	25.	299.	40.
10-15	1.7	1590.	28.	498.	51.
15-20	1.5	1770.	27.	608.	41.
20-25	0.0L	500.	32.	521.	28.
25-30	0.0L	1590.	26.	423.	45.
30-35	1.8	1550.	31.	264.	62.
35-40	0.0L	1270.	36.	179.	86.
40-45	1.8	1550.	35.	313.	163.
45-50	1.5	2310.	39.	110.	80.
50-55	1.1	1830.	21.	0.L	62.
55-60	1.5	1130.	28.	51.	58.
60-65	2.0	1240.	26.	0.L	69.
65-70	3.0	1570.	25.	0.L	74.
70-75	4.0	1660.	15.	0.L	51.
75-80	3.1	990.	17.	0.L	63.
80-85	3.8	1530.	26.	0.L	73.
85-90	2.9	1640.	18.	0.L	57.
90-95	5.9	1630.	29.	0.L	82.
95-100	5.6	2210.	22.	0.L	60.
100-105	3.2	1150.	20.	0.L	42.
105-110	2.3	860.	15.	0.L	29.
110-115	2.8	990.	18.	0.L	42.
115-120	3.5	1370.	17.	0.L	49.
120-125	3.0	1220.	17.	0.L	53.
125-130	3.3	1540.	19.	0.L	128.
130-135	3.6	1090.	14.	0.L	100.
135-140	7.4	1660.	20.	0.L	76.
140-145	7.2	2230.	20.	0.L	48.
145-150	8.3	1970.	25.	0.L	88.
150-155	6.2	3580.	26.	0.L	55.
155-160	6.8	2260.	22.	0.L	81.
160-165	3.8	2030.	36.	724.	58.
165-170	3.4	4280.	49.	2320.	116.
170-175	6.1	4450.	120.	3060.	238.
175-180	2.0	4420.	72.	6000.	318.
180-185	4.3	3140.	88.	4450.	264.
185-190	6.0	830.	59.	2220.	261.
190-195	4.8	740.	34.	1400.	287.
195-200	3.8	620.	32.	766.	278.
200-205	0.0L	530.	57.	1870.	299.
205-210	0.0L	330.	45.	1370.	385.
210-215	1.6	284.	49.	1020.	357.
215-220	2.4	990.	40.	1490.	250.
220-225	0.0L	221.	32.	721.	281.
225-230	0.0L	123.	39.	493.	337.
230-235	0.0L	115.	41.	640.	380.
235-240	0.0L	132.	38.	316.	344.
240-245	0.0L	152.	42.	599.	350.
245-250	0.0L	107.	40.	349.	391.

Table 1. (continued)

## NG31 CHEMICAL DATA

SAMPLE	ELEV	DEPTH	SI	TI	AL	FE	MG	CA	MA	K
5-10	6971.5	7.5	0.6	0.06	1.5	0.42	0.13	5.00	0.00L	0.47
10-15	6966.5	12.5	0.6	0.07	1.7	0.28	0.14	2.50	0.00L	0.52
15-20	6961.5	17.5	0.6	0.07	1.9	0.98	0.15	1.60	0.00L	0.52
20-25	6956.5	22.5	0.6	0.08	2.2	1.10	0.16	0.28	0.00L	0.54
25-30	6951.5	27.5	0.6	0.10	2.5	1.40	0.16	0.25	0.00L	0.64
30-35	6946.5	32.5	0.6	0.16	3.4	1.20	0.27	0.62	0.00L	1.00
35-40	6941.5	37.5	0.6	0.12	3.0	1.10	0.25	2.00	0.00L	0.79
40-45	6936.5	42.5	0.6	0.20	4.0	1.90	0.29	0.57	0.00L	1.00
45-50	6931.5	47.5	0.6	0.10	2.6	1.40	0.18	0.67	0.00L	0.55
50-55	6926.5	52.5	0.6	0.10	2.7	1.40	0.20	0.67	0.00L	0.60
55-60	6921.5	57.5	0.6	0.11	2.5	0.99	0.18	0.20	0.00L	0.55
60-65	6916.5	62.5	0.6	0.17	3.1	1.00	0.23	0.12	0.00L	1.00
65-70	6911.5	67.5	0.6	0.23	4.2	2.10	0.28	0.18	0.00L	2.00
70-75	6906.5	72.5	0.6	0.20	4.1	2.60	0.31	0.11	0.00L	1.90
75-80	6901.5	77.5	0.6	0.25	4.9	2.20	0.61	0.65	0.00L	2.10
80-85	6896.5	82.5	39.	0.27	5.2	3.10	0.76	0.58	0.00L	2.20
85-90	6891.5	87.5	37.	0.28	5.4	2.80	0.98	0.82	0.00L	2.20
90-95	6886.5	92.5	37.	0.29	5.3	2.80	1.10	0.91	0.00L	2.30
95-100	6881.5	97.5	38.	0.25	4.7	2.50	0.92	1.00	0.00L	1.90
100-105	6876.5	102.5	36.	0.24	4.7	2.90	0.89	1.00	0.00L	2.00
105-110	6871.5	107.5	34.	0.32	5.9	3.10	1.10	0.93	0.00L	2.30
110-115	6866.5	112.5	34.	0.31	5.8	2.90	1.10	0.84	0.00L	2.40

Table 1. (continued)

## NG31 CHEMICAL DATA-continued

SAMPLE	AG	AS	B	BA	BE	CD	CO	CR	CU	GA
5-10	1.5	35.	57.	1330.	2.2	59.0	2.4	66.	113.	0.L
10-15	1.8	24.	72.	1170.	2.1	41.0	0.0L	72.	125.	0.L
15-20	1.7	68.	68.	1410.	2.5	49.0	1.8	68.	171.	0.L
20-25	0.0L	53.	70.	1680.	2.5	39.0	0.0L	43.	146.	0.L
25-30	0.0L	78.	81.	2360.	2.5	75.0	1.7	38.	114.	0.L
30-35	1.1	54.	103.	2140.	2.8	52.0	5.2	98.	96.	0.L
35-40	1.2	36.	90.	2320.	3.6	167.0	4.2	90.	245.	0.L
40-45	1.3	55.	111.	2560.	2.2	138.0	2.1	63.	100.	0.L
45-50	1.4	26.	68.	1770.	1.8	142.0	1.7	53.	103.	0.L
50-55	1.7	19.	59.	2510.	1.8	125.0	4.3	56.	138.	12.
55-60	1.6	42.	57.	6070.	1.5	51.0	1.3	54.	100.	0.L
60-65	1.0	25.	55.	15940.	1.4	36.0	0.0L	59.	110.	0.L
65-70	0.0L	11.	34.	5860.	1.3	39.0	1.5	57.	82.	0.L
70-75	0.0L	9.	43.	3260.	1.5	44.0	1.6	51.	63.	0.L
75-80	0.0L	9.	43.	1060.	2.0	169.0	9.5	59.	62.	0.L
80-85	0.0L	15.	58.	4180.	2.1	95.0	28.0	54.	84.	11.
85-90	0.0L	11.	73.	950.	2.3	3.8	18.0	56.	82.	11.
90-95	0.0L	9.	83.	890.	2.2	1.6	12.0	60.	77.	11.
95-100	0.0L	12.	65.	890.	2.0	1.6	9.9	53.	63.	0.L
100-105	0.0L	12.	73.	860.	1.9	1.8	9.1	51.	81.	0.L
105-110	0.0L	10.	83.	900.	2.2	2.6	11.0	64.	65.	12.
110-115	0.0L	10.	76.	910.	2.2	2.1	12.0	66.	73.	12.

Table 1. (continued)

## NG31 CHEMICAL DATA-continued

SAMPLE	HG	LA	MO	MN	NI	PB	SB	SC	SE	SR
5-10	0.0L	27.	0.L	0.L	67.	13.	22.	0.L	10.	385.
10-15	1.9	0.L	0.L	0.L	45.	10.	19.	0.L	10.	264.
15-20	1.4	0.L	0.L	0.L	110.	13.	35.	0.L	20.	174.
20-25	1.6	0.L	11.	0.L	111.	15.	29.	0.L	10.	125.
25-30	0.0L	0.L	47.	0.L	153.	12.	25.	0.L	50.	143.
30-35	0.0L	24.	13.	0.L	102.	20.	29.	0.L	50.	185.
35-40	0.0L	32.	0.L	0.L	161.	19.	28.	0.L	1000.	174.
40-45	1.5	30.	0.L	0.L	85.	38.	31.	0.L	0.6	152.
45-50	0.0L	30.	0.L	0.L	58.	29.	61.	0.L	0.6	77.
50-55	0.0L	24.	36.	0.L	106.	18.	50.	0.L	0.6	84.
55-60	2.1	0.L	17.	0.L	43.	15.	29.	0.L	0.6	78.
60-65	0.0L	24.	11.	0.L	41.	11.	18.	0.L	0.6	139.
65-70	0.0L	26.	0.L	0.L	60.	11.	4.	0.L	150.	106.
70-75	0.0L	25.	0.L	0.L	64.	10.	0.L	0.L	500.	104.
75-80	0.0L	27.	0.L	0.L	173.	8.	0.L	0.L	200.	80.
80-85	0.0L	39.	0.L	0.L	565.	12.	2.	10.	15.	100.
85-90	0.0L	36.	0.L	0.L	375.	9.	2.	11.	10.	99.
90-95	0.0L	35.	0.L	0.L	263.	8.	0.L	0.L	0.1	98.
95-100	0.0L	32.	0.L	0.L	197.	10.	0.L	0.L	0.1	87.
100-105	0.0L	32.	0.L	0.L	158.	10.	0.L	0.L	0.1	90.
105-110	0.0L	40.	0.L	0.L	144.	9.	0.L	0.L	0.1	90.
110-115	0.0L	38.	0.L	0.L	121.	10.	0.L	12.	0.1	88.
				331.						
				216.						
				700.						
				561.						
				373.						
				360.						
				364.						
				392.						
				144.						
				158.						
				197.						
				263.						
				375.						
				565.						
				173.						
				64.						
				60.						
				41.						
				43.						
				106.						
				58.						
				85.						
				161.						
				102.						
				153.						
				111.						
				110.						
				45.						
				67.						

Table 1. (continued)

## NG51 CHEMICAL DATA-continued

SAMPLE	TL	V	Y	ZN	ZR
5-10	2.6	1070.	38.	173.	0.L
10-15	2.2	980.	28.	158.	0.L
15-20	2.5	1860.	29.	379.	32.
20-25	2.7	2000.	20.	515.	28.
25-30	3.4	1680.	18.	645.	44.
30-35	3.0	1280.	29.	492.	125.
35-40	3.0	2140.	42.	394.	88.
40-45	18.0	4090.	28.	286.	208.
45-50	8.3	0.6	25.	110.	112.
50-55	12.0	0.6	27.	199.	72.
55-60	8.6	0.6	22.	0.L	93.
60-65	1.9	1270.	19.	0.L	166.
65-70	2.0	320.	19.	132.	218.
70-75	1.4	630.	14.	194.	178.
75-80	0.0L	134.	27.	520.	217.
80-85	1.3	193.	26.	3790.	308.
85-90	0.0L	189.	25.	1350.	275.
90-95	0.0L	197.	26.	740.	267.
95-100	0.0L	165.	23.	560.	271.
100-105	0.0L	165.	23.	490.	249.
105-110	0.0L	195.	25.	470.	255.
110-115	0.0L	199.	24.	490.	236.

Table 1. (continued)

## NG47 CHEMICAL DATA

SAMPLE	ELEV	DEPTH	SI	TI	AL	FE	MG	CA	MA	K
65-70	7055.5	67.5	0.6	0.11	2.4	0.40	0.20	0.58	0.00L	0.76
70-75	7050.5	72.5	0.6	0.08	2.2	0.57	0.17	2.10	0.00L	0.54
75-80	7045.5	77.5	0.6	0.11	2.8	0.91	0.22	0.91	0.00L	0.80
80-85	7040.5	82.5	0.6	0.13	3.0	0.54	0.28	0.15	0.00L	0.84
85-90	7035.5	87.5	0.6	0.11	2.6	0.31	0.22	0.09	0.00L	0.63
90-95	7030.5	92.5	0.6	0.11	2.4	0.16	0.17	0.14	0.00L	0.52
95-100	7025.5	97.5	0.6	0.09	2.3	0.38	0.16	0.42	0.00L	0.45
100-105	7020.5	102.5	0.6	0.11	2.7	0.48	0.23	3.50	0.00L	0.61
105-110	7015.5	107.5	0.6	0.10	2.1	0.40	0.21	0.37	0.00L	0.67
110-115	7010.5	112.5	0.6	0.07	1.7	0.49	0.15	2.90	0.00L	0.48
115-120	7005.5	117.5	0.6	0.09	2.0	0.34	0.16	0.33	0.00L	0.65
120-125	7000.5	122.5	0.6	0.07	1.6	0.44	0.15	0.07	0.00L	0.50
125-130	6995.5	127.5	0.6	0.08	1.8	0.51	0.14	0.07	0.00L	0.59
130-135	6990.5	132.5	0.6	0.10	2.0	0.76	0.15	0.07	0.00L	0.69
135-140	6985.5	137.5	0.6	0.10	2.3	0.80	0.19	0.08	0.00L	0.76
140-145	6980.5	142.5	0.6	0.09	2.1	0.69	0.19	0.06	0.00L	0.72
145-150	6975.5	147.5	0.6	0.08	1.9	0.54	0.17	0.34	0.00L	0.63
150-155	6970.5	152.5	0.6	0.09	2.0	0.81	0.18	0.07	0.00L	0.69
155-160	6965.5	157.5	0.6	0.09	2.1	0.78	0.18	0.19	0.00L	0.68
160-165	6960.5	162.5	0.6	0.10	2.1	0.77	0.17	0.32	0.00L	0.70
165-170	6955.5	167.5	0.6	0.09	2.0	0.93	0.15	0.46	0.00L	0.66
170-175	6950.5	172.5	0.6	0.10	2.3	0.89	0.17	0.25	0.00L	0.75
175-180	6945.5	177.5	0.6	0.16	3.8	2.00	0.23	0.16	0.00L	1.00
180-185	6940.5	182.5	0.6	0.10	2.3	0.84	0.17	0.74	0.00L	0.91
185-190	6935.5	187.5	0.6	0.18	4.0	1.50	0.33	1.00	0.00L	1.60
190-195	6930.5	192.5	0.6	0.27	5.3	2.40	0.49	0.42	0.00L	2.30
195-200	6925.5	197.5	39.	0.24	5.1	3.20	0.44	0.61	0.22	2.50
200-205	6920.5	202.5	40.	0.28	4.8	1.90	0.38	0.21	0.00L	2.10
205-210	6915.5	207.5	0.8	0.00B						
210-215	6910.5	212.5	0.6	0.27	4.8	2.00	0.37	0.24	0.00L	2.20
215-220	6905.5	217.5	0.6	0.28	4.5	1.90	0.35	0.34	0.00L	1.90
220-225	6900.5	222.5	40.	0.27	4.1	1.80	1.20	1.40	0.00L	1.90

Table 1. (continued)

## N647 CHEMICAL DATA-continued

SAMPLE	AG	AS	R	BA	BE	CD	CO	CR	CU	GA
65-70	1.0	10.	88.	1230.	2.1	8.4	1.1	55.	91.	0.1
70-75	1.1	23.	90.	1340.	2.1	18.0	1.1	53.	82.	0.1
75-80	0.0L	22.	81.	1320.	2.4	18.0	0.0L	63.	87.	0.1
80-85	1.1	21.	105.	2150.	2.3	11.0	3.2	68.	73.	10.
85-90	0.0L	13.	80.	1370.	2.0	5.6	1.7	59.	68.	0.1
90-95	1.6	14.	75.	1530.	2.5	9.5	2.5	83.	97.	0.1
95-100	1.7	27.	78.	2330.	3.3	15.0	2.8	82.	70.	12.
100-105	1.8	25.	93.	2070.	4.7	38.0	4.4	107.	62.	12.
105-110	1.6	61.	144.	1920.	2.8	72.0	5.4	62.	71.	0.1
110-115	1.8	38.	103.	1560.	3.0	39.0	5.9	66.	40.	12.
115-120	0.0L	29.	93.	2480.	2.5	17.0	2.8	45.	101.	0.1
120-125	0.0L	46.	93.	1470.	1.9	30.0	2.5	36.	85.	0.1
125-130	0.0L	33.	85.	1300.	1.9	25.0	3.4	32.	72.	0.1
130-135	0.0L	34.	89.	1680.	2.1	44.0	4.8	29.	70.	0.1
135-140	0.0L	43.	105.	1610.	2.5	170.0	6.6	38.	82.	0.1
140-145	0.0L	44.	119.	1180.	2.8	0.06	6.7	43.	88.	0.1
145-150	1.1	57.	103.	980.	2.5	0.06	6.2	48.	91.	0.1
150-155	0.0L	46.	99.	1160.	2.1	0.06	5.5	39.	81.	0.1
155-160	0.0L	64.	95.	1390.	2.4	0.06	6.5	39.	86.	0.1
160-165	0.0L	42.	91.	1670.	2.5	148.0	7.9	35.	83.	0.1
165-170	0.0L	47.	84.	1610.	2.2	128.0	5.9	35.	80.	0.1
170-175	0.0L	36.	85.	1750.	2.1	44.0	5.8	29.	71.	0.1
175-180	0.0L	58.	113.	2450.	2.7	37.0	12.0	41.	71.	0.1
180-185	1.5	53.	100.	1590.	2.6	123.0	8.4	54.	87.	0.1
185-190	1.3	42.	148.	1820.	2.8	70.0	12.0	73.	101.	0.1
190-195	1.0	39.	0.6	1470.	3.3	25.0	16.0	118.	106.	10.
195-200	1.1	65.	199.	4970.	3.5	31.0	14.0	88.	83.	0.1
200-205	1.6	57.	167.	2080.	2.8	52.0	14.0	75.	83.	0.1
205-210	0.0B	0.3	0.8	0.8	0.0B	0.0B	0.0B	0.8	0.8	0.8
210-215	1.5	51.	187.	2490.	2.9	29.0	13.0	77.	76.	10.
215-220	0.0L	57.	166.	1650.	2.5	15.0	15.0	73.	79.	0.1
220-225	0.0L	57.	147.	1540.	2.2	13.0	12.0	52.	60.	0.1

Table 1. (continued)

## NG47 CHEMICAL DATA-continued

SAMPLE	HG	LA	MO	MN	NI	PB	SB	SC	SE	SR
65-70	0.0L	22.	0.0L	0.0L	21.	12.	18.	0.0L	20.	80.
70-75	0.0L	0.0L	0.0L	0.0L	16.	12.	36.	0.0L	100.	152.
75-80	0.0L	0.0L	0.0L	0.0L	23.	12.	27.	0.0L	50.	92.
80-85	0.0L	24.	23.	0.0L	17.	11.	37.	0.0L	150.	130.
85-90	0.0L	0.0L	16.	0.0L	15.	11.	40.	0.0L	100.	61.
90-95	0.0L	22.	13.	0.0L	22.	11.	30.	0.0L	500.	58.
95-100	0.0L	31.	31.	0.0L	28.	9.	39.	0.0L	700.	80.
100-105	0.0L	45.	47.	0.0L	67.	6.	29.	0.0L	500.	353.
105-110	0.0L	25.	104.	0.0L	116.	8.	28.	0.0L	1000.	122.
110-115	0.0L	29.	70.	220.	70.	8.	25.	0.0L	500.	362.
115-120	0.0L	24.	59.	0.0L	77.	9.	23.	0.0L	700.	102.
120-125	0.0L	0.0L	96.	0.0L	76.	8.	44.	0.0L	300.	79.
125-130	0.0L	0.0L	73.	0.0L	107.	8.	24.	0.0L	300.	66.
130-135	0.0L	0.0L	91.	0.0L	152.	8.	22.	0.0L	30.	134.
135-140	0.0L	23.	102.	0.0L	209.	10.	32.	0.0L	100.	140.
140-145	0.0L	27.	101.	0.0L	208.	9.	34.	0.0L	100.	139.
145-150	0.0L	0.0L	116.	0.0L	211.	10.	45.	0.0L	70.	64.
150-155	0.0L	0.0L	125.	0.0L	203.	9.	38.	0.0L	70.	59.
155-160	0.0L	0.0L	128.	0.0L	242.	9.	49.	0.0L	50.	70.
160-165	0.0L	0.0L	87.	0.0L	197.	8.	30.	0.0L	20.	107.
165-170	0.0L	0.0L	64.	0.0L	147.	13.	33.	0.0L	30.	116.
170-175	0.0L	0.0L	62.	0.0L	138.	9.	25.	0.0L	15.	102.
175-180	0.0L	31.	97.	0.0L	265.	10.	31.	0.0L	20.	172.
180-185	0.0L	25.	80.	0.0L	198.	12.	37.	0.0L	50.	90.
185-190	0.0L	28.	57.	0.0L	213.	14.	31.	0.0L	30.	150.
190-195	0.0L	38.	38.	264.	227.	15.	17.	12.	15.	115.
195-200	0.0L	50.	38.	240.	249.	18.	40.	13.	15.	392.
200-205	0.0L	40.	64.	0.0L	267.	17.	27.	10.	20.	156.
205-210	0.0B	0.0B								
210-215	0.0L	41.	63.	0.0L	236.	14.	28.	11.	15.	207.
215-220	0.0L	40.	82.	0.0L	301.	14.	16.	0.0L	15.	155.
220-225	0.0L	35.	71.	208.	254.	21.	27.	0.0L	0.0L	113.

Table 1. (continued)

## NG47 CHEMICAL DATA-continued

SAMPLE	TL	V	Y	ZN	ZR
65-70	2.5	240.	50.	83.	42.
70-75	3.1	1390.	30.	0.L	23.
75-80	2.4	1650.	41.	76.	43.
80-85	11.0	2710.	24.	0.L	0.L
85-90	8.4	1740.	25.	0.L	0.L
90-95	1.8	1960.	45.	0.L	0.L
95-100	4.0	5460.	65.	0.L	0.L
100-105	1.3	4700.	76.	0.L	29.
105-110	2.0	2790.	33.	381.	21.
110-115	2.5	5270.	37.	0.L	0.L
115-120	2.0	3410.	63.	130.	32.
120-125	4.2	3060.	20.	237.	20.
125-130	3.1	2680.	18.	188.	0.L
130-135	3.0	1730.	18.	139.	30.
135-140	4.0	3190.	25.	681.	48.
140-145	2.9	3480.	23.	940.	33.
145-150	3.7	2940.	42.	2240.	30.
150-155	4.2	2820.	16.	2280.	20.
155-160	3.2	2870.	36.	2410.	30.
160-165	1.4	1930.	26.	1590.	46.
165-170	2.5	1480.	26.	1260.	26.
170-175	1.9	1250.	23.	901.	24.
175-180	4.1	1610.	35.	2060.	144.
180-185	3.5	1630.	53.	2090.	92.
185-190	2.7	1130.	39.	1710.	122.
190-195	3.6	570.	56.	612.	192.
195-200	5.9	570.	64.	820.	207.
200-205	8.0	700.	47.	1770.	282.
205-210	0.08	0.3	0.B	0.B	0.B
210-215	6.4	540.	41.	1320.	284.
215-220	7.1	540.	50.	787.	283.
220-225	9.8	530.	36.	523.	317.