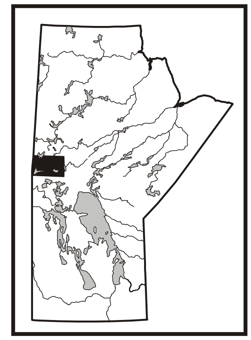
GS-2 THE APPLICATION OF RARE EARTH ELEMENT ANALYSES IN THE EXPLORATION FOR VOLCANOGENIC MASSIVE SULPHIDE TYPE DEPOSITS IN MANITOBA

by G.H. Gale and M.A.F. Fedikow



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SUMMARY

Rare earth element (REE) data for host rocks from the alteration zones of massive sulphide deposits in Paleoproterozoic volcanic rocks of the Flin Flon - Snow Lake area, Manitoba have chondrite-normalized REE profiles that are depleted in REE relative to unaltered host rocks. The intensely altered portions of the alteration zones show greater Eu depletion than less altered parts of the same zone. Layered sulphide ores and exhalites proximal to the deposits typically have positive Eu anomalies and are enriched in light REE. In contrast, barren sulphide facies iron formations show chondrite normalized patterns that have negative or 'flat' Eu values relative to Sm and Gd. Eu data for these deposits reflect the hydrothermal pathways of the mineralizing fluids. Eu is selectively leached by hot, low pH fluids in zones of intense alteration, and redeposited together with sulphides and/or silicates in: the uppermost parts of the alteration zones; 2) the sulphide lenses at the hydrothermal vent sites; and, 3) precipitates derived from the hydrothermal fluids within approximately a kilometre of vent sites. REE data can be used by explorationists to determine the presence of 'off-hole' metal-bearing sulphide zones, to distinguish metal-poor sulphidic layers related to 'economic' hydrothermal activity from barren sulphide facies iron formation, and to determine the presence of 'ore-equivalent' strata in some volcanic rocks.

INTRODUCTION

Positive Eu anomalies are common in VMS deposits and associated exhalite material from the Paleoproterozoic Flin Flon -Snow Lake district (Trans-Hudson Orogen) of Manitoba. The positive Eu signatures extend well beyond the limits of the known sulphide ores. In addition, REE patterns for rocks from stratigraphically underlying alteration zones and 'barren sulphides' are distinctively different than the patterns for exhalite-bearing material and iron sulphide bearing 'ore-equivalent' strata. We suggest that these differences in REE contents can be utilized in the understanding of, and the exploration for, VMS deposits.

The Flin Flon Belt has 25 past- or presently- producing mines and a number of subeconomic deposits. The Zn-Cu, and Cu-Zn deposits are associated with rhyolite and occur mainly in tholeiitic and calc-alkaline submarine arc assemblages; several small Cu - rich deposits and the 63 mt Flin Flon deposit are associated with primitive arc assemblages. The regional geological setting of this prolific VMS district is described by Syme and Bailes (1993) and Bailes and Galley (1996). The deposits are described by Gale and Eccles (1988) and Fedikow et al. (1989, 1993).

The immediate host rocks to many of the VMS deposits in the Flin Flon - Snow Lake area are commonly an interlayered sequence of felsic tuff, felsic tuffaceous rocks, minor amounts of locally derived volcaniclastic material and disseminated and/or layered sulphides. These rocks commonly contain variable amounts of metasedimentary material that is interpreted as metamorphosed chemical sediments and exhalite-derived silicate minerals and minor amounts of slate that probably represents metamorphosed pelagic sediments. The 'exhalite' content of these rocks, commonly referred to as 'tuffaceous exhalite', varies from layer to layer and ranges from nearly pure chemical sedimentary rock to tuffaceous material with only trace amounts of exhalite-derived minerals both vertically within the sequence and laterally away from the VMS sulphide deposits. Laterally, these 'ore-equivalent' rocks may extend for kilometres away from the sulphide deposits or vent sites, but the component of 'exhalite derived' material and contained base metals decrease. A direct visual or chemical correlation with metal-producing hydrothermal systems is not always readily apparent to even experienced explorationists.

REE data from the various deposits vary systematically along the fluid pathways that conceptually produce a VMS deposit, namely: a) the host rocks that stratigraphically underlie the deposits and were altered by the hydrothermal fluids; b) the sulphides deposited in ore lenses from the hydrothermal fluids upon contact with sea water either at or beneath the rock-water interface; c) tuffaceous exhalites deposited in part from hydrothermal fluids at and near the vent sites; and d) tuffaceous exhalite deposited in part from fluids that dispersed away from the hydrothermal vent sites to form distal ore-equivalent' rocks.

FOOTWALL ALTERATION

The intensity of alteration in rocks stratigraphically below the solid sulphide lenses varies from zones with complete destruction of the original minerals, large scale removal of components and the addition of abundant sulphides and chlorite to zones with weakly developed alteration on the periphery of the alteration envelope where original feldspar outlines are still recognizable and only subtle changes in chemistry are present (Gale et al., 1997). REE mobility in alteration zones was demonstrated by Campbell et al. (1984). Eu depletion is greatest in the most intensely altered portions of the alteration zone and decreases towards the periphery. These observations are supported by the experimental work that indicates REE mobility and Eu enrichment in hydrothermal fluids increases with decreasing pH and increasing temperatures (Haas et al., 1995).

Samples from the sulphide-rich portions of the alteration zone, i.e., the 'stringer zone', have overall negatively sloped chondrite-normalized REE patterns and Eu_d values (=(Eu_n/(1/2Sm_n+1/2Gd_n)-1*100), where $_n$ is the chondrite-normalized value) for these rocks are < -30. Altered felsic rocks that stratigraphically underlie the solid sulphide lenses at the Spruce Point deposit exhibit typical negative Eu anomalies and have Eu_d values < -40 (Fig. GS-2-1). The Eu_d values for samples within an alteration zone vary dramatically and are dependent not only on the position of the sample in the alteration zone, but also on the initial Eu contents of the rocks.

SULPHIDE ORES

Hydrothermal fluids have been observed depositing sulphides and other chemical sediments at vent sites (Francheteau et al., 1977; Edmond et al., 1982) and are today considered to be the process involved in the formation of ancient VMS deposits such as those in these Paleoproterozic rocks.

In general, samples of layered solid sulphide (SS, i.e., rocks with more than 90% sulphide minerals) typically have enriched LREE and a positive Eu_d, but commonly have HREE concentrations that are below detection limits. In comparison, near solid sulphide (NSS; i.e., 50 - 90 % sulphides) ores have HREE contents that are well above detection limits and LREE chondrite normalized values that are the same or higher than Yb and Lu. This mineralization is characterized by high positive Eu_d values that range from 50 to 150 and represent an overall 50% to 150% increase of Eu_n (Fig. GS-2-2). Similar chondrite normalized REE patterns were obtained for layered sulphides from the Brunswick deposit (Graf, 1977), layered and breccia matrix sulphides from the Halfmile Lake VMS deposit (Adair, 1992) and ores of the Broken Hill sediment hosted deposits (Lottermoser, 1989).

Some samples of NSS and SS ores obtained from a number of the producing mines in Manitoba have near zero or negative Eu_d. These samples were collected from mobilized ores, the stratigraphically lowermost portions of the sulphide lenses, or the uppermost portions of the alteration zones. We attribute the negative Eu_d values of these sulphide ores to the absence of an exhalite component in both the mobilized ores and the stratigraphically lowermost portion of the deposits, or selective mobility of Eu relative to other REE during modification of the deposit by late stage hydrothermal fluids.

Both Graf (1977) and Lottermoser (1989) reason that Eu enrichment in the sulphide ores is related to hydrothermal fluids and represents an exhalite component of the sulphides. We have not found any significant statistical correlations between base metal contents or other elements.

and Eu contents and have not been able to establish a relationship between visual estimates of sulphide minerals and positive Eu$_d$ values. We concur that Eu-enriched chondrite-normalized REE patterns, i.e., positive Eu$_d$ values, are a hydrothermal fluid signature in these rocks.

We ascribe the absence of high positive Eu$_d$ values in some samples adjacent to some ores as the result of only small amounts of exhalite material in the rocks. This can be explained by the formation of some sulphide lenses below the water-rock interface, i.e., the rocks are literally part of the alteration zone. Alternatively, ongoing or repeated pulses of hydrothermal fluid activity may have altered and stripped previously deposited exhalite and REE after initial deposition of the ore lense.

TUFFACEOUS EXHALITE

In active paleovolcanic environments it is reasonable to expect that material derived from hydrothermal fluids at the vent site would mix with clastic material and/or volcanic ejecta to form deposits of tuffaceous exhalite similar to those obtained from the present day oceans (Barrett et al., 1990). We have sampled several drill core sections identified as "ore equivalent strata" by exploration and mining company geologists as well as chip samples from the 274 m and 574 m drifts that cut across strata hosting the Spruce Point deposit. The 274 m drift was cut adjacent to an ore lense and the 574 m drift (Fig. GS-2-1) was cut 140 m from the nearest known ore lense. Both the footwall and hanging wall felsic rocks at the Spruce Point deposit show negative Eu$_d$ values whereas the metal-poor sulphidic rocks immediately above and along strike from the ore have Eu$_d$ values that are near zero or strongly positive. These rocks have REE patterns and positive Eu$_d$ values that are similar to layered sulphide ores. In addition, positive Eu$_d$ values extend for approximately 20 m into the hanging wall rocks beyond the strata identified by mine geologists as 'ore equivalent' (Fig. GS-2-1).

A sample of 'ore equivalent' material collected approximately 100 m from known ore at the Bigstone deposit has a positive Eu$_d$, whereas sulphide-rich sedimentary and tuffaceous rocks from adjacent hanging wall and footwall strata have negative Eu$_d$ values. Tuffaceous exhalite samples collected 120 m along strike from the Photo Lake deposit, 400 m along strike from a prospect known as Deposit X and 120 m from known ore at the Bruce Morgan deposit all have light REE enriched chondrite normalized patterns and positive Eu$_d$ values. These data confirm that Eu can be deposited hundreds of metres away from the sites of base metal deposition.

A drill core sample collected 250 m into the hanging wall of the Photo Lake deposit has a Eu$_d$ value of 167 (Fig. GS-2-2). This sample contained approximately 5% pyrite and other than Eu, the major and trace element data for this sample do not indicate proximity to a mineralized zone. A hole

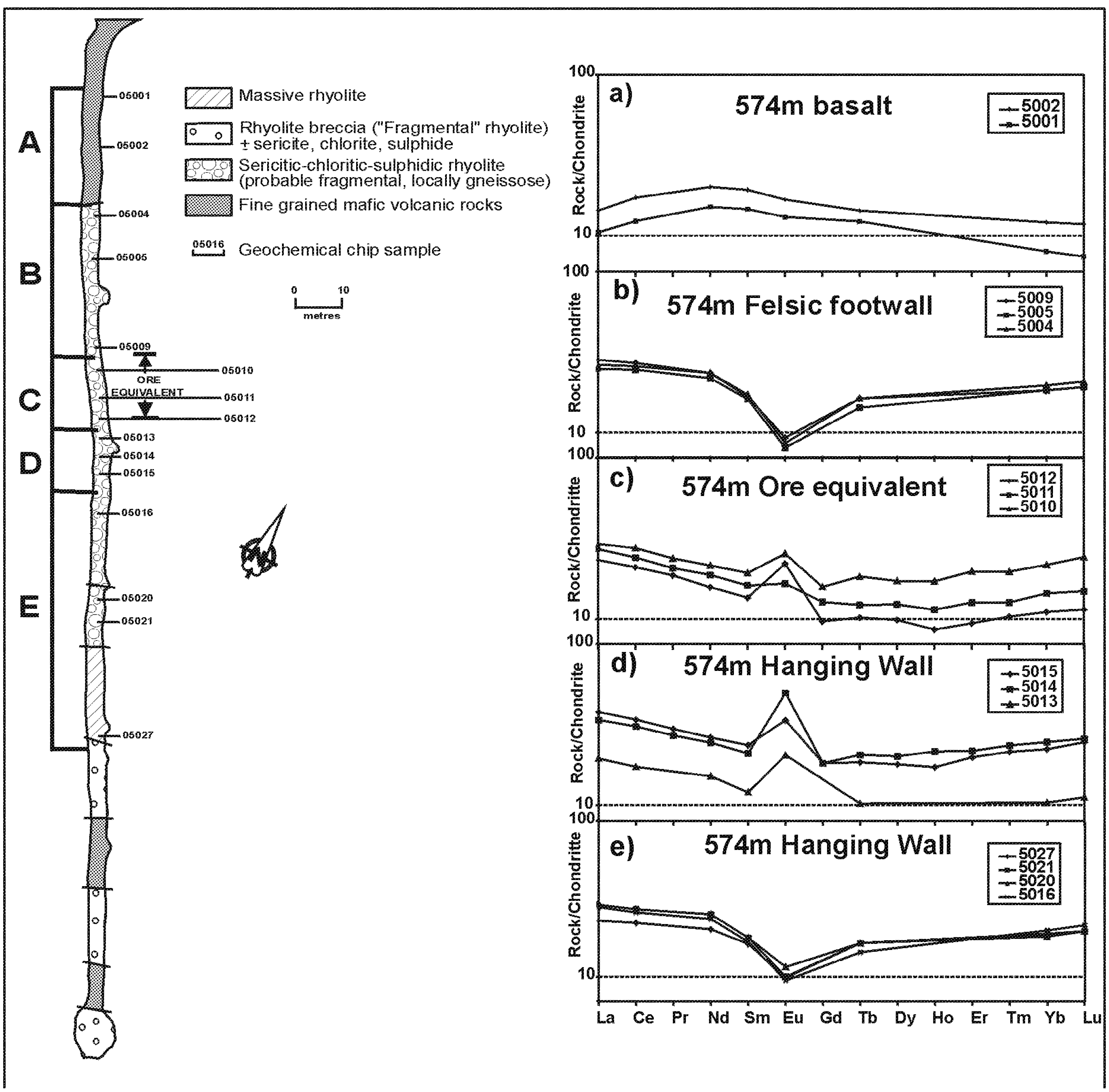

Figure GS-2-1: Geology, sample locations and REE patterns for samples from the 574 m level of the Spruce Point Mine. Cross-cut is approximately 140 m from known ore (after Gale et al., 1997).

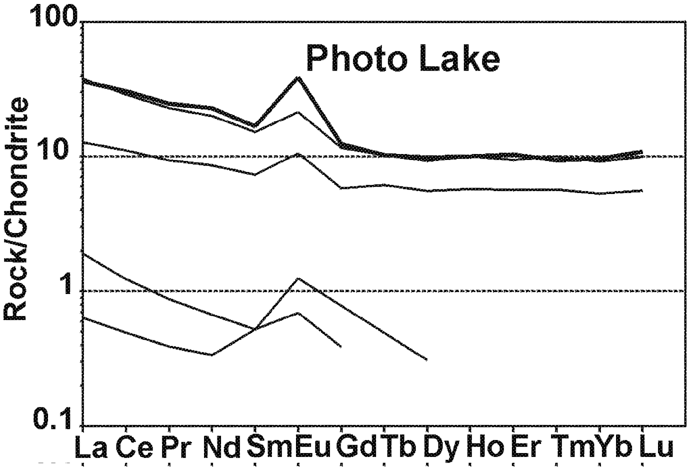

Figure GS-2-2: REE patterns for samples of ores and tuffaceous exhalite from the Photo Lake Mine. Heavy line represents sample from hanging wall zone 250 m statigraphically above the deposit.

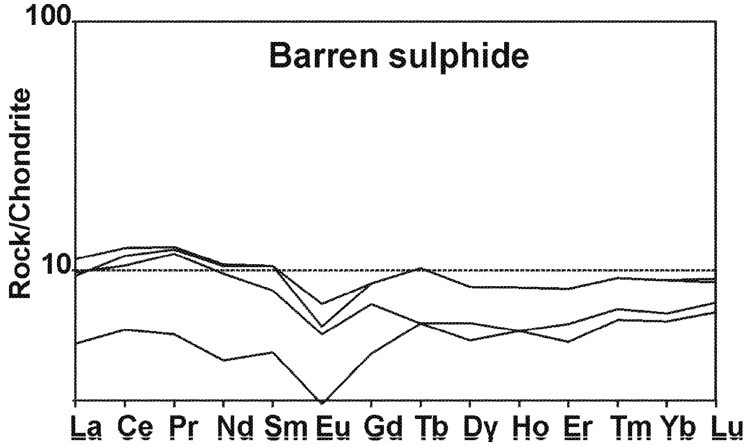

Figure GS-2-3: Typical REE patterns for samples of barren sulphide muds and SFIF from the 20 km long Foot-Mud unit at Snow Lake

drilled 20 m along strike intersected significant sphalerite-rich VMS type mineralization. Samples of sulphide-bearing tuffaceous exhalite from Cu-Zn prospects identified as VMS type occurrences (Fedikow et al., 1993) also have high positive Eu_d values. This example suggests that systematic REE analyses is warranted for even low-sulphide bearing tuffaceous exhalite.

Similar light REE enriched patterns with positive Eu_d values are reported for: a) exhalites proximal to the Broken Hill sediment hosted deposits in Australia (Lottermoser, 1989); b) tuffaceous exhalite and chemical sedimentary rocks associated with the Matagami (Liaghat and MacLean, 1992) and Brunswick 12 (Peter and Goodfellow, 1996) VMS deposits; and, c) sediments adjacent to submarine hydrothermal vent sites (Barrett et al., 1990). Lottermoser (1989), Barrett et al. (1990) and Peter and Goodfellow (1996) interpret the observed positive Eu anomalies as a mixing an hydrothermal fluid derived component and detrital material.

A sample collected approximately 400 m along strike from Deposit X, has a Eu_d value of 40. Samples collected 1800 m along strike from the Photo Lake deposit and approximately 300 m west of the Bigstone deposit, have Eu_d values near zero. A low positive Eu_d value has been found in 'ore equivalent strata' approximately 1 km from the Ruttan deposit. Lottermoser (1989) clearly showed a change from positive Eu_d values in exhalites proximal to the Broken Hill ore bodies to low negative Eu_d values in the Hores Gneiss distal to the ore bodies. Kalogeropoulos and Scott (1983) showed that the "tetsusekiei" or ferruginous cherts several kilometres distal to, and associated with, the Japanese Kuroko deposits do not have positive Eu anomalies, yet Kuroko type ores have strong positive Eu anomalies (Shikazono and Matsumoto, 1989). Although we have not systematically sampled a tuffaceous exhalite away from a particular VMS deposit (cf. Peter and Goodfellow, 1966), our data suggests that Eu^{2+} complexes are deposited relatively close to hydrothermal vents, high positive Eu_d values occur within approximately a kilometre of a hydrothermal vent, and positive Eu anomalies decrease with increasing distance from the deposits.

BARREN SULPHIDES

Sulphide facies iron formations (SFIF) consisting of 50% or more pyrite and or pyrrhotite and 0-10% graphite are common in the vicinity of VMS deposits in the Flin Flon - Snow Lake area (Gale et al., 1980; Fedikow et al., 1989; Gale and Eccles, 1992). The REE patterns for samples that include sulphides, argillite and siltstone from drill holes through these regional geophysical conductors show low to moderately negative Eu_d values (Fig. GS-2-3). The LREE portions of the REE patterns from these barren sulphide zones are either enriched, flat or lower than the HREE portions. The differences in LREE fractionation are probably due to local environments of deposition or provenance of the material rather than sulphide content.

Several of the SFIF samples show weak Ce anomalies that probably reflect an above average pelagic sediment content or the result of extensive mixing of hydrothermal fluids and seawater in some of these layered rocks (cf. Barrett et al., 1990; Ruhlin and Owen, 1986).

It is clear from the examples studied that barren layered sulphide facies iron formations do not have a recognizable REE hydrothermal fluid signature. Consequently, barren and distal SFIF are readily distinguishable from vent proximal, but metal poor, sulphide-bearing strata associated with VMS deposits by the absence of positive Eu_d values. Because exploration for VMS deposits is often complicated by difficulties in evaluating the significance of drill core from sulphide-bearing strata that do not contain significant base metals, the recognition of a hydrothermal fluid signature in these rocks could assist exploration.

In addition, the identification and tracing of 'ore equivalent' strata within faulted and folded rocks in the vicinity of some known deposits can be a major problem in mine scale exploration. The hydrothermal signature provided by REE data can assist not only in the recognition and definition of the 'ore equivalent' strata, but REE analyses of footwall rocks can aid in the recognition of unknown hydrothermal vent sites along defined ore-bearing strata.

Explorationists can utilize the marked differences in REE patterns between SFIF within tuffaceous exhalite associated with VMS deposits and barren SFIF to determine the residual potential of a previously drilled property.

CONCLUSIONS

Several projects have been initiated with industry geologists to provide further documentation of REE behaviour around deposits and to test the observations reported here in active exploration programs. Detailed studies of cores and rocks from the Lew deposit in the Flin Flon area and the Ruttan Mine are in progress in cooperation with company geologists. In addition, available drill cores from the subPaleozoic rocks in the Reed Lake area have been sampled in an attempt to use REE to determine residual exploration potential in an unexposed area that is known to contain abundant felsic volcanic rocks. Analyses of sulphidic rocks in three drill cores from a property in the Snow Lake area have identified Eu positive anomalies that increase in amplitude along strike; this sulphidic zone was previously considered to be a barren sulphide by the property holder.

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