

GEOLOGY, GEOCHEMISTRY AND MINERALOGY OF CARBONATES HOSTED LEAD ZINC DEPOSITS



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ABSTRACT

Lead-zinc deposit hosted by carbonate rocks occur principally in dolomites with less occurrence in limestones. Such carbonate rocks have a primary peripheral structural association with sedimentary basins. Carbonate – hosted lead – zinc deposits are epigenetic in origin. The origin or the metal-bearing solution is uncertain. However, there is a striking similarity of the mineralizing fluids to the highly saline formation waters encountered at depths in all fields. This suggests that the deposits were formed by ascending hot metal-bearing solutions derived from sedimentary basins associated with the host rocks. The metals were transported as metal – chloride complexes. Precipitation of the ores from the complexes resulted from the reduction of the metal-bearing brines by fluids containing hydrogen sulphide (H₂S), reduction of sulphate phases, change in the pH of solution and dissolution of the metal-bearing liquids by oxidizing ground waters. Homogenization temperatures of fluid inclusions in the range of 50^o – 200^oc show that these deposits are low-temperature types. The deposits are almost exclusively stratabound sulphide mineralization of sphalerite, galena, pyrite, baryte, fluorite and marcasite. The high porosity and permeability of the host rocks favour the deposition of the sulphide as vuggy ores or bedded replacements. These deposits are found in Paleozoic and Mesozoic carbonate rocks. In Nigeria, they are found at Arufu and Akwana, both in the Nigeria lead-zinc belt. Lead/zinc deposits with the aforementioned characteristics are also termed Mississippi valley – type (MVT) lead/zinc deposits.

INTRODUCTION

In spite of their chemical dissimilarity, geologic conditions favour the simultaneous formation of lead/zinc deposits. Because of this, it is pertinent that both lead and zinc should be treated together. Goldschmidt (1958), classified lead and zinc as chalcophile elements because of their high affinity for sulphide phase. In other words, lead and zinc normally combine strongly with sulphur to form metallic sulphides which are important group of non-ferrous metals, thereby constituting the raw materials for most of the world's supplies of non-ferrous metals. The association of lead and zinc sulphides and their oxidation products have over the years been of economic importance to man. As early as 2000 B.C., the Chinese had used these elements for various purposes ranging from coinage, ornaments, making of alloys to uses such as for vases. The ancient Romans found extensively used for plumbing purposes. Nowadays, these elements are used widely in the electronic, chemical, medical and agriculture industries.

Lead and zinc mineralization can occur in an igneous or sedimentary environment, one of such sedimentary environments being carbonate rocks. These carbonate rocks that host these lead and zinc deposits are often known to be associated with all fields, where there is abundant organic matter to enhance a reducing condition for the precipitation of the metals from solution. The source rock of the metals is same as that for petroleum. Thus there is a relationship between lead/zinc deposits in carbonate rocks and petroleum.

Lead/zinc mineralization in carbonate rocks comes under a category of deposits recognized as stratabound deposits, though some could be stratiform. Stratabound deposits are those deposits that occur as discordant, cross-cutting veins, pore space and breccia fillings, minor layers and are

confined to particular stratigraphic horizons (Stanton, 1972). These deposits could be epi- or syngenetic in nature. By epigenetic, they are said to have been formed after the host rock might since have been formed and by syngenetic; they were formed simultaneously with the host rocks. The host rocks for these lead/zinc deposits are commonly dolomites and less oftenly limestones. A large percentage of the world's production of lead and zinc are from these stratabound deposits of lead and zinc which are typified by those of the Mississippi valley in the United States of Americas. Hence, this type of mineralization is often referred to as Mississippi Valley – Type (MIV) lead/zinc deposits.

The aim of this research was to survey and to discuss the current state of knowledge regarding lead/zinc mineralization of carbonate rocks. The scope of the work was limited to the following aspects:

- i. Geology of the mineralization: the conditions which made possible the precipitation of lead/zinc ores in carbonate rocks; the origin of the mineralization by taking into account the various views of different workers in this field, as well as the different modes in which the mineralization occurs in carbonate rocks.
- ii. Geochemistry: how these elements had been transported from their source rocks to their sites of deposition as well as to geochemical survey methods and the geotechniques that could be employed to reduce the probable problems that would be encountered during the geochemical exploration for these metals.
- iii. Mineralogy of such mineralization, which according to field evidence is simple and is restricted to the sulphides of the elements.

Carbonate rocks that host lead-zinc deposits occur along the margins of miogeosynclines; though most oftenly, they occur on the adjacent shelf outside a geosyncline (Barnes *et al*, 1981). Also, nearly all carbonate-hosted lead-zinc deposits accumulated in either the shelf areas or on epeiric seas landward of passive continental margins (Mitchell and Garson, 1981). These host rocks are highly porous and permeable. The porous layers develop from the dissolution of these carbonate rocks by oxidation processes. The porosity can also result from brecciation of the host rock caused by the acidity of the ore-transporting fluids during sulphide mineralization (Barnes 1983). The porosity of limestone is also enhanced by complete dolomitization (Guillet, 1967). These carbonate (host) rocks are known to be associated with reefal build-ups in some cases. (Liberty and Bolten, 1970). These reefal host of which are brachiopods, corals and crinoids (Magaritz, 1975). Because of their highly porous nature, these reefs are thought to have served as escape route for mineralizing fluids during the dewatering process of sediments in associated basins.

These host rocks are often impregnated by petroliferous materials such as bitumen, exudanites, gilsonite (Sangster and Liberty, 1971, Tworo, 1985). They are also in some cases overlain by an impervious shale cover which tends to restrict further upward movements of the mineralizing fluids (Anderson, 1983). They (host rocks) could at times be mottled, fine, medium or coarse grained as well as being massive and scraggy or possessing sugary crystalline texture. The development of typical karst topography with steep limestone hills, sinkholes, cavities or caverns (Diehl and Mern, 1981), are peculiar to these rocks in some areas.

The breccias, cavities, caverns and permeable porous layers, present in these host rocks, apart from having temperature and pressure conditions necessary for ore disposition, also act as receptacles for the deposition of the lead-zinc ores. In addition, under the influence of heated water, carbonate rocks are subject to replacement by metallic ores such as galena and sphalerite (Lindgren, 1933). Principal occurrences of lead-zinc deposits in carbonate rocks are in dolomites with lesser occurrences in limestone.

The mode of occurrence of these lead/zinc mineralization in carbonate rocks are mostly cavity-filling and replacement types (Liberty and Bolten (1970); Park and MacDiarmid (1975), Mitchell and Garson (1981). Bateman, (1950) broadly classified the cavity-fillings as fissure veins, breccias

fillings, cave fillings pitches and flats. The replacement deposits were also classified as massive deposits, replacement lodes and disseminated deposits.

Lindgren (1933) reports that in the Moresnet District in Sangium and Luxemburg, the host rocks are cut by large faults and that it is these dislocations that the ores are found as filled veins, replacement deposits or are deposited in the intersections of the faults. The mineralization also occurs as cavity, vug and crevices fillings. The ores also fill spaces of faulted and solution breccias. In Morocco, the mineralization are chiefly; replacement in the host rocks (Lamey, 1966). In Western Thailand, the ores form stratabound lenses, bands and in places occur as disseminated layers. Some of the ores show “boundinage” structures with lens-shaped inclusions of limestone host rocks. There are occurrences of sphalerite concretions in the Bruce Peninsula of Southern Ontario (Sangster and Liberty 1971). The sphalerite concretions could be disc-shaped or massive. These sphalerite concretions were precipitated as a result of the reaction between zinc (zn) present in the sediments and sulphate-reducing bacteria which provided a source of sulphur. Thus, the sphalerite in the concretions have a biogenic origin.

Carbonate – hosted lead-zinc deposits therefore occur within specific sedimentary units as cave and solution-cavity linings, pore space and breccias fillings, as cross cutting veins in faults and fractures and are confined most of the time, to particular stratigraphic horizons. Based on their mode of occurrence, they can be referred to as stratabound deposits (Stanton, 1972).

CRYSTAL CHEMISTRY OF LEAD AND ZINC

In carbonate environments, lead/zinc deposits are mostly sulphides. Most metal sulphides are known to be crystalline solids and can thus be represented using ionic models in which the ions are considered to be charged spheres of constant radius. This approach is useful in considering the geometrical relationships between the atoms in the sulphides structures and between different structure types. (Vaughan and Craig, 1978).

THE GALENA (HALITE STRUCTURE) GROUP

The halite (cubic) structure typical of halite (NaCl) occurs in galena (Vaughan and Craig, 1978). This structure is based on the cubic close – packing of the anions. The lead – zinc atoms are at the corners and face centres. The coordination of the ions is such that each lead atom is surrounded by 4 atoms of sulphur, Fig. 1.

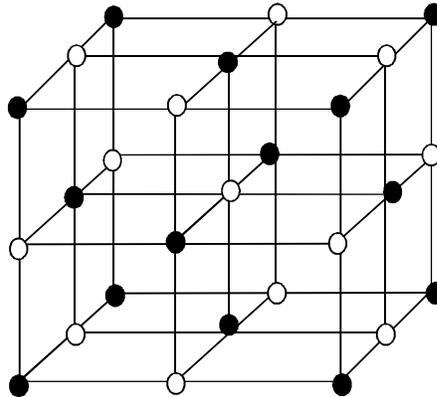


Fig. 1: The halite (NaCl) structure of galena showing coordination of ions.

THE SPHALERITE GROUP

The sphalerite (B-Zns) structure is a unit cube with zinc (Zn) atoms at the corners and face centres. The co-ordination of the ions is such that a sulphur atom lies at the centre of a regular tetrahedron of zinc atoms with each zinc at the centre of a regular sulphur tetrahedron for a given unit cell, (Figure 2).

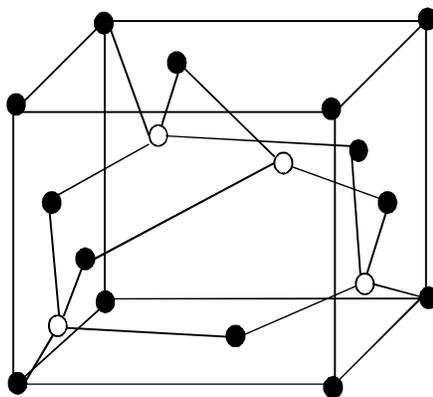


Fig. 2: The sphalerite (B-Zns) structure showing coordination of ions.

THE WURTZITE GROUP

There could also be the wurtzite structure of wurtzite (α - Zns). Here, each atom is tetrahedrally surrounded by four atoms of the opposite kind. However, the tetrahedral arrangement is such that a lattice with hexagonal instead of cubic symmetry is formed. This can be attained by the slight elongation of the unit cell in the c- direction to achieve a deformation of the zinc – sulphure tetrahedra (Vaughan and Craig, 1978).

Lead (Pb) and Zinc (Zn) are normally classified as B-metals, since they form a borderline transition series in a given period (Lowrie and C – Ferguson, 1971). Most of these B – metals are known to occur as oxides but mostly as sulphides, (they can thus said to be lithophil and chalcophil respectively). This is so because their ions are easily polarized (distorted) same as the anions of sulphides (Lowris and C – Ferguson, 1971). The ions of B-metals because of their easy polarization form covalent bonding. The effect of this is that, they enter into complex formation and election – pair formation very easily. They also show variable valency by exhibiting 2 states i.e.: the inter-pair effect.

TEMPERATURE OF FORMATION OF THE ORES

Carbonate rocks that host lead/zinc deposits are found on the margins of sedimentary basins and these are at shallow depths where diagenesis, burial metamorphism can take place. The mineral association here are known to indicate that deposition was at shallow depths where temperature and pressure conditions are not very different from those prevailing at the surface. The presence of marcasite, a common accessory mineral in these ores, strongly suggest deposition near the surface since marcasite is not stable at high temperature, (Lindgren, 1933). Table 1 shows estimated deposition temperature of some Mississippi Valley Type deposits.

Table 1: Estimated deposition temperature of some Mississippi Valley Type deposits, (source, Giordano and Barnes, (1981).

District	Temperature °C	Method of determination
Illinois Wisconsin	75 – 220 52 – 227	Inclusion in sphalerite, (sphalerite – galena).
Central Tennessee and Central Kentucky	73 – 132	Inclusion in sphalerite, barite, fluorite
Northern Arkansas	80 – 132	Inclusion in sphalerite, quartz, dolomite
Southern Illinois	145 – 195	Sphalerite – galena
Pinepoint, Northwest Territories	50 – 97 90 - 100	Inclusion in sphalerite Inclusion in calcite.

CONCLUSION

It has been found that of the carbonate rocks that host lead-zinc deposits, dolomite is the principal host rock with less occurrences of the deposits found in limestones. These host rocks are highly porous, permeable and occur peripheral to, rather than within sedimentary basins. Carbonate-hosted lead-zinc deposits consist of vuggy ores, veins and some bedded replacements strongly controlled by individual strata. They are thus said to be stratabound and are epigenetic as symbolised by the slumping, brecciation and thinning of the host rock. These carbonate-hosted lead/zinc deposits are mostly sulphide mineralizations and they contain galens, sphalerite, marcasite, pyrite, barite, dolomite, calcite, quartz etc. The origin of the metal-bearing solution is uncertain but it is most probable to have been generated in the adjoining sedimentary basins, since the metal-bearing solutions are similar to oil filed brines. Such similarities include; the low homogenization temperature, high salinities, aqueous inclusions, co-existing petroleum inclusions and occurrence on the flanks of sedimentary basins.

Lead-zinc deposits in carbonate rocks are low temperature types as shown by the occurrence of low temperature minerals such as pyrite, marcasite, barite etc in these deposits. Homogenization temperatures of fluid inclusions are generally low in the range of 50^o – 200^oC. these deposits also occur at shallow depths generally less than 600m. The exact mode of transportation of the metals from source to sites of deposition is not known. Thus, a variety of models of explain this have been put forward.

These include the:

- i. single solution model in which both the metals and sulphide were transported in the same solution;
- ii. the mixing model fluid and the sulphide transported separately in another fluid, with precipitation taking place where the two fluids mixed.

However, any of the models applied to certain specific deposits as shown by field and laboratory studies. Carbonate-hosted lead/zinc deposits are fairly widespread in the world and are found almost exclusively in Paleozoic and Mesozoic dolomites and limestones.

The problems of lack of knowledge of the appropriate transportation mechanism; origin of ore solutions as well as the time of emplacement of the ore bodies in the host rocks tend to becloud a better understanding of these lead-zinc deposits in carbonate rocks. To overcome these barriers, we suggest a future work on these deposits in the direction of field-oriented as well as laboratory-oriented research as the integration of the two lines of research is essential. This would significantly improve our understanding of these Mississippi Valley-Type (MVT) or carbonate-hosted lead/zinc deposits.

REFERENCES

- Anderson, G. M. (1973). The Hydrothermal Transport and Deposition of Galena and Sphalerite near 100^oC. *Econ. Geol.* 82(2), p. 457 – 470.
- Barnes, H. L. (1983). Ore depositing Reactions in Mississippi Valley – Type Deposits: in Kisvarsanyi, G. Grant, S. K., Pratt, W. P. and Koenig, J. W., eds., *International Conference on Mississippi Valley Type Lead Zinc deposits. Proceedings volume: Rolls, Univ. Missouri Rolla*, P. 77 - 85
- Barnes, H. L., Adams, S. S., Rose, A., (1981). Ores formed by Diagenetic and Metamorphic Processes: in Mineral Resources: Genetic Understanding for Practical Applications: *Geophysics Study Comm., National Academy Press, Washington*, p. 77-79.
- Bateman, A. M. (1950). Economic Mineral Deposits 2nd edition. *John Wiley and Sons Inc.*, New York
- Giordana, T. H. and Barnes, H. L. (1981). Lead Organic Geochemistry of two Mississippi Valley – Type Ore solution. *Econ. Geol.* 76(8), P. 2200 – 2211.
- Goldschmidt, V. M. (1958). *Geochemistry. Oxford Univ. Press, London.*

- Guillett, G. R. (1967). Notes on Zinc-Lead Mineralization in Silurian Dolomites of the Niagara Escarpment and Bruce Peninsula, Ontario. *Miscellaneous paper MPB; Ontario Department of Mines*. P. 1-17.
- Lamey, C. A. (1966). *Metallic and Industrial Mineral Deposits*. McGraw Hill Inc.
- Liberty, B. A. and Bolten, T. E. (1970). Palaeozoic Geology of the Bruce Peninsula Area, Ontario. *Memoir 360, Geol. Survey, Canada* p. 89-90
- Lingren, W. (1933). *Mineral Deposits*, 4th ed. McGraw-Hill Book Company Inc., New York
- Lowrie, R. S. and Campbell-Ferguson, H. J. (1971). *Inorganic and Physical Chemistry. An Integrated Approach*. Pergamon Press, London
- Magaritz, M. (1975). Epigenetic Dolomitization and Mineralization in Jurassic rocks from Mount Hermon and Northern Neger, Israel. *Chemical Geology*, 16, p. 265-306.
- Mitchell, A. H. G. and Garson, M. S. (1981). *Mineral Deposits and Global Tectonics Settings*. Academy Press Inc. London, p. 103-105.
- Park, Charles and Macdiarmid (1975). *Ore-Deposits*, 3rd ed.; M. H. Freeman and Company, San Francisco.
- Sangster, D. F. and Liberty, B. A. (1971). Sphalerite Concretions from Bruce Peninsula Southern Ontario, Canada. *Econ. Geol.* 66, p. 1145-1152.
- Stanton, R. L. (1972) *Ore-Petrology*. McGraw-Hill Inc., New York. P. 543-553.
- Twoo, A. G. (1985). The Nature and Origin of Lead -Zinc Mineralization, Middle Silurian Dolomites, Southern Ontario. *Unpublished M. Sc Thesis. Abs, Univ. Waterloo, Ontario*.
- Vaughan, D. J. and Craig, J. R. (1978). *Mineral Chemistry of Metal Sulphides*. Cambridge Earth Science Series Camb. Univ. Press.