## Carbonate-hosted, Nonsulphide Zn–Pb (supergene) Mineral Deposit Profile B09

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### **IDENTIFICATION**

#### SYNONYMS

Zinc-oxides, Calamines, Galman

COMMODITIES (*BYPRODUCTS*) Zn, Pb (*Ag, Cu, barite, Cd*)

#### **EXAMPLES**

(British Columbia - Canada/International): Redbird (MINFILE 082FSW024), Lomond (MINFILE MacDonald 082FSW018), Reeves (MINFILE 082FSW026), Annex (MINFILE 082FSW219), Caviar (MINFILE 082FSW060), HB (MINFILE 082FSW004), Oxide (MINFILE 082FSW022), Cariboo Zinc (which comprises Canopener, DeBasher (MINFILE 093A 050), Flipper Creek, Dolomite Flats, Main (MINFILE 093A 065), Gunn, and Que (MINFILE 093A 062); Leadville (Colorado, USA), Balmat (New York, USA), Sierra Mojada, Mapimi (Mexico), Accha, Mina Grande (Peru), Ariense (Brazil), Tynagh, Silvermines and Galmoy (Ireland), La Calamine (Belgium), Reocin (Spain), Silesia-Cracow district (Poland), San Giovanni (Italy), Lavrion (Greece), Touissit (Morocco), Um Gheig (Egypt), Zamanti district (Turkey), Jabali (Yemen), Angouran, Mehdiabad, Irankuh, Kuh-e-Surmeh (Iran), Shaimerden (Kazakhstan), Skorpion (Namibia), Padaeng (Thailand), Long Keng (Myanmar), Cho Dien (Vietnam), Jinding, Qiandong Shen Shen (China), Magellan (Australia).

## **GEOLOGICAL CHARACTERISTICS**

#### **CAPSULE DESCRIPTION**

Nonsulphide deposits are commonly hosted in carbonate rocks. The main minerals are hemimorphite, smithsonite, hydrozincite, cerussite, Fe-oxyhydroxides (including goethite), and hematite. The deposits are broadly divided into three subtypes: the more common -1) direct replacement and 2) wallrock replacement; and the less common -3) residual and karst-fill. Direct

replacement deposits have similar shape as the sulphide protore from which they are derived and may contain vestiges of sulphide mineralization. Wallrock replacement deposits are located at various distances from the protore, have simpler mineralogy and higher Zn/Pb ratio than direct replacement deposits, and occur as irregular masses encrustations, tabular bodies, and open-space fillings. Residual and karst-fill deposits form generally small, high grade, irregular bodies of partly consolidated material that may have detrital component. Some nonsulphide deposits may share characteristics of more than one of these subtypes.

### **TECTONIC SETTING(S)**

Supergene nonsulphide deposits derived from Mississippi Valley-type (MVT) and Irish-type deposits are located in carbonate platform settings, typically in relatively undeformed orogenic foreland rocks, commonly in foreland thrust belts inboard of clastic rock-dominated passive margin sequences, and in continental rift systems. Those derived from sedimentary exhalative (SEDEX) deposits are located in intracratonic or continental margin environments in fault-controlled basins and troughs. Volcanic-hosted massive sulphide (VHMS)-derived supergene nonsulphide deposits are emplaced under extensional crustal regime, such as oceanic or back-arc spreading ridges, continental rifts, back-arc basins, oceanic ridges close to continental margins, and rift environment within, or perhaps behind, an oceanic or continental margin arc.

# DEPOSITIONAL ENVIRONMENT / GEOLOGICAL SETTING

Hostrocks of supergene nonsulphide Zn-Pb deposits are mostly deposited in platform successions within shallow and deep water environments. The nonsulphide deposits are found in both arid and tropical environments; however, many of the best supergene nonsulphide deposits recognized to date formed in semi-arid environments. Some are found in cold, wet climates at higher latitudes.

#### AGE OF MINERALIZATION

Ages of nonsulphide mineralization are commonly poorly constrained. Ore formation coincides with or postdates the exhumation of the hostrocks and generally postdates the main tectono-metamorphic event. Most of

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the nonsulphide deposits formed during the late Cretaceous to late Tertiary *(i.e.,* Paleocene to Pliocene) and younger times.

#### **HOST / ASSOCIATED ROCK TYPES**

Dolostone, limestone, dolomitized limestone and argillaceous carbonate are the most common hostrocks. Siliciclastic rocks, such as calcsilicate rocks, carbonaceous black shale, siltstone, cherty argillite, quartz-rich conglomerate and arkosic meta-arenites, and volcaniclastic and metasedimentary rocks are also potential hosts.

#### **DEPOSIT FORM**

The direct replacement deposits (also referred to as "red ores") occur as a) irregular and poorly defined masses that replaced primary sulphides and carbonate hostrocks (Figure 1), whereby selective replacement within specific horizons may yield stratabound morphologies; and b) veins and open-space fillings within primary breccias of sulphide mineralization and carbonate hostrocks (Figure 2), where the morphologies of the



Figure 1. Lomond deposit; an example of a supergene direct replacement nonsulphide deposit, southeastern British Columbia.



Figure 2. Galena and nonsulphides forming part of a vein-breccia system crosscutting the host dolostone, Cariboo Zinc property, east-central British Columbia.

nonsulphide zones are comparable to those of the related primary sulphides (*i.e.* stratabound zones and/or crosscutting pipes, fracture-fill zones, veins). The depth of oxidation can be variable from a few metres to several hundred metres. The wallrock replacement deposits are Zn-rich irregular and lens-shaped or tabular (subvertical to subhorizontal) bodies adjacent to or distal to direct replacement bodies. The residual and karst-fill deposits occur as accumulations of ferruginous, "earthy" and hemimorphite-clay mixtures, within karst cavities that cut through the replacement or open-space filling mineralization. These deposits have, irregular geometry, and can form high-grade nonsulphide bodies. Geometry is controlled by basement topography.

#### **TEXTURE / STRUCTURE**

Nonsulphides form irregular stratabound masses, pods or lenses; breccias of sedimentary and tectonic origin, disseminations, fracture fill, and veins are also very common. Due to intense oxidation, the primary textures of sulphides and hostrock are often obscured. Ore textures are varied and complex, ranging from massive to highly brecciated, from compact to powdery and from vuggy to dense. Nonsulphide minerals occur as earthy to crystalline aggregates replacing primary sulphides and/or carbonate hostrocks (Figures 3 and 4). They form crusts, concretions, and stalactites on outer surfaces, and botryoidal, colloform and crystalline aggregates of euhedral and subhedral crystals in intergranular voids, cavities, fractures, and breccias.

#### **ORE MINERALOGY (Principal and subordinate)**

Smithsonite, hemimorphite, hydrozincite, sauconite, cerussite, anglesite, litharge, pyromorphite, mimetite, and plumbojarosite, *minrecordite, zincian aragonite, willemite, goslarite, loseyite, descloizite, hetaerokite, hydrohetaerolite, chalcophanite, hopeite, aurichalcite, woodruffite, tarbuttite, scholzite.* Where the sulphidebearing protolith was not entirely converted to nonsulphides, primary sulphides remain intermixed with



**Figure 3.** Hemimorphite-rich mineralization, Oxide deposit, southeastern British Columbia. The hemimorphite replaced the carbonate groundmass.



**Figure 4.** Microphotographs (polarised light) of A) concentric aggregates of radiating crystals of hemimorphite replacing the carbonate groundmass and tabular crystals of hopeite filling up crosscutting veinlets, and B) aggregates of tabular crystals of hemimorphite lining cavities.

the nonsulphide minerals to form "mixed ores". The primary sulphides may contain anglesite-coated nodules of galena and remnants of sphalerite. Chalcocite, malachite, and azurite are present in some deposits.

## GANGUE MINERALOGY (Principal and subordinate)

Carbonates (dolomite, calcite, aragonite), hematite, goethite, other Fe-oxyhydroxides, gypsum, minor quartz.

#### ALTERATION MINERALOGY

Coarse crystalline dolomite spatially associated with MVT-type protore may survive in proximity to nonsulphide deposits and contrast with regional finely crystalline dolostone. Local alteration may also include silicification and rare secondary barite, both a result of the alteration and breakdown of feldspar (*e.g.*, Skorpion). The sulphide weathering and near surface alteration of protore corresponds to formation of supergene mineralization.

#### WEATHERING

The nonsulphide mineralization forms by weathering of sulphides. Multicyclic oxidation and leaching of nonsulphides is a part of the ore-forming process and may affect even previously formed wallrock replacement bodies (see genetic model). Such bodies may be gradually converted into porous brown to reddish smithsonite intergrown with hemimorphite. Further leaching may result in mixture of hemimorphite, sauconite, hematite- or goethite-dominated iron oxides, and hematitic chalcedonic silica, and ultimately transformed into a barren goethite-chalcedonic silica rock.

#### **ORE CONTROLS**

Most favourable conditions for oxidation are achieved in hot, arid or semiarid climates, which maximize the quantity of metals available for transport by supergene solutions. Sedimentary successions containing carbonate rocks are the most common regional hosts for nonsulphide lead and zinc deposits. In general, the oxidation of the protore takes place above water table. Karst, faulting, fracturing and to lesser extend porosity are important in enhancing the depth and intensity of the oxidation. Major faults represent channels for oxygenated solutions and permit oxidation to depths exceeding 500 m. Faults also increase the reactive surface of hostrocks (i.e. provoking changes in pH and Eh). Direct replacement deposits are confined to protore envelope. Wallrock replacement orebodies are commonly located near the level of the paleo and/or present water table.

#### **GENETIC MODEL**

Supergene nonsulphide Zn-Pb deposits form when base metal sulphide mineralization is subject to intense weathering and metals are liberated by the oxidation of sulphide minerals. The formation of nonsulphide minerals is influenced by the composition, size and morphology of the preexisting sulphide body. During the formation of a direct replacement deposit, primary ore (protore) is oxidized, and base metals pass into solution and are redistributed and trapped within space originally occupied by the protore. If the base metals liberated by the oxidation of sulphides are not trapped locally, they are transported by percolating waters down and/or away from the sulphide protore, and under favourable geological conditions may form wallrock replacement deposits. Wallrock replacement deposits can be located in proximity to protore or several hundreds of metres away. Lead is less mobile in the supergene environment than zinc, so in general, it is left behind as relict galena nodules and lead carbonate or lead sulphates. Wallrock replacement deposits tend to have higher Zn content and higher Zn/Pb ratios than direct replacement deposits. Residual and karst-fill deposits are formed as accumulations of mechanically and/or chemically transported zinc-rich material in karstic cavities or lows in basement topography. Some nonsulphide zinc deposits are assigned a hypogene origin. These deposits are

characterized by willemite or willemite-franklinite-zincite assemblages (Hitzman *et al.*, 2003) and formed at higher temperatures than the supergene deposits. Their temperature of formation is estimated from less than  $100^{\circ}$  to nearly  $300^{\circ}$ C.

#### ASSOCIATED DEPOSIT TYPES

Mississippi Valley-type Pb-Zn (E12), Irish-type carbonate-hosted Zn-Pb (E13), sedimentary exhalative Pb-Zn-Ag (E14), veins, and Pb-Zn skarns (K02); rarely volcanic-hosted massive sulphide (G04 to G06).

#### COMMENTS

British Columbia has prospective strata for supergene nonsulphide deposits in the miogeoclinal carbonate platform rocks of the Ancestral North America continental margin and in pericratonic rocks of the Kootenay terrane. The association of many known carbonate-hosted nonsulphide zones with directly underlying massive sulphide orebodies, in combination with nonsulphide mineralogical characteristics, suggests that a large proportion of known nonsulphide mineralized zones in southern and central British Columbia are of the direct replacement type.

## **EXPLORATION GUIDES**

#### **GEOCHEMICAL SIGNATURE**

Colorimetric field test for secondary zinc minerals ("Zinc Zap") is very useful (Figure 5). Portable hand-held x-ray fluorescence spectrometry was successfully tested in British Columbia on supergene nonsulphide Pb-Zn deposits. Depletion in Zn, Pb, Cu, Fe, and Mn in and around former Zn-bearing sulphide gossans. Readily detectable positive anomalies of Zn and Pb in residual soils and stream sediments; elevated concentrations of Cu, Fe, Ag, Mn, As, and Cd can also be detected. Analysis of heavy mineral concentrates (identification of Zn-Pb nonsulphides) in stream and overburden may be effective



**Figure 5.** Typical bright red stain caused by reaction of "Zinc Zap" solution with zinc-rich mineralization, east-central British Columbia.

in areas lacking deep weathering. Where residual sulphide oxidation is taking place, soil gas geochemical techniques (SO2 surveys) may be an applicable exploration technique. Many supergene minerals, such as hydrozincite and smithsonite, give distinct spectral responses in the short-wave infrared portion of the spectrum. Hyperspectral imaging holds promise as a useful tool for accurate mapping of structures, lithologies, and alteration.

#### **GEOPHYSICAL SIGNATURE**

There is no simple approach to use geophysical methods in exploration for nonsulphide-bearing Pb-Zn deposits. The mineralogy, textures, homogeneity, friability, porosity, and degree of saturation by water vary widely. These properties affect the density, resistivity, magnetic susceptibility, and seismic properties of the rocks. Interpretation methodologies may be district specific. Where sulphide mineralization is present at depth, methodology used in exploration for MVT, VHMS, and SEDEX deposits applies.

#### **OTHER EXPLORATION GUIDES**

Most of the supergene nonsulphide base metal deposits are derived from the oxidation, or near-surface weathering, of primary carbonate-hosted sulphide deposits, such as Mississippi Valley-type, sedimentary exhalative, Irish-type or vein-type deposits and, to lesser extent, Pb-Zn skarns and rarely volcanic-hosted massive sulphide. Any carbonate-hosted, sulphide zinc district that has undergone geochemically mature weathering in semiarid to wet climatic (or paleoclimatic) conditions and concomitant tectonic uplift and/or water table depression is prospective for supergene nonsulphide deposits. Within these settings, exploration could be further focused on areas where favourable water table level, optimum oxidoreduction conditions, permissive hydrological characteristics (permeability and porosity of the hostrocks, karsts, and fracture and fault zones), rocks with ability to control the pH of the metal-bearing solutions, topography and slow(?) rate of uplift, coexisted. Discovery of outcropping supergene Zn-Pb nonsulphide deposits depends on recognition of common nonsulphide ore minerals. Areas not affected by glaciation have higher potential to contain preserved, soft, nonsulphide deposits than glaciated ones.

## **ECONOMIC FACTORS**

#### TYPICAL GRADE AND TONNAGE

Tonnages for nonsulphide Zn-Pb deposits range from <1 Mt to 50 Mt with grades of 2% to more than 30% Zn. If mixed ores are considered, some deposits and districts have tonnages comparable to world-class sulphide deposits. Skorpion (Namibia) has 60 Mt of mixed resource grading 6–8% Zn and 1–2% Pb, and 24.6 Mt of oxide resource grading 10.6% Zn. Mehdiabad (Iran) has a mixed oxide-sulphide resource of 218 Mt grading 7.2% Zn, 2.3% Pb, and 51 g/t Ag. Direct replacement

nonsulphide Zn-Pb deposits could be also significant sources of Pb, as illustrated by the exploitation of the Magellan deposit, which has ore reserves of 8.5 Mt grading 7.12% Pb.

#### **ECONOMIC LIMITATIONS**

The economic value of nonsulphide ores is dependent on the physical setting of individual deposit, the specific characteristics of the mineralogical association and the nature of the gangue minerals. The large, near-surface deposits are amenable to high volume, open pit mining. Underground mining is less common. Depending on the type of ore and mineralogy, a dedicated processing plant may be required. However, there is also the possibility that limited quantities of zinc-rich carbonates or silicatebearing material (with low levels of impurities) may be used by conventional smelters as a sweetener (instead of Ca carbonate that is commonly used to control the pH) or as source of silica; this should be investigated.

#### IMPORTANCE

Nonsulphide deposits were the main source of zinc prior to the 1930s. Following the development of differential flotation and breakthrough in smelting technology, the mining industry turned its attention almost entirely to sulphide ores. Today, most zinc is derived from sulphide ore. The nonsulphide deposits provided roughly 7% of the world's zinc production in 2009. The successful operation of a dedicated processing plant at the Skorpion mine to extract zinc, through direct acid leaching, solid-liquid separation, solvent extraction and electro winning from nonsulphide ore has attracted more attention to these types of deposits. These deposits are attractive targets because they are characteristically low in lead, sulphur and other deleterious elements, offer low-cost onsite production, and are environmentally friendly.

## ACKNOWLEDGMENTS

This manuscript benefited from reviews by Donald Sangster (Geological Consultant, Ottawa) and David Lefebure (British Columbia Geological Survey Branch). The project started under the umbrella of the Cordilleran Targeted Geoscience Initiative-3 Program of the Geological Survey of Canada, and was done in collaboration with the British Columbia Geological Survey Branch. Geoscience BC is acknowledged and thanked for funding the laboratory component required to complete this project.

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