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Vectoring volcanogenic massive sulphide deposits using rare earth elements and other pathfinder elements at the Ruttan mine, Manitoba (NTS 63B5)

by G.H. Gale

Summary

This article summarizes the results of geochemical studies undertaken at the Ruttan mine in 2002. Assay pulps and grab samples from drillcores that intersected the Cu-rich East Lens and the Zn-rich Zinc Zone were analyzed for major, trace and rare earth elements (REE). In addition, selected samples were analyzed from a series of five cores from drillholes located at approximately 100 m intervals northeastward along the strike of the ore zone and associated tuffaceous exhalite. Europium deviation (Eud) in the ‘upper exhalite’ provides a reliable vector to volcanogenic massive sulphide (VMS) mineralization at a distance of over 400 m from significant Zn assay values. Commonly used VMS ‘pathfinder elements’ (e.g., Cu, Zn, Pb, Ag, Mo, Sn and Ba) are present within both the ores and related exhalites. These elements do not show a systematic variation away from the deposit within the uppermost tuffaceous exhalite, which is stratigraphically equivalent to the Zinc Zone. Both Eud and ‘pathfinder’ elements identify the lowermost tuffaceous exhalite, which overlies the footwall alteration zone and appears to be stratigraphically equivalent to the Cu-rich East Lens.

Introduction

This project forms part of a larger program initiated in 1997 to characterize the behaviour of REE within the ores and hostrocks of the Ruttan mine for possible use as a guide to exploration for VMS mineralization. Drillcore samples collected in 2002 from the Ruttan mine and stratigraphically equivalent rocks to the northeast were analyzed for major elements, base metals and trace elements, including the rare earth elements, using the ‘4Litho standard’ analytical method at Activation Laboratories Ltd. in Ancaster. The objectives of this portion of the project are to 1) test the proposal (Gale et al., 1997) that Eud values could be used to vector VMS mineralization, and 2) investigate the eastward extension of strata hosting the deposit for indications of additional mineralization. The inclusion of high-quality base-metal and other trace-element data permit a comparison of the effectiveness of using standard ‘pathfinder elements’ (Govett, 1983), together with the REE data, to vector VMS mineralization. This article is a preliminary report on the viability of using REE and other ‘pathfinder’ elements to both characterize the hostrocks and vector VMS mineralization at distances of more than 400 m from a known orebody. Cores from all surface drillholes sampled were relogged in detail with the aid of company drill logs. Additional follow-up samples were collected in 2003, and further analyses will be undertaken.

This report provides analytical data for ores, exhalites and a section through the ‘ore equivalent’ and footwall alteration zone, approximately 600 m distal to the orebody. It includes data for solid sulphide and near-solid sulphide samples from the compositionally contrasting Cu-rich and Zn-rich orebodies and disseminated sulphide-bearing ores. Multiple analyses of exhalite-bearing rocks and hostrocks along the northeast extension of a sequence of rocks considered here to be the ‘upper exhalite’ provide geochemical information on exhalites and hostrocks. These data permit potential users of this methodology to observe the variations in REE and ‘pathfinder elements’ encountered within different ores and ‘ore equivalent’ rocks over a strike distance of approximately 600 m from the orebody.

A geochemical profile through portions of drillhole 91-06, situated approximately 600 m east of the orebody, provides limited data for approximately 400 m of both unaltered and altered footwall rocks, and detailed information for approximately 60 m of ‘ore equivalent’ rocks that stratigraphically overlie the footwall alteration zone. The data for drillcore 91-06 are organized to illustrate the variations from stratigraphically unaltered rocks in the footwall of the deposit, through the footwall alteration zone and ‘ore equivalent’ rocks, and into the unaltered hangingwall rocks. The ‘ore equivalent’ rocks contain a number of beds of exhalite (chert-like rocks, quartz-sericite± pyrite schist and porphyroblastic chlorite-cordierite-sericite-biotite rocks) interlayered with mafic, intermediate and felsic volcanic sedimentary rocks. Consequently, for the purposes of this report, the ‘ore equivalent’ rocks are separated into ‘lower exhalite’, ‘middle exhalite’ and ‘upper exhalite’ sequences.

1 Eud = % deviation of chondrite-normalized Eu from Eu* (see Gale et al., 1997, 2002)
Geology of the Ruttan deposit

The Ruttan deposit consists of a number of stacked sulphide lenses (Fig. GS-9-1) that are enclosed in extensively altered, reworked felsic volcanic or volcaniclastic rocks. The sulphide lenses are underlain by a thick sequence of altered rocks of ‘dacitic’ composition that form a footwall alteration zone to the massive sulphide deposit (Speakman et al., 1982; Baldwin, 1988). The deposit and its hostrocks were folded, metamorphosed to the amphibolite facies, and subsequently faulted and extensively sheared. Porphyroblasts of cordierite, staurolite, andalusite, anthophyllite, chlorite, biotite, sericite and gahnite are common in schist, derived from altered rocks, that encloses the sulphide lenses. Locally, chalcopyrite, sphalerite, galena and anhydrite are mobilized into late fractures. Although individual ore lenses have been disrupted by faults, boudins and shears, the deposit and its hostrocks consistently young towards the south (Fig. GS-9-1; Speakman et al., 1982). This is confirmed not only by the superposition of the Zinc Zone stratigraphically above the Cu-rich East Lens, but also by the distribution of metal-zoned sulphide lenses overlying alteration in a ‘classic’ VMS configuration (Fig. GS-9-2, -3) in the lower portion of the East Lens (Gale et al., 2002). Although altered rocks occur in the hangingwall of some solid sulphide lenses, metal zonation within individual ore lenses and between lenses, together with a clearly defined footwall alteration zone, confirm that the deposit occurs on the north limb of an upward-facing synform.

The ‘North Wall Shear’ is a late fault that appears to displace the sulphide deposit upward relative to the footwall alteration that occurs to the northwest of this fault. Ames and Taylor (1996) deduced from drillcore and underground examinations that there was a sinistral component to the movement in the area northwest of the fault. Their interpretation favours placement of the ‘ore equivalent’ strata at the position of exposed exhalites in an area north-northeast of the deposit.

Figure GS- 9-1: General geology of the Ruttan VMS deposit (after Speakman et al., 1982); location of Figure GS-9-2 indicated by cross-section.
Correlation of rock units, especially the ‘ore equivalent’ rocks, north of the ‘North Wall Shear’ is uncertain. Additional mapping and chemistry are required to assess the significance of an approximately 100 m thick sequence of reworked felsic sedimentary rocks, mapped as quartz-feldspar porphyry by Ames (1996), in establishing the ‘ore equivalent’ rocks beyond the ‘North Wall Shear’; consequently, data for drillcores from north of this fault are not discussed here.

Chemistry of the Ruttan deposit ores

Grab samples collected from the mineralized portion of drillcore UX5730 provide a section through the Cu-rich East Lens (Fig. GS-9-3). Assay pulps from three drillcores (UD5711, UD5791 and UD5792) through the Zinc Zone provide continuous geochemical sections through portions of the footwall alteration zone, ores and hangingwall of the markedly different and stratigraphically overlying Zn-rich ore lenses. Drillhole UD5711 (not shown) intersected abundant altered rocks and narrow sections of layered sulphides near the end of an ore lens approximately 210 m along strike from the one intersected in drillholes UD5791 (Fig. GS-9-4) and UD5792; analytical data for drillholes UD5711 and UD5792 will be presented in a later publication.

East Lens and Zinc Zone

A lithological profile through drillhole UX5730 (Fig. GS-9-3) illustrates company assay data and the relative position of REE profiles for representative grab samples. This diagram illustrates the Cu-rich basal and Zn-rich upper parts of the solid sulphide zone. The REE profiles for grab samples from the ores show a marked light REE enrichment in all samples, a nearly flat heavy REE profile and a pronounced negative Eu\(^d\) anomaly that is typical of footwall alteration rocks associated with VMS deposits. A silicic rock that is interpreted as recrystallized chert has Eu\(^d\) values near zero, and the REE profiles have a pronounced negative slope from La to Lu. The absence of positive Eu\(^d\) values in the sulphides in this zone may be a function of fluid chemistry at the time of deposition, or mobilization of Eu by later fluids that deposited mineralization in the Zinc Zone.

Figure GS-9-4 illustrates metal concentrations, lithology and schematic REE profiles for drillhole UD5791 through the Zinc Zone on mine section 49+00. In this drillhole, there is a progressive change from negative Eu\(^d\) values in the footwall of the ore zone, to moderately positive Eu\(^d\) values within the zone, to strongly positive Eu\(^d\) values in the uppermost part of the ore zone. The uppermost samples in this drillhole have negative Eu\(^d\) values that are comparable to those of hangingwall rocks not associated with mineralization.

Trace metals that are commonly deposited distal to VMS deposits are used as indicators or ‘pathfinder’ elements to identify VMS-bearing strata (Govett, 1983). A number of these elements are present in the both the Cu-rich and Zn-rich ores. Figure GS-9-5 illustrates that anomalous Eu\(^d\) values (−10 to +195%) are associated with anomalous concentrations of Zn, Ag and Pb in the ores. Other potential ‘pathfinder’ elements (Co, As, Sn, Sb, Ba, and Bi) are also present in the Zn-rich ores but do not show a systematic relationship to Zn concentrations.

Geochemical data from drillholes UD5711 and UD5792 (not shown) are similar to data obtained from drillhole UD5791, in that positive Eu\(^d\) values are associated with some of the near-solid sulphide and solid sulphide layers, whereas other sulphide-rich layers have Eu\(^d\) values that are near zero. Altered rocks that occur between sulphide layers in an ore zone may have strongly negative or near-zero Eu\(^d\) values. There is no direct correlation between Cu and Zn contents, Eu\(^d\) values or the presence of other pathfinder elements within the ore zones. The data from drillhole UD5711 indicate that strong positive Eu anomalies are present at several different stratigraphic levels within some parts of the Zinc Zone. This suggests that ‘zone refinement’ by later metal-depositing fluids did not occur (McClenaghan et al., 2003) and the Zinc Zone probably represents the stratigraphically highest mineralization in this deposit. Local
repetition of sulphide layers by small-scale isoclinal folds within individual ore lenses cannot be ruled out at this time.

The REE profiles for samples from drillcores UX5730 and UD5791 are shown in Figures GS-9-6a and -6b. There is an absence of positive Eu anomalies in all of the solid sulphide samples from drillcore UX5730; these samples are from the lowermost and Cu-rich sulphide lens and probably represent higher temperature fluids than those that deposited the stratigraphically higher Zinc Zone. The quartz-rich rocks (‘chert-like’) near the top of the sulphide lens have distinctive near-zero Eu\textsuperscript{d} values and strongly negative REE profiles that are similar to those observed in other samples of chert and ‘chert-like’ rocks.

The presence of REE profiles with strongly depleted Eu in footwall rocks to the Cu-rich East Lens indicates that this zone occurs directly over a hydrothermal vent with high-temperature and low-pH fluids (Gale et al., 1999). The low REE contents observed in some of the solid sulphide samples from the Cu-rich zone are probably an indication that these elements, for the most part, either remained in solution during deposition of the base metals or, if deposited together with the sulphides, were stripped by later, hot, reducing fluids during postdeposition ‘zone refinement’ processes (McClenaghan et al., 2003). Either of these processes can be invoked to explain the absence of positive Eu\textsuperscript{d} values in the Cu-rich ore zone.

There is an absence of strong negative Eu anomalies in both the sulphide- and silicate-rich samples from drillcore UD5791 through the Zinc Zone. This suggests that the hydrothermal fluids depositing the Zinc Zone were either lower...
temperature than those that deposited the Cu-rich East Lens or the mineral-producing vent was situated some distance from the site of deposition (i.e., parts of the Zinc Zone are distal deposits).

**Chemistry of distal exhalites**

Core from five drillholes that tested exhalites and hostrocks along the extension of the Ruttan ‘ore equivalent’ stratigraphy at approximately 100 m intervals were analyzed together with core from two drillholes that were designed to intersect the extension of the Ruttan exhalites north of the ‘North Wall Shear’ (Fig. GS-9-7). The data for samples collected from drillholes 89-05 and 96-02 are inconclusive in defining exhalites and are not discussed here. Drillholes 89-12, 93-08, 93-07 and 91-06 intersected exhalites related to the Ruttan deposit and the data clearly define a decrease in Eu\(^d\) values with increasing distance from the deposit along the ‘upper exhalite’ zone. The presence of weakly altered and unaltered hostrocks immediately below the ‘upper exhalite’ suggests that these exhalites were deposited distal to their hydrothermal vent site.

Five samples of the ‘upper exhalite’ in drillcore 89-12 with 0.03 to 5% Zn have Eu\(^d\) values that range from +6 to +220% (Fig. GS-9-8a). In contrast, a sample of the hangingwall rocks (89-12-107’6") has a Eu\(^d\) value of approximately

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**Table GS-9-1: Legend for Figures GS-9-3, GS-9-4, GS-9-5; unit numbers and abbreviations are those used by staff at the Ruttan mine.**

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
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<tbody>
<tr>
<td>1a</td>
<td>Altered footwall volcaniclastic rocks</td>
</tr>
<tr>
<td>2</td>
<td>Quartz-rich rocks: 2a, includes ‘chert-like’ rocks</td>
</tr>
<tr>
<td>3</td>
<td>Solid sulphides with high Cu and/or Zn</td>
</tr>
<tr>
<td>4</td>
<td>Near-solid sulphides</td>
</tr>
<tr>
<td>5</td>
<td>Solid sulphides with low Cu and/or Zn</td>
</tr>
<tr>
<td>6</td>
<td>Schistose rocks, commonly sheared</td>
</tr>
<tr>
<td>7</td>
<td>Sedimentary rocks: a, felsic; b, mafic; I, intermediate</td>
</tr>
<tr>
<td>9</td>
<td>Dikes: b, mafic; I, intermediate</td>
</tr>
<tr>
<td>10</td>
<td>Porphyroblastic schist</td>
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<tr>
<td>11</td>
<td>Siliceous dikes: Q, quartz porphyry; F, feldspar porphyry</td>
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<td>Rhyolite</td>
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<td>14</td>
<td>Andesite</td>
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<tr>
<td>15</td>
<td>Basalt</td>
</tr>
</tbody>
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**Mineral abbreviations:**

- M: magnetite
- P: pyrite
- R: pyrrhotite
- C: chalcopyrite
- Z: sphalerite
- Q: quartz
- M: magnelite
- N: gahnite
- m: actinolite
- n: andalusite
- y: anhydrite
- l: anthophyllite
- o: biotite
- q: chert
- c: chlorite
- r: cordierite
- h: hornblende
- s: sericite
Figure GS-9-4: Cu, Zn, Fe, lithology and schematic REE profiles for drillhole UD5791 through the Zinc Zone; see Table GS-9-1 for legend.

−30%. High values of the ‘pathfinder’ elements Cu, Zn, Ag, Sb, Sn and Pb are also present. Assay values of up to 5% Zn were obtained from the uppermost mineralized zone in this drillcore. This mineralization can be followed in other drillcores along strike to the deposit and represents the same stratigraphic level as the Zinc Zone.

Four samples from drillcore 93-08 (Fig. GS-9-8b) contain a maximum of 606 ppm Zn, 222 ppm Cu, 141 ppm V, 5.5 ppm Ag and 151 ppm Pb. These samples have consistently strong positive Eu^d^ values; one of the samples has a Eu^d^ value of over 450%. The interval sampled represents the eastward extension of the ‘upper exhalite’ intercept in drillcore 89-12.

Samples from drillcores 93-07, 89-03 and 91-06 also show positive Eu^d^ values that decrease in magnitude with increased distance from the VMS deposit along the ‘upper exhalite’, but the ‘pathfinder’ elements are not consistently distributed along this unit.

Drillhole 91-06

Fifty-three samples were collected from drillcore 91-06, in part during an earlier investigation of alteration-zone chemistry at the Ruttan deposit and as part of this study to establish variations in REE and trace elements beyond the limits of the ore zones. This 1391 m long drillhole provides a unique section through the eastern limits of the alteration zone. It intersected approximately 900 m (3000 ft.) of hangingwall rocks and 60 m (200 ft.) of ‘ore equivalent’ rocks, and extended approximately 400 m (1300 ft.) into the ‘footwall’ rocks. Metamorphosed ‘chert-like’ rocks are interlayered
with relatively unaltered intermediate and felsic volcaniclastic rocks at several intervals in the ‘ore equivalent’ section, which also contains abundant quartz±sericite±biotite±pyrite schist. The relatively unaltered rocks are predominantly felsic and intermediate sandstone and grit; thin, medium-grained, intermediate and mafic dikes intrude the other rocks. Grab samples (approximately 30 cm of core) and continuous sections (commonly 1.5 m intervals) were collected for analysis from material below the 900 m interval in the drillcore in order to characterize the extent of alteration, distribution of ‘pathfinder’ elements and behaviour of the REE some 600 m beyond the limits of the orebody.

Drillcore rock types are indicated on Figure GS-9-9. The section is ‘right way up’, with the oldest rocks at the bottom of the drillcore. Below approximately 975 m (3200 ft.), the rocks are predominantly quartz-sericite-pyrite schist derived from altered rhyolitic and/or dacitic volcaniclastic rocks that represent the eastern margin of the ‘footwall alteration zone’ to the Ruttan deposit. These rocks are overlain by the ‘ore equivalent’ rocks, which are separated into three segments, ‘lower exhalite’, ‘middle exhalite’ and ‘upper exhalite’, for the purpose of this report (Fig. GS-9-9). The quartz-rich sericitic and pyritic rocks immediately above the alteration zone are overlain by relatively unaltered felsic sandstone and quartz-sericite-pyrite schist that extend upwards to approximately 950 m (3130 ft.); these are collectively referred to as the ‘lower exhalite’. Between 952 and 931 m (3123 and 3056 ft.), the ‘middle exhalite’ includes interlayered intermediate sandstone (greywacke), quartz–sericite±biotite±pyrite schist, minor tuffaceous basaltic rocks and several thin units of quartz-rich ±pyrite rocks. Between 931 and 915 m (3056 and 3007 ft.), the rocks are predominantly intermediate sandstone and felsic volcaniclastic rocks with minor tuffaceous basaltic rocks that are interlayered with quartz-rich and quartz-sericite–rich rocks; these are referred to as the ‘upper exhalite’ unit.

**Footwall alteration zone**

Sample 91-06-4538, collected near the base of the drillcore and located north of the Hanging Wall Shear (Fig. GS-9-1), has 69% SiO₂ and the overall chemistry of rhyodacite-rhyolite. This sample is not depleted in Na or enriched...
Figure GS-9-6: REE profiles for assay pulps from drillcores a) UX5730 and b) UD5791. Note that, in drillcore UX5730, samples UX5730-186 and -190.5 represent ‘chert-like’ rocks, and the spiky patterns for the samples with near-chondrite values are typical of the low concentrations found in many iron sulphide–rich solid sulphide samples. The two samples with heavy REE values near chondrite represent sphalerite-rich near-solid sulphide.
in K, but has a TiO₂/Zr ratio that plots away from the footwall rhyolite on Figure GS-9-10a; this suggests that it represents unaltered dacitic footwall rocks (cf. Ames, 1996). Visibly altered footwall rocks that occur between approximately 975 and 1035 m (3200 and 3400 ft.) in the drillcore have TiO₂/Zr ratios that are typical of rhyolite found elsewhere in the Flin Flon–Snow Lake area (Gale and Dabek, 1996). These footwall rhyolitic rocks are strongly depleted in Na and enriched in K (2.2–3.8% K₂O) because most of the samples plot close to the K = 1 line on alkali alteration plots (Fig. GS-9-10b, -10c; Stanley and Madeisky, 1994). The REE profiles for the altered footwall rocks and sample 91-06-4538 are nearly identical (Fig. GS-9-11) and suggest a common magmatic source. In addition, several of the samples (91-06-3361, -3372) exhibit a marked depletion in Eu relative to the other rhyolitic samples (Fig. GS-9-11); strong negative Eu anomalies are typical of footwall rocks found in many VMS alteration zones that were subjected to hot acidic fluids (Gale et al., 1997, 1999).

**‘Lower exhalite’**

Sample 91-06-3192, from an interval of quartz–sericite±pyrite schist, has a TiO₂/Zr ratio similar to the altered footwall rocks, and a Eu-negative REE profile that is similar to the least altered footwall rhyolitic rocks (Fig. GS-9-11). The higher total REE contents may be the result of removal of some minerals during alteration, as indicated by the low SiO₂ (63%) and Na₂O (0.5%) and/or the addition of aluminous clay minerals, as indicated by the high K₂O (6.12%) and Al₂O₃ (20%) contents.

Samples (91-06-3187, -3181) of similar quartz–sericite±pyrite (‘chert-like’) rocks that immediately overlie sample
Figure GS-9-8: a) REE profiles for samples from the ‘upper exhalite’ in drillcore 89-12; note that sample 89-12-107′6″ represents unaltered hanging wall rocks; b) REE profiles for samples from the ‘upper exhalite’ in drillcore 93-08.

91-06-3192 have TiO₂/Zr ratios that are similar to the altered footwall rocks. This indicates that they are derived from felsic volcaniclastic rocks. Although they have slightly different heavy REE contents, their light REE contents are identical and their overall REE patterns are similar to those of the ‘rhyolitic’ footwall rocks. The moderately positive Eu anomalies are considered to be derived as precipitates from hydrothermal fluids (Gale et al., 1999). Anomalously high ‘pathfinder’ elements (Zn, Pb and Ag) are also present, but similar values also occur in the underlying altered footwall rocks. This quartz-sericite-pyrite schist is clearly discriminated from other quartz–sericite±pyrite rocks in this section by its positive Eu anomalies. The TiO₂/Zr ratios and REE profiles are quite different from those of other ‘chert-like’ rocks. Therefore, these rocks are considered to be tuffaceous exhalites that are a mixture of felsic volcaniclastic material (sandstone?) and exhalite-derived precipitates and/or detritus.

In contrast, rock samples from ‘felsic sandstone’ (unit 7a, Fig. GS-9-9), immediately overlying the ‘chert-like’ rocks, have the same TiO₂/Zr ratios as the footwall rocks, but exhibit neither Na depletion nor K enrichment. They have abnormal amounts of pyrite (7 to 12% Fe₂O₃) for rhyolite, and several samples show minor enrichments in Ag and Ba. Their REE profiles are typical of rhyolite and are not enriched in Eu; these rocks are considered to be unaltered rhyolite-derived sandstone.

‘Middle exhalite’
Drillcore in the interval 925 to 954 m (3065 to 3126 ft.) consists predominantly of quartz-rich, quartz–sericite and
quartz–biotite±sericite schist. These rocks are commonly white to pale grey and interlayered with rocks that contain abundant chlorite±biotite±cordierite schist. Drillcore logs indicate that these rocks include intermediate sedimentary rocks (greywacke), mafic tuffaceous sedimentary rocks and altered (exhalite-derived?) rocks. Most of the samples have lower SiO$_2$ and significantly different TiO$_2$/Zr ratios than the underlying footwall ‘rhyolitic’ rocks. In general, TiO$_2$ values are much higher than those commonly found in rhyolitic rocks and they plot well away from the footwall rhyolitic rocks on the TiO$_2$/Zr diagram (Fig. GS-9-12a). The two samples on Figure GS-9-12a with the same TiO$_2$/Zr ratio as the footwall rocks are ‘chert-like’ rocks (91-06-3089, -3096). These occur between an intermediate sedimentary rock (91-06-3118) and a tuffaceous basaltic rock (91-06-3120) that plot below line C on Figure GS-9-12a, in the field commonly occupied by andesite and basalt.

Five samples have low Na contents (<1% Na$_2$O) and five have >3% K$_2$O. Six of the samples plot close to the feldspar model line (line B) on Figure GS-9-12b; this suggests that they have not undergone extensive alkali metasomatism (Stanley and Madeisky, 1994). Sample 91-06-3120, a weakly altered mafic tuffaceous rock (?), and samples 91-06-3086, -3101 and -3104, from intermediate intrusions, all plot near the feldspar model line on Figure GS-9-12b. Quartz-rich rocks (‘chert-like’) also plot close to the feldspar model line. These samples have undergone minor alkali metasomatism (Fig. GS-9-12c) because they plot to the left of the vertical line that represents unaltered felsic rocks; unaltered intermediate and mafic rocks plot to the right of the vertical line on this diagram. Therefore, the chemical variations in these rocks cannot be explained by alkali metasomatism. Some of the other samples in this segment of
Figure GS-9-10: TiO₂/Zr and alkali variation diagrams for ‘footwall’ and ‘lower exhalite’ rocks from drillcore 91-06:
a) TiO₂/Zr ratios for samples of ‘lower exhalite’ and footwall rhyolitic rocks in drillcore 91-06; sample 4538 is from the base of the drillhole and probably represents the footwall ‘dacite’ of Ames (1996); b) Alkali molar ratios for samples shown in (a); most of the footwall samples plot on or near the sericite line (line C), whereas the overlying rocks, in the ‘lower exhalite’ section, plot near the feldspar model line (line B), which indicates that they have undergone only minor, if any, alkali alteration and are probably derived from rhyolite; on this diagram, dacite, andesite and basalt plot away from the origin and between lines B and A (the upper limit for unaltered basaltic rocks); c) Potassium alteration diagram based on molar ratios; altered footwall samples and sample 3192 plot near the line K = 1, which indicates extensive Na and Ca depletion and K addition, whereas most of the samples from the ‘lower exhalite’ plot near the vertical line representing unaltered rhyolitic rocks. See Stanley and Madeisky (1994) for details on plots 10b and 10c.
drillcore exhibit strong alkali metasomatism because they plot towards the K = 1 line on Figure GS-9-12c.

The REE plots for samples from the ‘middle exhalite’ core interval are separated into ‘lower’ and ‘upper’ parts for clarity (Fig. GS-9-13a, -13b). Both the quartz-sericite schist and the intermediate sedimentary rocks (greywacke) have similar REE patterns, with higher heavy REE values and less light REE enrichment than the underlying ‘rhyolitic’ rocks (cf. Fig. GS-9-11, -13). This suggests that the protolith for most, if not all, of the quartz-sericite (‘felsic’) rocks in the ‘middle exhalite’ segment of this drillcore is altered intermediate (andesitic?) volcaniclastic sandstone.

Sample 91-06-3120 is a fine-grained amphibole-bearing rock with 49% SiO₂, 8% MgO, 4% K₂O, 0.7% TiO₂, 195 ppm V, 250 ppm Cr, 516 ppm Cu, 564 ppm Zn, 1.3 ppm Ag, 14 ppm Cs and 66 ppm Pb. The low heavy REE contents and slight light REE enrichment for this rock are similar to some basalt and mafic to intermediate intrusions in the Ruttan area (cf. Ames, 1996); however, the positive Eu anomaly is unusual. The high MgO, TiO₂, V and Cr are different than any of the chlorite- and amphibole-rich exhalites. Consequently, this sample is considered to be representative of a magmatic rock rather than a hydrothermal vent signature; however, its origin is uncertain because its Al/Zr ratio is quite different from known magmatic rocks in the area (Fig. GS-9-12b).

Eight samples (91-06-3104, -3101, -3096, -3089, -3086, -3084, -3081 and -3079) on Figure GS-9-13b exhibit ‘abnormal’ REE profiles relative to the samples of intermediate sedimentary rocks (Fig. GS-9-13a, -13b). Samples 91-06-3104, -3101 and -3086 have lower SiO₂, and higher Fe₂O₃, MgO, TiO₂, V, Cr and Ni than the intermediate sedimentary rocks. Their REE profiles also differ from the other rock types and their Eu⁴⁺ values are close to zero. Although the high TiO₂ and Cr contents indicate that these rocks are probably representative of intrusions, a tuffaceous exhalite origin cannot be ruled out at this time. The two samples of ‘chert-like’ rocks, samples 91-06-3089 and -3096, have major-element compositions that are similar to those of ‘rhyolite’. Their flat to slightly positive Eu anomalies and intensely depleted heavy REE contents give REE patterns quite unlike those of rhyolite but identical to the REE patterns obtained for ‘chert-like’ rocks that overlie the East Lens solid sulphide layers (Fig. GS-9-6a). The major-element compositions and enhanced Eu contents of samples 91-06-3084 and -3081 (Eu⁴⁺ near zero) and sample 91-06-3079 (Eu⁴⁺ = -20%) indicate that these rocks are probably tuffaceous exhalite. These rocks are probably derived by the addition of minor exhalative material to intermediate volcanosedimentary rocks, as suggested by their anomalously high Zn, As, Ag, Pb and Bi; sample 91-06-3081 also contains abundant pyrite (14% Fe₂O₃).

Samples 91-06-3084, -3083 and -3081, from a section of porphyroblastic sericitic and pyritic rocks with cordierite
Figure GS-9-12: TiO\textsubscript{2}/Zr and alkali variation diagrams for 'middle exhalite' rocks in drillcore 91-06: a) TiO\textsubscript{2}/Zr variation diagram; line A represents the average TiO\textsubscript{2}/Zr ratio of footwall 'rhyolitic' rocks (cf. Fig. GS-9-10a); lines B and C indicate the limits of intermediate rocks in this segment of drillcore; numbers on this and subsequent diagrams indicate specific samples discussed in the text; b) molar ratio alkali variation diagram for 'middle exhalite' rocks, illustrating that some of the intermediate rocks exhibit some degree of alkali alteration because they plot towards or on the sericite line (line C), whereas the 'chert-like' rocks and intermediate intrusions plot close to the feldspar model line (line B); however, the Al/Zr ratio of these rocks forces them to plot well away from the fields occupied by felsic and intermediate volcanic rocks and attests to their high Al and/or low Zr contents; c) diagram illustrating the variable degree of potassium metamorphism in the 'middle exhalite' rocks; 'chert-like' and high TiO\textsubscript{2} rocks cluster near the vertical line, which represents the feldspar model line for unaltered felsic rocks.
and anthophyllite, directly underlie quartz-sericite schist with abundant (<20%) pyrite and trace amounts of sphalerite (e.g., sample 91-06-3079). Samples 91-06-3081 and -3079 contain the highest concentrations of the 'pathfinder' elements Zn (5000 ppm), Pb (1483 ppm), Ag (2.3 ppm), As (60 ppm) and Bi (8.5 ppm) of any quartz-rich sericitic and pyritic rocks in the 'middle exhalite'. Most of these samples have REE profiles that are similar to the intermediate sedimentary rocks, but both 91-06-3084 and -3081 have enhanced Eu values that are contributed either directly from the mineralizing fluids or indirectly from erosion of Eu-rich precipitates from the adjacent sulphide body. Although the enhanced Eu concentrations in samples 91-06-3084 and -3081 indicate the presence of an active hydrothermal vent capable of producing VMS mineralization (Gale et al. 1999), the 'pathfinder' elements in this instance provide a stronger indication of proximity to a VMS deposit.

Upper exhalite

Samples from the core interval 915 to 931 m (3000 to 3056 ft.) represent ‘chert-like’, exhalite, felsic sandstone, intermediate sandstone and mafic sedimentary rocks. Most of the samples have similar TiO$_2$/Zr ratios and plot well within the same field as the underlying intermediate sedimentary rocks (cf. Fig. GS-9-12a, -14a). These rocks have a wide range in TiO$_2$ (0.4 to 0.8%) and Zr (100 to 160 ppm). Four samples from a unit of porphyroblastic biotite-sericite-cordierite-andalusite-pyrite schist (91-06-3056, -3052, -3046, -3045), with SiO$_2$ contents of 60 to 69%, have TiO$_2$/Zr
Figure GS-9-14: Variation diagrams for 'upper exhalite' rocks in drillcore 91-06: a) TiO$_2$/Zr variation diagram; line A represents the average TiO$_2$/Zr ratio of footwall 'rhyolitic' rocks (cf. Fig. GS-9-11a); lines B and C indicate the limits of intermediate sedimentary rocks in the 'middle exhalite' segment of the drillcore; b) molar ratio alkali variation diagram for 'upper exhalite' rocks; diagram illustrates that most of the rocks exhibit little alkali alteration because they plot close to the feldspar model line (line B), although the porphyroblastic schist samples plot close to the sericite line (line C).

ratios that are similar to those of quartz-sericite-rich rocks with >70% SiO$_2$ (samples 91-06-3030, -3029, -3026); this suggests a common source. The flat heavy REE, moderately depleted Eu and weakly enriched light REE patterns for samples 91-06-3026a to -3056 in Figure GS-9-15a also suggest a common parentage for most of these layered rocks. The lower heavy REE values for samples 91-06-3019, -3020.5 and -3022 may be due to a slightly different (more mafic?) source material, as indicated by TiO$_2$/Zr ratios that fall in the basalt field on Figure GS-9-14a.

Most of these rocks are not extensively altered because they plot close to the feldspar model line (line B, Fig. GS-9-14b) on the alkali metasomatism diagram of Stanley and Madeisky (1994). Variation in their positions on Figure GS-9-14a appears to be the result of higher Al$_2$O$_3$ contents in rocks with the lower SiO$_2$ contents; this probably reflects high clay contents in the sediment. The variation in composition of these rocks is probably a result of mixing volcanioclastic material and alteration detritus (sericite) rather than in situ alteration. Samples that plot close to the sericite line on Figure GS-9-14b are porphyroblastic schist (91-06-3045 to -3056).

The REE profiles for the remaining four samples (Fig. GS-9-15b) include sample 91-06-3007, an intermediate volcaniclastic rock from the hangingwall. It has a REE profile that is quite similar to the basaltic andesite of island-arc tholeiite affinity exposed elsewhere in the Ruttan area (Ames, 1996). The REE profile for this rock differs from those of the stratigraphically underlying intermediate sedimentary rocks, in that it does not have a Eu depletion anomaly and the rock has over 100 ppm V. This sample also plots in the field for basaltic rocks on both the TiO$_2$/Zr and alkali metasomatism diagrams.
Samples 91-06-3026i and -3055, both with over 1% TiO$_2$, plot in the fields commonly occupied by andesite and basalt on several variation diagrams (Fig. GS-9-14a, -14b). These rocks have REE profiles that are similar to mafic to intermediate rocks of uncertain origin in the ‘middle exhalite’ unit (cf. Fig. GS-9-15b, -13b). The presence of a positive Eu anomaly in sample 91-06-3055 suggests that it represents a different rock type than sample 91-06-3026i.

Sample 91-06-3051 differs markedly from the other samples in that it has the flat heavy REE profile of both the intermediate and ‘rhyolitic’ sedimentary rocks and the light REE enriched profile of the ‘rhyolitic’ rocks, in addition to a strong positive Eu anomaly. The low SiO$_2$ (61%) and high Fe$_2$O$_3$ (7%), MgO (3.7%), CaO (4.2%), TiO$_2$ (0.85%), P$_2$O$_5$ (0.24%) and V (117 ppm) preclude an affinity with sample 91-06-3055. Sample 91-06-3051 is from the same unit of porphyroblastic rocks as samples 91-06-3045 to -3056. The REE profile for this sample indicates a provenance similar to that of the porphyroblastic schist, and the positive Eu anomaly indicates derivation, at least in part, from the hydrothermal vent that produced the deposit.

**Discussion**

This study reinforces the conclusions of Gale et al. (1997, 1999) that Eu anomalies can be used to vector VMS mineralization. Drillcores that intersect the northeast extension of the Ruttan orebody show a systematic decrease in Eu within the uppermost exhalite unit with increasing distance from the deposit (Fig. GS-9-16). This behaviour of Eu can be directly applied to the exploration for VMS-type deposits where favourable rock types with only trace quantities of metals are intersected in early stages of exploration programs.
Drillhole 89-12 is the most distant drillhole from the margin of the orebody that contains significant metal assays, and drillhole 91-06 is located approximately 400 m along strike to the northeast. Both drillholes intersected a number of quartz–sericite±pyrite (i.e., ‘chert-like’) schist horizons that represent tuffaceous exhalite derived, in part, from an active hydrothermal vent. Sodium depletion and potassium enrichment are prevalent below the ‘lower exhalite’ at approximately 972 m (3190 ft.) in the drillcore, and altered footwall rocks are present down to the ‘North Wall Shear’

Figure GS-9-16: Schematic representation of Eu$^d$ values obtained for drillcores, relative to approximate distance from the eastern rim of the open pit; note the wide range in Eu$^d$ values found in the ores; dots below 8912 represent Eu$^d$ values obtained from samples of drillcore 89-12.
at approximately 1050 m. Between approximately 970 m (3180 ft.) and 1050 m (3390 ft.), the hostrocks are predominantly rhyolitic in composition, whereas the rocks above this interval are predominantly a mixture of intermediate and felsic volcanogenic sedimentary rocks. The quartz–sericite±pyrite rocks that constitute the ‘lower exhalite’ contain anomalous Zn (440 ppm), Ag (1.6 ppm) and Pb (160 ppm); these rocks (tuffaceous exhalite) appear to be stratigraphically equivalent to the Cu-rich East Lens of the Ruttan mine. Similar ‘pathfinder’ metal values are also present in the altered footwall rocks and overlying sedimentary rocks. The Eu\(^{4+}\) values of ±30% in the tuffaceous exhalite are distinctly different from the –30% Eu\(^{4+}\) found in both the weakly altered footwall rocks and the overlying felsic sedimentary rocks. Hydrothermal fluids capable of transporting Eu need to be reducing, low-pH and high-temperature (>250°C) fluids similar to those that form metal-rich VMS deposits (Gale et al., 1999). Consequently, positive Eu anomalies in similar rocks (‘chert-like’, quartz-sericite schist or tuffaceous exhalite), with or without accompanying ‘pathfinder’ elements, clearly indicate proximity to a hydrothermal vent capable of producing a VMS deposit.

The ‘middle exhalite’ includes an approximately 3 m thick unit of ‘chert-like’ rocks within a thick unit of porphyroblastic schist and quartz–sericite±pyrite schist. Most of the volcanogenic rocks in this section of the drillcore are of intermediate composition and have TiO\(_2\)/Zr ratios that suggest derivation from andesitic to dacitic volcanic material. Some of the ‘chert-like’ rocks have compositions that are similar to those of ‘chert-like’ rocks near the stratigraphic top of the East Lens orebody and do not have a positive Eu\(^{4+}\). The only anomalous ‘pathfinder’ element present in this ‘chert-like’ unit is Pb (159 ppm). Quartz–sericite±pyrite schist above the adjacent porphyroblastic schist is anomalous in Zn, As, Bi, Ag and Pb. The ‘chert-like’ rocks, porphyroblastic schist and quartz–sericite±pyrite rocks in the ‘middle exhalite’ have only weakly negative or near-zero Eu anomalies. The ‘middle exhalite’ sequence is approximately the same thickness as the hostrocks that separate the Cu-rich East Lens and the Zn-rich Zinc Zone. It is postulated that, during deposition of the ‘middle exhalite’ rocks, the hydrothermal vent was waning and the supply of fluid and exhalite-derived material to the basin were restricted to ‘near vent’ sites. The presence of ‘pathfinder’ elements in tuffaceous exhalite without a positive Eu anomaly may be a reflection of fluid compositions incapable of transporting Eu, or derivation of the ‘pathfinder’ elements by mass wasting of vent-deposited material that was low in Eu. Discrimination of this type of fluid composition at an early stage in a grassroots exploration program can prevent follow-up drilling on metal-poor, low-temperature, tuffaceous exhalite strata.

The ‘upper exhalite’ includes a sequence of rocks that contains altered and unaltered intermediate sedimentary rocks, beds of quartz-rich sericite schist and porphyroblastic schist with sericite-, biotite-chlorite- and cordierite-rich varieties. Most of the intermediate rocks in this segment of drillcore have the same provenance as similar rocks in the ‘middle exhalite’ because they have similar TiO\(_2\)/Zr ratios and REE profiles. The porphyroblastic schist horizons show evidence of K enrichment and Na depletion and are interlayered with quartz-sericite schist that is not depleted in Na or enriched in K, but weakly to moderately enriched in Eu. This quartz-sericite schist and porphyroblastic schist are tuffaceous exhalite that can be traced in drillcore along strike back to the uppermost Zinc Zone of the Ruttan orebody. In drillcore 91-06, approximately 400 m from the last significant Zn assay in this stratum, the only significant ‘pathfinder’ element in addition to Eu is Zn (400 ppm).

Although drillcore 91-06 intersects a number of quartz-rich (‘chert-like’) and quartz–sericite±pyrite schists, most of the rocks in the 60 m thick ‘ore equivalent’ segment are not useful in vectoring to the VMS deposit because they contain neither anomalous ‘pathfinder’ elements nor enhanced Eu anomalies. This is probably a result of precipitation of the silica-rich (‘chert-like’) rocks from low-temperature fluids that had already been stripped of their base metals and Eu closer to the active vent sites. This study also demonstrates that not all positive Eu anomalies are related to mineralizing activity.

**Economic Considerations**

Studies of drillcore from exhalite units northeast of the Ruttan mine show that the Eu\(^{4+}\) within the ‘upper exhalite’ decreases systematically away from the VMS deposit. At this time, geological controls are not sufficient to determine with certainty that the same beds are sampled in each drillcore; however, it appears from the available data that the intervals sampled do represent the same overall time-stratigraphic position in the volcanioclastic sequence. This study may assist exploration in the Ruttan area by determining the geochemical signature and lateral extent of the ‘ore equivalent’ strata north of the ‘North Wall Shear’ and elsewhere (e.g., the Darrol Lake area). Although the drillcores extend for approximately 400 m beyond the eastern margins of the orebody, the Eu\(^{4+}\) values obtained from this study indicate that explorationists may be able to easily detect VMS mineralization for distances of at least a kilometre from a source vent in this area. The application of this type of REE study in grassroots exploration programs, especially during exploration of ‘favourable strata’ in both the Ruttan and Darrol Lake area, may improve the chance of exploration success (Gale et al., 1999).
References


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