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SOME CHEMICAL FEATURES OF LEAD-
ZINC DEPOSITS IN CARBONATE ROCKS

(Report and 10 figures)

D. F. Sangster

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ABSTRACT

The major chemical features of lead-zinc deposits in carbonate rocks can be expressed in terms of two 'systems': Cu-Pb-Zn and Pb-Zn-Ag. In the Cu-Pb-Zn 'system', the ores are markedly bimodal in terms of the Zn/Zn + Pb atomic ratio and are characteristically copper-poor relative to lead and zinc. In the Pb-Zn-Ag 'system', most ores from carbonate-host lead-zinc deposits are relatively low in silver, except for those few orebodies which produce by-product copper and/or contain polymetallic minerals.

Host-rock carbonate from three selected Canadian deposits were analyzed for trace amounts of Cu, Pb, and Zn. These studies show that, as the size (i.e. tonnage) of the orebody increases, the Cu:Pb:Zn atomic ratio in the host rock approaches that of the ore.

Trace element content in sphalerite from four Canadian deposits are presented as Fe-Mn-Cd, Cu-As-Ag, and Cr-Ni-Co atomic ratios. Sphalerite from one of these deposits, which field relations indicate has more 'hydrothermal features' than the other three, is distinguished by its relative enrichment in Mn, Ag, and Ni.

SOME CHEMICAL FEATURES OF LEAD-ZINC DEPOSITS IN CARBONATE ROCKS

INTRODUCTION

For the past three years the author has been engaged in a systematic geological study of Canadian lead and zinc deposits. For several reasons the study of this important commodity group began with those deposits which are found in carbonate rocks. As a group, these deposits are a major factor in Canada's mineral production; in the period 1956-66, 24 per cent of Canada's lead and 17 per cent of her zinc was produced from orebodies in carbonate rocks.

Study of the chemistry of these orebodies was initiated in order to demonstrate the range in composition of the ores, to see if they could be sub-divided on the basis of their chemical make-up, to see if there was any correlation between the composition of the ore and the geological features of the deposit, to compare and contrast certain chemical features of the ore with the same features in the host rock, and to attempt to outline metallogenic belts or areas using the chemical data in conjunction with the geological data. There is not yet enough data to delineate metallogenic areas but some progress has been made in meeting the other objectives.

With few exceptions, these are all what are commonly geologically classified as the Mississippi Valley type according to criteria suggested by Ohle (1959). The origin of this type of mineral deposit has been debated for many years, the most recent suggestion being by Jackson and Beales (1967). It is not the author's intention to review these arguments; rather, it is to present on a factual, or empirical, basis, some of the chemical data that have resulted from the study to date.

These data have been summarized for presentation and will be discussed as groups of element ratios rather than absolute values. Furthermore, to remove the bias resulting from differences in atomic weights of the elements, the ratios are expressed on an atomic rather than a weight basis.

Acknowledgments

CHEMISTRY OF THE ORE

Because it is the chemistry of the orebodies that makes them rather unique and valuable rock types, it is of interest to compare the bulk compositions of lead-zinc ores in carbonate rocks with lead-zinc ores in non-carbonates. Besides iron, of course, copper is the most common 'extra' metallic constituent of lead-zinc deposits. In Figure 1 the atomic ratios of Cu, Pb, and Zn in 114 lead- and/or zinc-bearing deposits have been plotted and contoured. Most of these ores are Canadian but a few, particularly the carbonate ones, are from outside the country. For purposes of illustration the data have been contoured in the same way that points on a stereonet petrofabric diagram are contoured except, of course, that a one-area-per cent triangle, rather than a one-area-per cent circle, was used (Turner and Weiss, 1963, pp. 58-64). In Figure 1, note the following:

1. A major chemical difference exists in the bulk compositions of ores in the two groups of deposits. Those in carbonate rocks are characterized by a low copper content relative to lead and zinc; those in non-carbonate rocks show a wide range of Cu-Pb-Zn ratios but most compositions fall in the smaller triangle formed by a line joining the mid-point of the Cu-Zn side with the mid-point of the Pb-Zn side. Expressed in another way, 90 per cent of the 'carbonate type' deposits contain less than 10 atomic per cent Cu whereas 70 per cent of the 'non-carbonate type' contain less than 10 atomic per cent Pb.

2. When projected into the $\dfrac{Zn}{Zn + Pb}$ scale, deposits in carbonate rocks show a bimodal distribution as illustrated in the left histogram of Figure 1. In other words, most of these deposits are either relatively zinc- or lead-rich, with very few of intermediate composition. One frequency distribution peak occurs at a $Zn/Zn + Pb$ ratio of about 0.3 and the other at about 0.85. Over 80 per cent of the 'carbonate type' orebodies have a
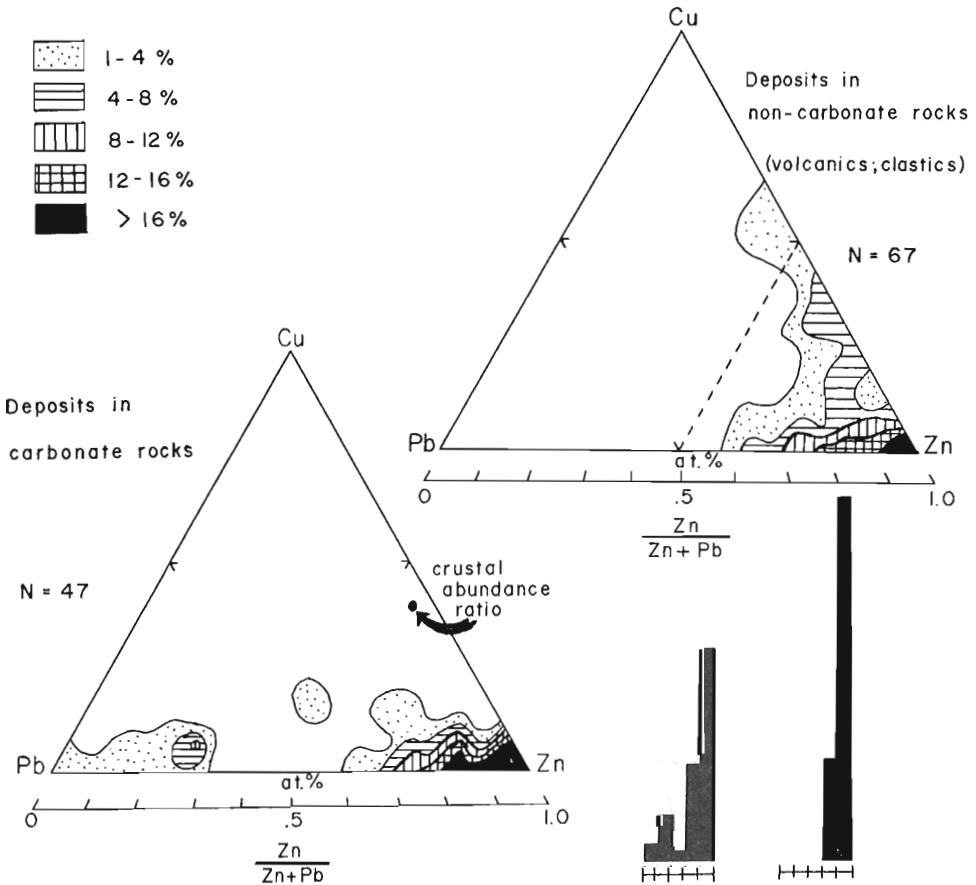
Figure 1. Cu-Pb-Zn atomic ratios of lead- and/or zinc-bearing ores in carbonate and non-carbonate rocks.

Zn/Zn + Pb ratio greater than 0.5, i.e. most are zinc-rich with respect to lead. Deposits in non-carbonate rocks (right histogram) show only a single peak at 0.9.

    3. When compared with the crustal abundance ratio of Cu, Pb, and Zn (values from Mason, 1958, p. 44), one can immediately see that the 'carbonate type' has apparently resulted from a strong partitioning of these elements as demonstrated by their relative lack of copper. Furthermore, that group of deposits in carbonate rocks 'peaking' at a Zn/Zn + Pb ratio of about 0.85 is practically identical to the average ratio of these two elements in the earth's crust (0.93). Such deposits show minimum 'fractionation' relative to the crustal ratio; maximum 'fractionation', however, is shown by
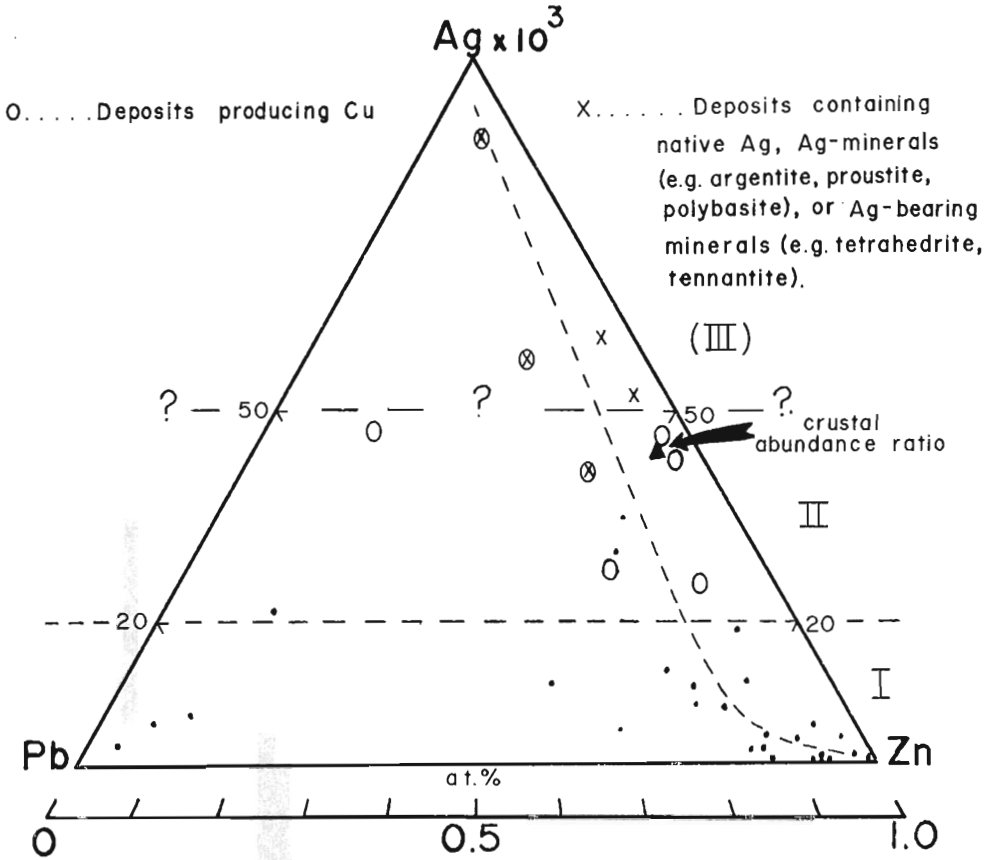
Figure 2. Pb-Zn-Ag atomic ratios in lead-zinc deposits occurring in carbonate rocks.

those deposits with a ratio less than 0.5. These ores are least similar to the average crustal ratio and show a relative depletion not only in copper but also in zinc.

Besides these major constituents, however, such ores commonly contain important amounts of silver and cadmium which are recovered as by-products. Cadmium substitutes for zinc in the sphalerite lattice and its abundance in the ore will be strongly dependent on the zinc content. Silver, on the other hand, can occur in solid solution in galena, sphalerite, pyrite, chalcopyrite, sulphosalts, as independent silver sulphides or as the native metal. Consequently it is of interest to examine the Pb-Zn-Ag ratios of 'carbonate type' lead-zinc ores.

In Figure 2 are plotted the Pb-Zn-Ag ratios of 36 deposits for which data were available. In order to get a good spread to the data, silver content was exaggerated a thousand-fold. From this diagram it is apparent that most of these ores are silver-poor relative to lead and zinc. It is important to remember that the plots are ratios and bear no direct relation to the absolute silver content of the ore. While it is true that, in absolute terms, the silver content of most ores will rise with increasing lead content, one can see from the diagram that Pb-rich ores do not necessarily contain proportionately more silver than do zinc-rich ores. In fact, Figure 2 suggests that the silver content of these Pb-Zn ores is more-or-less independent of the Zn/Zn + Pb ratio.

The ratio Ag/Pb + Zn in most of these ore deposits appears to be substantially less than that in average crustal rocks (see Fig. 2). This implies a fractionation away from silver during the ore-forming process. Some deposits, however, are substantially enriched in silver and are anomalous for this reason.

When the mineralogy of the deposits represented in Figure 2 is taken into consideration, it becomes apparent that the diagram can be divided into two, and possibly three parts. In Part I, the metallic mineralogy is simple (ZnS, PbS, FeS_2, $Fe_{1-x}S$) and the relative silver content of the ore is low. Canadian examples of this type of ore would be Pine Point or any of the conformable deposits in the Kootenay Arc of British Columbia (Fyles, 1966). Orebodies plotting in Part II of the diagram are characterized not only by a higher relative silver content but they also contain enough copper to be recovered as a by-product although, as demonstrated in Figure 1, the copper content of these ores (relative to lead and zinc) is generally low. In Part II, then, it is probably safe to say that the extra silver in the ore is brought in at the expense of introducing another phase (generally chalcopyrite) into the 'system'. Examples of this type of ore would be the Tynagh deposit in Ireland, the Errington Mine in Ontario, or the Silver Giant Mine in British Columbia. Although the data are meagre, there is a suggestion that Figure 2 could be further divided into a Part III where, in addition to or instead of chalcopyrite, the ores contain independent silver minerals and/or high-silver sulphosalts. Canadian examples would be the Walton Mine in Nova Scotia or the Tetrault Mine in Quebec.

As suggested in an earlier paragraph, the ores, in general, show little relation between relative silver content and the Zn/Zn + Pb ratio. In Part I of Figure 2, however, ores with a high Zn/Zn + Pb ratio seem to show a rather marked tendency toward an increase in silver content with increase in lead content as shown by the dashed line passing through these points. This curve relating Ag and Zn/Zn + Pb ratio increases exponentially until it reaches the boundary between Part I and Part II where it levels off. Beyond this point relative silver content in the ore rapidly increases with little or no relation to the Zn/Zn + Pb ratio which remains more-or-less constant at about 0.85. By definition, ores in Part I do not contain recoverable amounts

of copper nor do they contain independent silver minerals. Therefore the silver recovered from these ores must be entirely contained in the sphalerite and galena; furthermore, sphalerite and galena from deposits plotting near the top of Part I should contain more silver than those in the lower half of Part I.

In summary, then, one might say that, in Part I of Figure 2, the simple Pb-Zn ore in the lower half is under-saturated with silver whereas ore in the upper half of Part I is near-saturated with silver. In Part II the silver content, relative to lead and zinc, is higher but the extra silver is probably contributed by an extra phase, i.e. chalcopyrite. In Part III, the 'system', including the copper phase, is over-saturated in silver; neither the ZnS, PbS, or $CuFeS_2$ can hold any more silver and it appears as independent silver minerals. Research on the trace element content of sulphides from representative deposits of Parts I, II, and III is currently underway to test this 'silver saturation' hypothesis.

CHEMISTRY OF THE HOST ROCK

Carbonate host rocks of several Canadian lead-zinc deposits have been systematically sampled and analyzed for selected major and minor elements in an attempt to: (1) determine whether or not chemical haloes surround the orebodies; (2) establish approximate background values, or range of values, for some of the ore-bearing carbonate horizons; and (3) compare the ratios of ore-forming elements in the host rocks with ratios of the same elements in the ore.

TABLE I

Average background values of base metals in carbonate
host rocks in three selected areas

	ppm		
	Cu	Pb	Zn
Southwestern Ontario (average of 49)	3	5	16
Leitch Gold Mines (average of 49)	3	6	83
Pine Point (average of 35)	3	65	342

Samples of host rock carbonate were collected over a distance of from a few feet to over a mile from known mineralization in three localities: Bruce Peninsula of southwestern Ontario, Leitch Gold Mines' deposit in
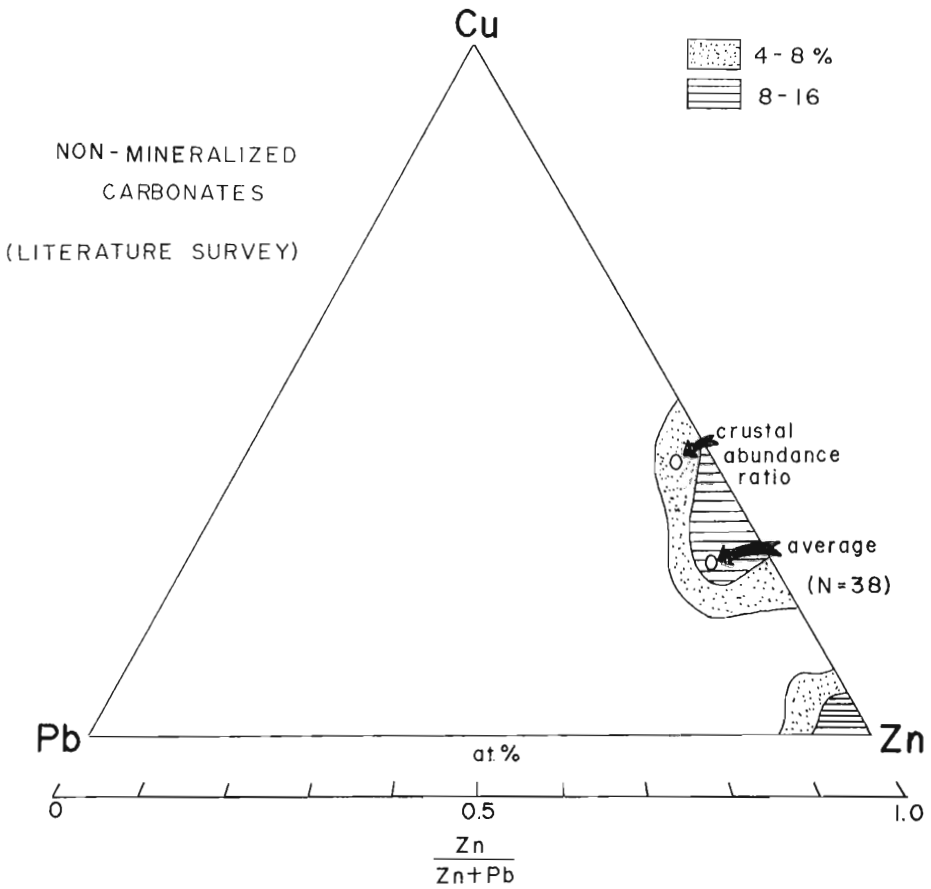
Figure 3. Cu-Pb-Zn atomic ratios in non-mineralized carbonate rocks.

northwestern Newfoundland, and Pine Point, Northwest Territories. In all cases, metal values (Cu, Pb, Zn) in host rock carbonate fell away to background very rapidly with distance from ore. Even the larger deposits could not be detected by these elements more than about 200 feet away from the edge of the orebody; for the smaller occurrences this 'detectable distance' was reduced to 75 feet or less. Similar negative results were found for Ni, Co, As, Sb, MnO, Al_2O_3, SiO_2, Fe_2O_3, and TiO_2. The samples were also analyzed for total CaO and MgO in an attempt to detect any major or consistent change in the dolomite-limestone ratio but none was found. Approximate background averages for Cu, Pb, and Zn in carbonate in the three areas are given in Table I.

Figures 3 to 6 illustrate ratios of these three base metals in non-mineralized carbonate as well as in carbonates from the three study areas. In Figure 3, note that the average for the 38 analyses from the literature approaches that of the average crustal abundance ratio. The latter is slightly richer in copper because silicate rocks generally contain more copper than do carbonates. In Figure 4 are plotted analyses from carbonate rocks in southwestern Ontario that contain several dozen, small, very low-grade occurrences (Guillet, 1967). Their average composition is shown by the
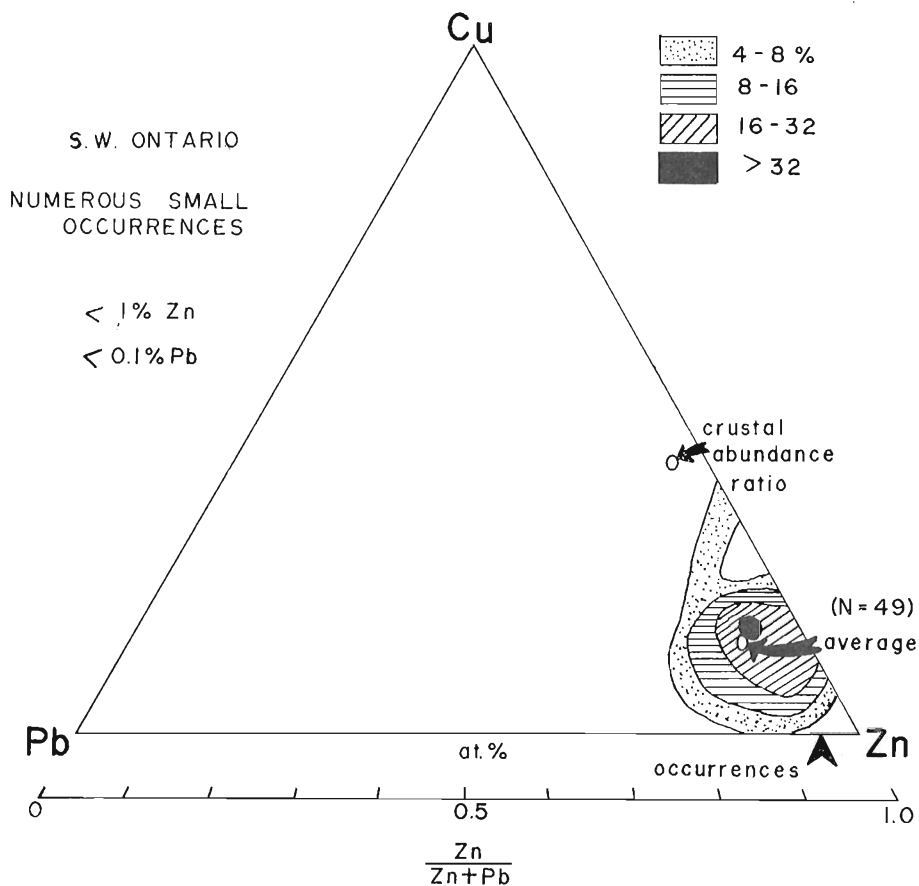
Figure 4. Cu-Pb-Zn atomic ratios in slightly mineralized carbonate rocks in southwestern Ontario. Composition of known mineralization in this area is indicated by the arrow in the lower right corner of the diagram.
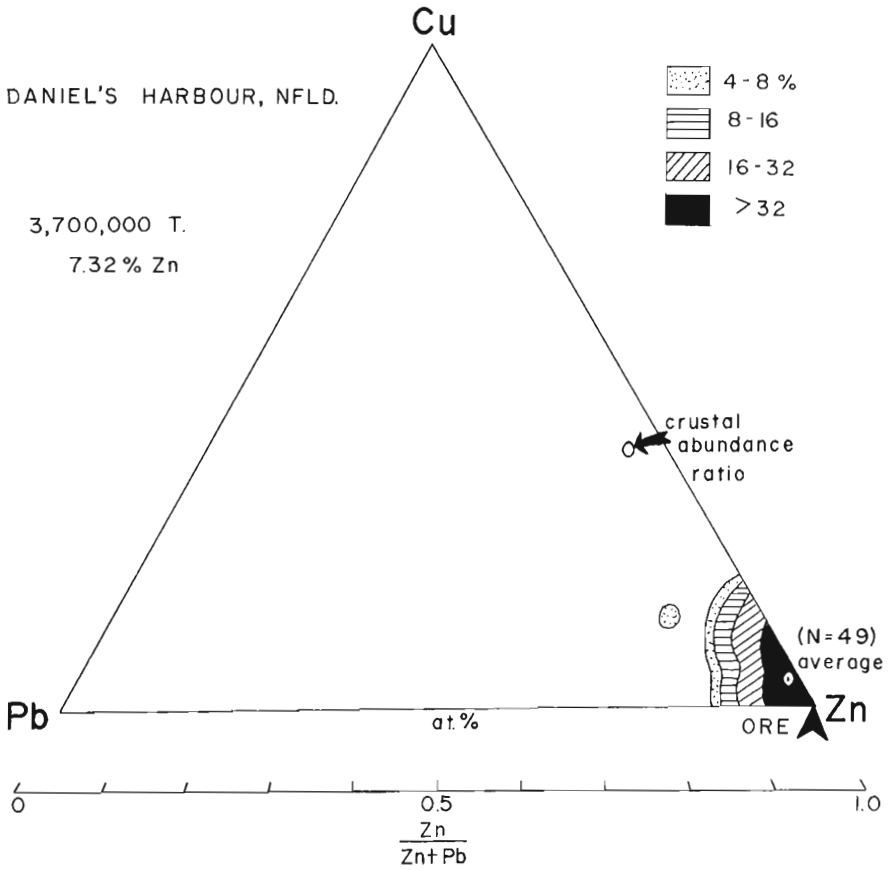
Figure 5. Cu-Pb-Zn atomic ratios in carbonate rocks in the Daniel's
Harbour area of northwestern Newfoundland. Composition of the
contained orebody is shown by the arrow in the lower right corner.

arrow near the Zn corner of the diagram. Compared with Figure 3 one can
see that the average for the Ontario carbonate rocks has moved in a direct
line away from the crustal ratio toward the ratio of these elements in the
small deposits. Results of analyses from Newfoundland are shown in Figure
5. The contained orebody is entirely zinc in composition as shown by the
arrow. Here the carbonate values form a tight concentration near the zinc
corner; furthermore, the average has moved well away from the crustal
abundance ratio, away from the average for non-mineralized carbonate, and
plots close to the composition of ore in this deposit. Finally, Figure 6 shows
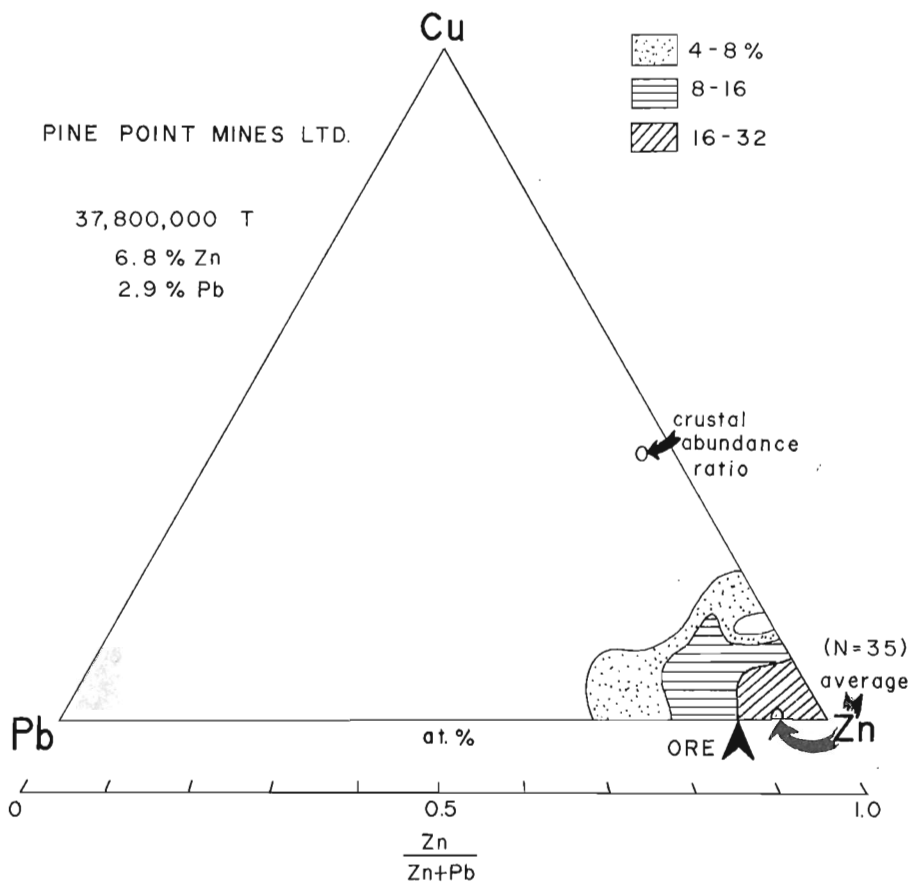
Figure 6. Cu-Pb-Zn atomic ratios in carbonate rocks in the Pine Point area, N.W.T. Composition of the ore is shown by the arrow in the lower right corner.

values in carbonate in the Pine Point area. In this case the average is close to the Pb-Zn side of the diagram and close to the average composition of ore.

Thus, in the examples shown, it would appear that as the size of the contained orebody increases, the ratio of Cu-Pb-Zn in the host rock carbonate approaches that of the ore. These deposits are all of the strata-bound, Mississippi Valley type and one interpretation of these results could be that the deposits are a product of the rock in which they are found. Both the size of the occurrence, as well as its composition relative to the trace element

Pine Point
(M.Devonian)

Daniel's Harbour
(L.Ordovician)

Monarch - Kicking Horse
(M.Cambrian)

S.W. Ontario
(M.Silurian)

500 miles

Figure 7.   Locations and age of host rock carbonates of lead-zinc deposits
             selected for detailed sphalerite analyses.

composition of the host rock, could be a reflection of the efficiency and selec-
tivity of the ore-forming (i.e. concentrating) processes.

CHEMISTRY OF SPHALERITE

As a final presentation in this review of some chemical features of
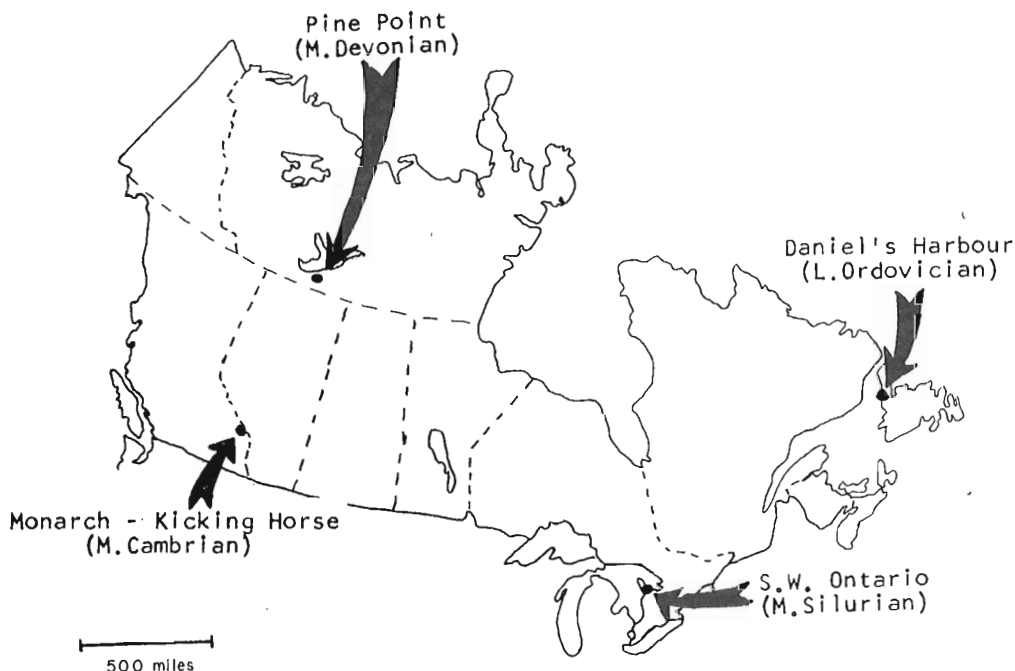lead-zinc deposits in carbonate rocks, some results of quantitative analyses
of sphalerite are given to illustrate the range in composition of this mineral
in four selected deposits. The locations of these are shown in Figure 7.
These were chosen for illustration because they span a wide range in size,
age of host rock, and geographic distribution. Although all are of the
Mississippi Valley type, the Monarch-Kicking Horse deposit in southeastern
British Columbia (Brown, 1948; Ney, 1957) could be said to have more
'hydrothermal features' (in the classical Lindgren sense) than the other three.
Some of these features are: (1) it is the only one of the four that has a nearby
possible source intrusion (the Ice River complex lies 18 miles to the south
and is rimmed with several small lead-zinc deposits; Allan, 1914); (2) min-
eralization is associated with several prominent faults or other structural
features; (3) the host rock is essentially limestone but the actual orebody is
enclosed in a halo of dolomite which could be interpreted as a hydrothermal
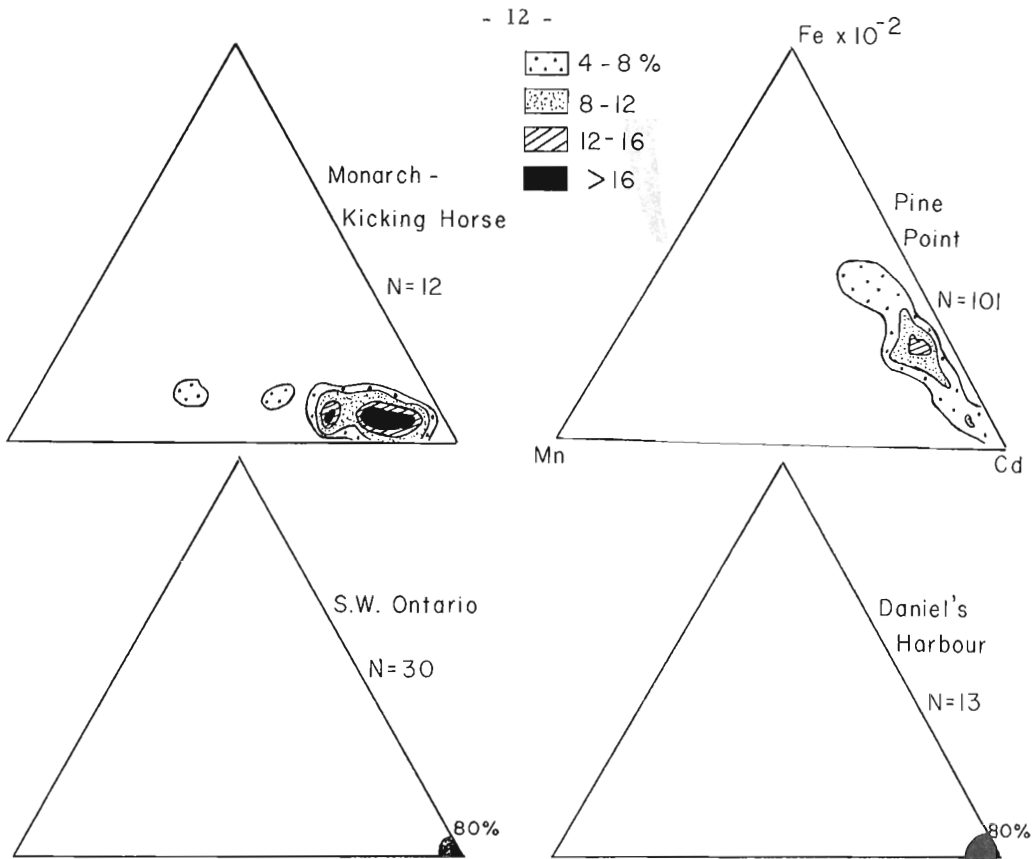
Figure 8. Fe-Mn-Cd atomic ratios in sphalerites from four selected
           Canadian deposits.

alteration feature. The other three deposits are enclosed in a widespread
dolomite unit; dolomitization does not appear to be as closely related to ore
as it is at the Monarch Mine.

        Ratios of Fe-Mn-Cd, the most common elements to substitute for
Zn in the sphalerite lattice, are shown in Figure 8. Analyzed sphalerites
from these deposits were better than 98 per cent pure concentrate and did not
contain any visible exsolved or included impurities except very small amounts
of galena. Some of the iron in the Pine Point and Monarch sphalerite might
be due to pyrite contamination but the other two ores do not contain pyrite.
Although there is an equal chance for pyrite contamination in both Monarch
and Pine Point samples, it should be noted that the former sphalerite is a
Mn-Cd type whereas Pine Point is an Fe-Cd type. The lack of iron in sphal-
erite from the other occurrences can be explained by the lack of iron in the
ore as demonstrated by the absence of pyrite. In spite of the abundance of
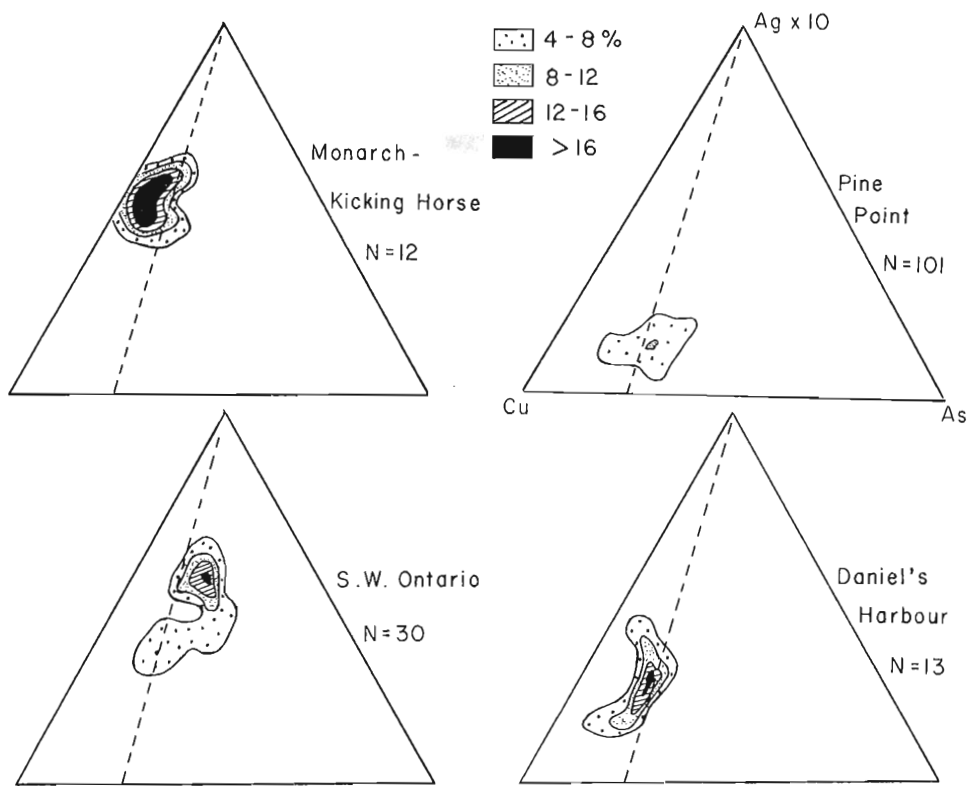
Figure 9.   Cu-As-Ag atomic ratios in sphalerites from four selected Canadian deposits.   Diagonal line in the diagrams represents the Cu:As ratio in ideal tennantite ($Cu_{12}As_4S_{13}$).

pyrite at the Monarch, however, sphalerite in this ore is relatively enriched in manganese and is rather anomalous in this respect.

Ratios of Cu-As-Ag are plotted in Figure 9. The reason for this particular grouping is that deposits with a high relative silver content (Part III in Fig. 2) frequently contained silver-bearing tetrahedrite (Cu-Sb sulphide) or tennantite (Cu-As sulphide) as independent minerals. None of the sphalerite from the four selected deposits contains appreciable antimony so the Cu-As-Ag grouping was chosen for presentation. Now, although all are from silver-poor deposits (they would plot in Part I of Fig. 2), it should be noted that these sphalerites contain Cu and As in about the same ratio as tennantite (Fig. 9). This mineral, like sphalerite, is isometric and the data suggest that these sphalerites contain, in solid solution, varying amounts of Ag-bearing tennantite. None of the polished sections of any of these ores revealed the presence of this mineral nor has it been reported by other workers. The Monarch and southwestern Ontario sphalerites have similar Ag/Cu + As ratios
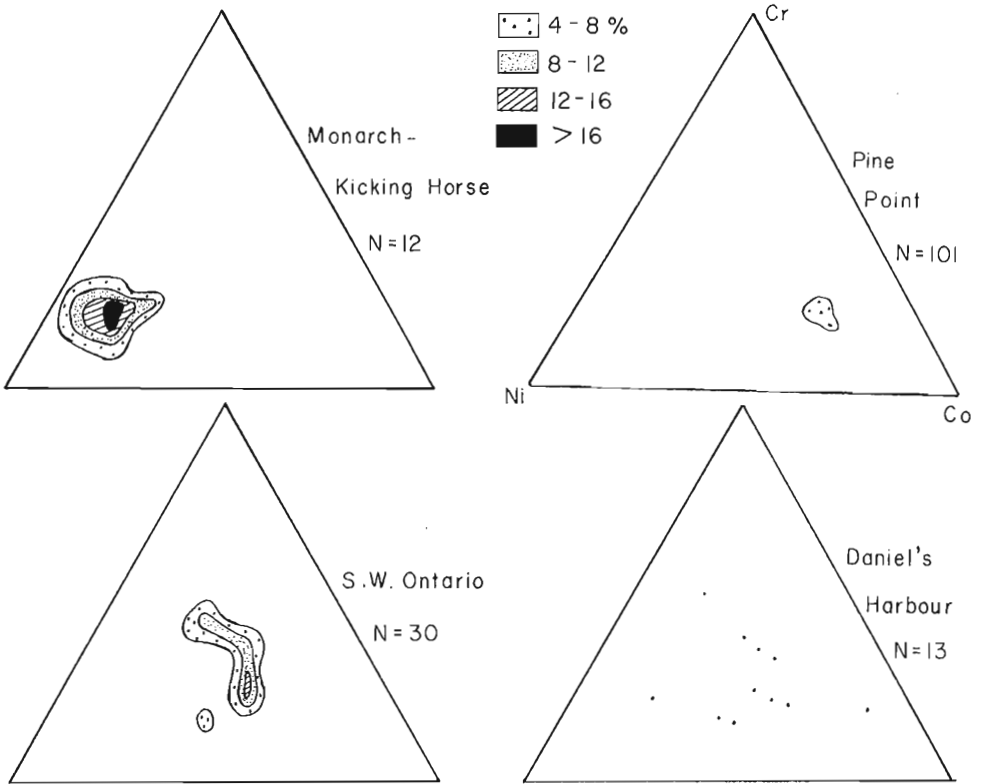
Figure 10. Cr-Ni-Co atomic ratios in sphalerites from four selected
Canadian deposits.

and are higher than in the other two occurrences, implying that the dissolved
tennantite in the two former deposits contain more silver. Comparing sphal-
erite from the Monarch-Kicking Horse Mine with that from southwestern
Ontario on an absolute rather than a relative basis, however, shows that the
former contains much more silver than the latter. Average silver content in
the Monarch sphalerites is 98 ppm whereas that from southwestern Ontario is
2.6 ppm (1 ppm = 0.032 oz/T). Therefore, on an absolute basis, Monarch
sphalerite is characterized by a high silver content but on a relative basis, it
is indistinguishable from other silver-poor sphalerites, at least on these Cu-
As-Ag diagrams.

Ratios of Cr-Ni-Co, the three most refractory elements analyzed,
are shown plotted in Figure 10. It must be noted that the range in the ratios
is very large in all sphalerites except those from the Monarch-Kicking Horse
Mine. These show a very marked tendency to concentrate near the Ni-corner
of the diagram whereas Pine Point, for example, shows a weak tendency to

plot near the Co-corner. The other two deposits seem to fall somewhere in between; ratios in Daniel's Harbour sphalerite were considered too scattered to contour. Nickel in all sphalerites fell roughly in the same concentration range (5-10 ppm) but, compared with Cr and Co, sphalerite from the Monarch-Kicking Horse Mine shows a decided Ni-rich trend. Thus, in the two 'systems', Cu-As-Ag and Cr-Ni-Co, Monarch sphalerite is characterized by its high absolute Ag content in the first case and by its high relative Ni content in the second.

This analysis of sphalerite compositions shows that a deposit such as the Monarch, which is geologically similar to three others yet possesses certain distinctive geological features, contains sphalerite which, although generally similar in composition to the other three, also possesses certain distinctive chemical features.

SUMMARY

From this initial chemical study of lead-zinc deposits in carbonate rocks, several features emerge which are so distinctive that they may eventually be recognized as being characteristic of this type of orebody.

Study of the bulk compositions of 47 deposits in terms of the Cu-Pb-Zn 'system' shows that 90 per cent of carbonate-host lead-zinc ores contain less than 10 relative atomic per cent copper. Furthermore, most of these ores show a bimodal distribution in terms of $Zn/Zn + Pb$ atomic ratio. One frequency distribution peak occurs at a ratio of 0.3, the other at 0.85.

In the Pb-Zn-Ag 'system', the ores fall into a three-fold division of increasing Ag relative to Pb + Zn. Ores in Part I with lowest relative silver are the true Mississippi Valley type ores with simple mineralogy and low precious metal content. In Part II, with relatively higher silver content, the extra silver is contributed to the 'system' by an additional phase (chalcopyrite). In Part III, ores with highest Ag content relative to lead and zinc, the silver appears as independent silver minerals in the ore. These observations have been tentatively interpreted in terms of a 'silver-saturation' hypothesis with ores in Part I being under- or just-saturated in silver and ores in Part III being over-saturated with respect to silver.

Primary haloes in bedrock adjacent to orebodies were searched for and found to be very narrow (less than 75 feet in most cases). The ratio of Cu:Pb:Zn in host rock carbonate, however, was found to be similar to that in ore and the similarity in the two ratios increased as the size of the contained orebody increased.

Ratios of Fe-Mn-Cd, Cu-As-Ag, and Cr-Ni-Co in sphalerite showed that, in the examples chosen, one deposit with more 'hydrothermal features' than the other three selected examples, was distinguished by its wide range

of Mn-Cd ratios and high Ni-Co ratio. All four deposits contain sphalerite
with similar Cu-As-Ag ratios and with Cu-As ratios suggesting that the
sphalerite contains tennantite in solid solution. On an absolute basis, how-
ever, the more 'hydrothermal' deposit is characterized by sphalerite of high
silver content (average 98 ppm versus 2-3 ppm for the other sphalerites).

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