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A BRGM contribution to the EEC finded Bioshale project WP6

Final report

BRGM/RP-55610-FR

June, 2007

BIO SHALE

Geoscience for a sustainable Earth

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Study carried out as part of
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Geoscience for a sustainable Earth

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Synopsis

To cope with the strong base and precious metal demand due to the growing economy of China and India, the mineral industry has to face several challenges: discovering new ore reserves and develop low cost methods for extracting them. The Bioshale project fit exactly with this major objective.

In the frame of the project, a bibliographic compilation of the major base metal districts associated with black shales in the world was performed. However, to better achieve one of the main objectives of the project, we restricted our investigation to the main polymetallic districts of the world associated with sedimentary, carbon rich shales. These include deposits classified in the Sedex type (Goddfellow W., Lydon J., 2005), those corresponding to the Kupferschiefer type and some disseminated sulfides disconnected from their submarine volcanic sources (VMS *lato sensu*) and deposited in anoxic basins.

Black shales are deposited in four major geodynamic contexts: deep enclosed basins, deep border land basin, shallow stratified basins and coastal intertidal zone of continental platform. Worldwide major anoxic events are well known in Proterozoic, Cambrian, Ordovician, Carboniferous, Permo-Triassic and Eocene, Oligocene periods.

Major low grade but very extensive base metals deposits are related to these events and usually classified in three main ore types: Sedex, Kupferschier or copper shales and distal Volcanogenic massive sulphide (VMS).

A short description of the major mineralized districts is provided: Proterozoic black schists of Finland, Early Silurian black shales of the Selwyn basin, Canada, the Cambrian carbonaceous shales of the Zunhyi district in China, the Paleoproterozoic Carpentaria belt of Australia, the Neoproterozic Congolese-Zambian copper belt, and the Lower Permian German-polish Kupferschiefer.

In ancient mining districts (Abitibi, Australian Carpentaria belt, Southern Iberian province, Rammelsberg district,…) a reassessment of the low-grade *in situ* resources has to be done including dumps materials according to the new price trend. Few data are published, but for example, in the Iberian Pyrite Province we know that more than 500 Mt of polymetallic ores would be easily accessible to new investors, using bioleaching technologies.

This new era opens new opportunities to develop new mines in well known enriched black schists like in the Selwyn Basin (more than 520 Mt resources of Pb-Zn ore with rare metals), in Canada, or in the Proterozoic belt of Finland, of Australia, and Paleozoic belts of Brittany and the Pyrenees in France and Spain.

Contents

List of figures

List of Tables

1. Introduction

1.1. SCOPE OF THE WORK

In the frame of the EEC funded Bioshale project, a bibliographic compilation of the major base metal districts associated with black shale in the world was performed to provide an overview of the tremendous potential of development for the numerous metal resources (Cu, Pb, Zn mainly but also Ni, Mo, V, U, Au, PGE) linked to this ore association in the near future using a new sustainable low cost beneficiation technology. Of course, bacteria leaching of ore is not restricted to low grade sulphide ores and the process is already used worldwide for bioprocessing Cu rich sulphide ore as well as polymetallic dumps materials in abandoned mines (see the Kasese Cobalt recovery for example).

However, to better fit with the major objectives of the project, we restricted our investigation to the main polymetallic districts of the world associated with sedimentary, carbon rich shales. These include deposits classified in the Sedex type (Goddfellow W., Lydon J., 2005), those corresponding to the Kupferschiefer type and some disseminated sulfides disconnected from their volcanic sources (VMS *lato sensu*) and deposited in anoxic basins. Unconformity related deposits like MVT or sandstone red bed types have not been retained in this preliminary attempt to compile the existing in situ reserves. No doubt that the fascinating increase of the base and precious metal prices during the last 5 years (Fig. 1) will urge the major mining producers to reassess their reserves classifications and develop new exploration strategies toward low grade extensive base and precious metal resources.

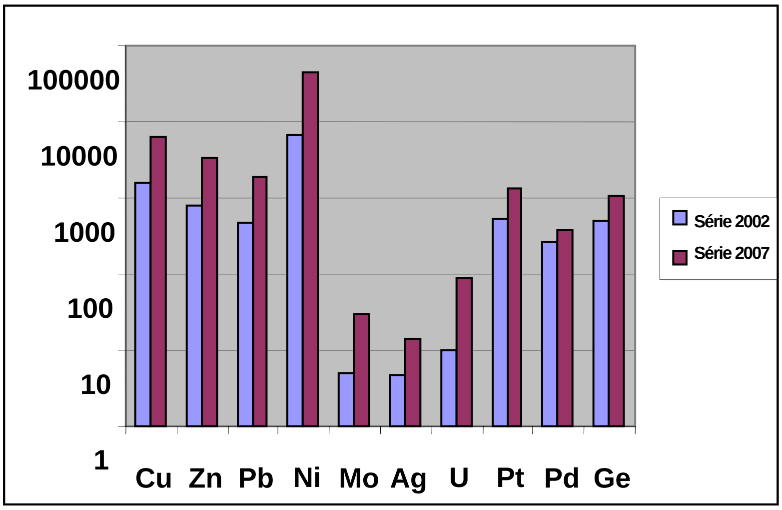


Figure 1 - Price evolution (in $ US) between 2002 and 2007 for the major base metals, U and Au, Pt, Pd.

1.2. BLACK SHALE: DEFINITION

Black shale are sedimentary rocks mainly composed of clays, fine grained detrital particles, and 1 to 5% organic carbon. These rocks are common in back arc basin, in continental sea or lake (rift) and interfingered with fan type fuvio-deltaic deposits, or turbidite deposited at the bottom of lakes, or deeper sea platform margin. The organic matter (OM) may be of continental origin (peat, coal,..) or marine origin: algal matts, plankton….

Three major steps are generally differentiated during basin burial evolution (Baudin *et al.*, 2007):

- diagenesis (1): 20-80°C. This T° mark the bacteria deadline;
- catagenesis (2): 80-120°C or 4,000m depth: most of the O, N, S atoms are disconnected from OM, oil and gas are free;
- metagenesis: T° >120°: only residual bitumen, kerogen remain in the shale.

During their later evolution, after compaction and temperature increase with burial metamorphism, the cristallinity of the clays and the purity of the carbon matter increase with the departure of the O and N compounds. The metallic elements are then disconnected from their weak boundings with organic metalloprophyrins during early diagenesis. At this stage, bacterial sulphide reduction (BSR) allows the first precipitation of base metal sulfides.

During the second stage, most of the organic acid formed during catagenesis (formic, acetic, oxalic, malonic acids...) are indeed, very efficient complexing agents to allow transport of Al, Fe, Mn, Mn, Cu, Zn, Pb, U in the interstitial fluids (Wood S.A., 1996, Sverjenski, D.A.,1987) and recristallize mainly as sulfides because of thermal sulfate reduction in these rocks..

Oil shale or tar shales are the residue of the initial black shale impoverished in light hydrocarbons. These rocks still contain heavy hydrocarbons and the associated heavy and precious metals. Mudrock containing high amounts of organic matter in the form of solid hydrocarbon or kerogen is known as oil shale or kerogen shale or kerogenites. Kerogen is a complex mixture of compounds with large molecules containing mainly hydrogen and carbon but also oxygen, nitrogen, and sulfur. Oil shales beds are often found accompanying coal and, in fact, grades into bituminous coal when carbonaceous material is present in large amounts. In higher metamorphic grade, these rocks are called black or graphitic schist. Numerous black shales districts in the world are host of base metal and or precious metal deposits (Fig. 2).

Figure 2 - Main black shales districts with their corresponding economic ressources in the world (after Pasava I., 2004).

1.3. SEDIMENTOLOGICAL MODEL

Geodynamic context

To obtain a thick organic rich black shale layer, it is necessary to have not only a high OM productivity, but also a stable continental margin to trap the material over a long period.

In deep border land, and marginal shoreland basin, the organic matter productivity is directly related to the major climatic variations:

- alternative regressive–transgressive phase related to worldwide glaciation induces severe impact on the bioplankton. A moving of the thermocline or the sudden temperature lowering of the ocean surface water by a change of density in the peri-oceanic circulation (for example due to ice melting of the Northern Ice kalott) will induce the massive death of micro-organisms and these will settle at the oceanic bottom. If anoxic conditions prevail at this stage, an organic layer will be developed interlayered with turbidites or pelagic clays;
- a moving of the salinity of the sea water towards extreme salinity by evaporation in a marginal sea will also produce a biogenic reservoir.

The development of coal layer from continental macroflora start with the aerial plant development under tropical climate at the carboniferous. Most of the organic matter in Precambrian era was deposited from the decay of marine algae.

On a world global scale the rate of organic matter (OM) storage increase with the sedimentation rate: indeed a quick transfer of the organic matter from marginal shoreline to deeper anoxic conditions will ensure its preservation. In a closed rift system like the black sea, there is also a direct correlation between the OM content and the finest fractions (clays) content of the sediment (Baudin *et al.*, 2007). Today, for example, sphalerite framboids are crystallizing in bottom anoxis sediments of the Kivu lake. Isotopic studies have shown both a volcanic and a biogenic contribution to the sulphur.

The sedimentology models of these black shale deposits have deeply evolved in the last years, mainly after intensive research on oil source rocks and secondary trapps in the modern litterature.

Black shales are the precursor of most of the intracontinental evaporitic deposits (Warren J., 2000; Lagny *et al.*, 2001). Their deposition require the preservation of organic matter (either of continental or marine origin) during their transfer through the marginal basin or ocean water column and the preservation of anoxic condition during their diagenesis.

Worldwide oceanic anoxic events are well known for example in the lower Proterozoic black schist of Finland, Australia, *in* lower Cambrian period (China, Africa, Europe) Ordovician associated with continental glacial deposits (tillites), in the Silurian period (black graptolitic shales), and in two periods of the Cretaceous: the Aptian-Albian event and the Turonian-Cenomanian (Arthur, Sageman, 1994).

Permian and carboniferous rifts are also the location for continental organic matter deposition leading to bitumen, coal deposits.

According to Arthur, Sagerman (1994), four main types of sedimentological models are recorded for black shales deposits (Fig. 3):

- (1) Deep enclosed basins (for example the Black sea): anoxic zone between –150m to 1,500m, high H_2S productivity;
- (2) Deep border land basins (like S California) or western continental slope: disoxic zone between 100m and 700m;
- (3) Shallow stratified basins (estuaries, fjords etc.. like Baltic sea) with two oxic layers;
- (4) Coastal, intertidal zone (lagoons, tidal flats).

Following to the paleogeographic model of Heckel (1991), for the deposition of Pennsylvanian black shales in North America, the distribution of black shales vary according to the sea level variations (Fig. 4):

- in low level stand, grey shales storing a part of the continental OM from emerged continent are located on the platform slope;

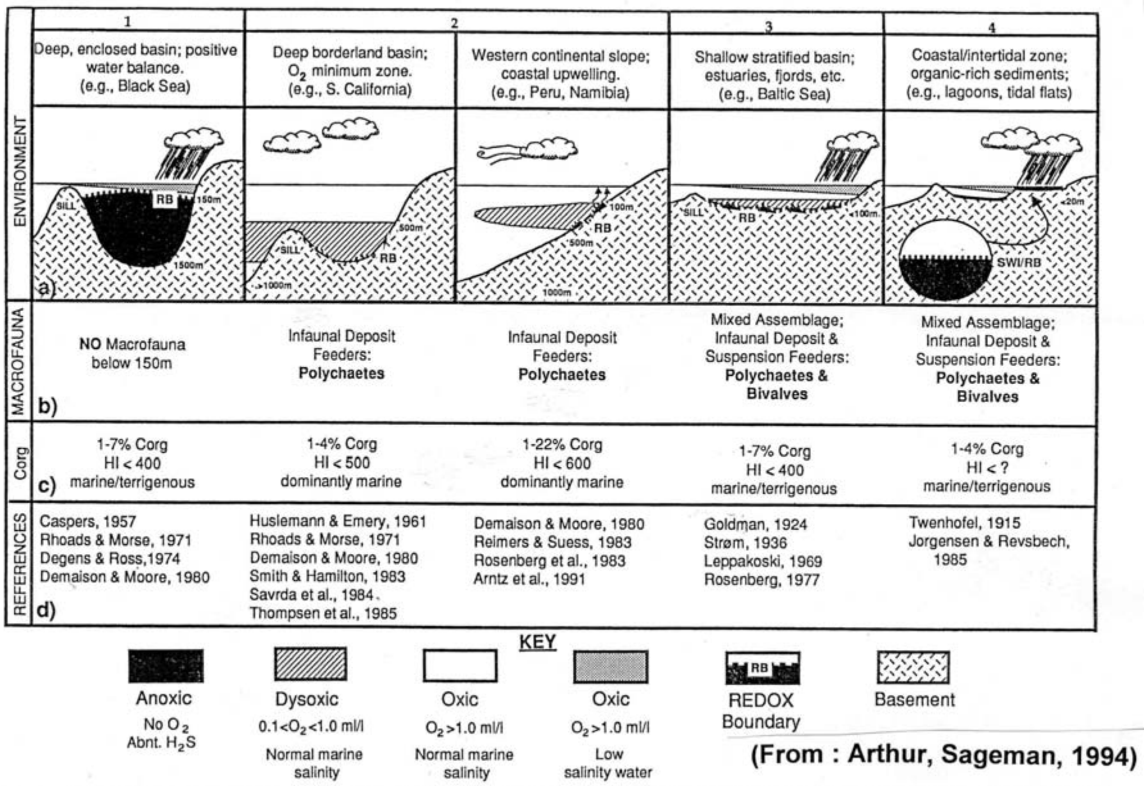


Figure 1 A summary of the major modern marine environments of organic matter accumulation showing: (*a*) idealized basin morphology and bathymetry, water mass distribution, dominant position of redox boundary (RB), and prevalent climate (rain cloud indicates precipitation > evaporation; cloud streamers indicate offshore winds); (*b*) predominant macrofauna reported from oxygen-deficient parts of each environment; (*c*) characteristics of organic matter associated with each environment; and (*d*) key references for each environment.

Figure 3 - Major modern environment of organic matter accumulation (Arthur, Sagerman, 1994).

- in high level stand, black shales are more extensive, being deposited in back ridge, in top of the anoxic zone, in shallow water with phosphate;
- in intermediate sea level stages, the CO_3 rich water precipitate the carbonates and grey shales are deposited inland with calcarenite and offshore on the steep margin of the platform.

The occurrence of dolomitic reef carbonates, mud craks etc. and abundant macrofauna indicates shallow conditions. When black shales are part of the turbidite cyclothems in sandstone deposits (like the Burundian sandstone in East Africa, Salpeteur I. *et al.*, 1992), they should correspond to gravity sediments deposition at the base of the continental slope.

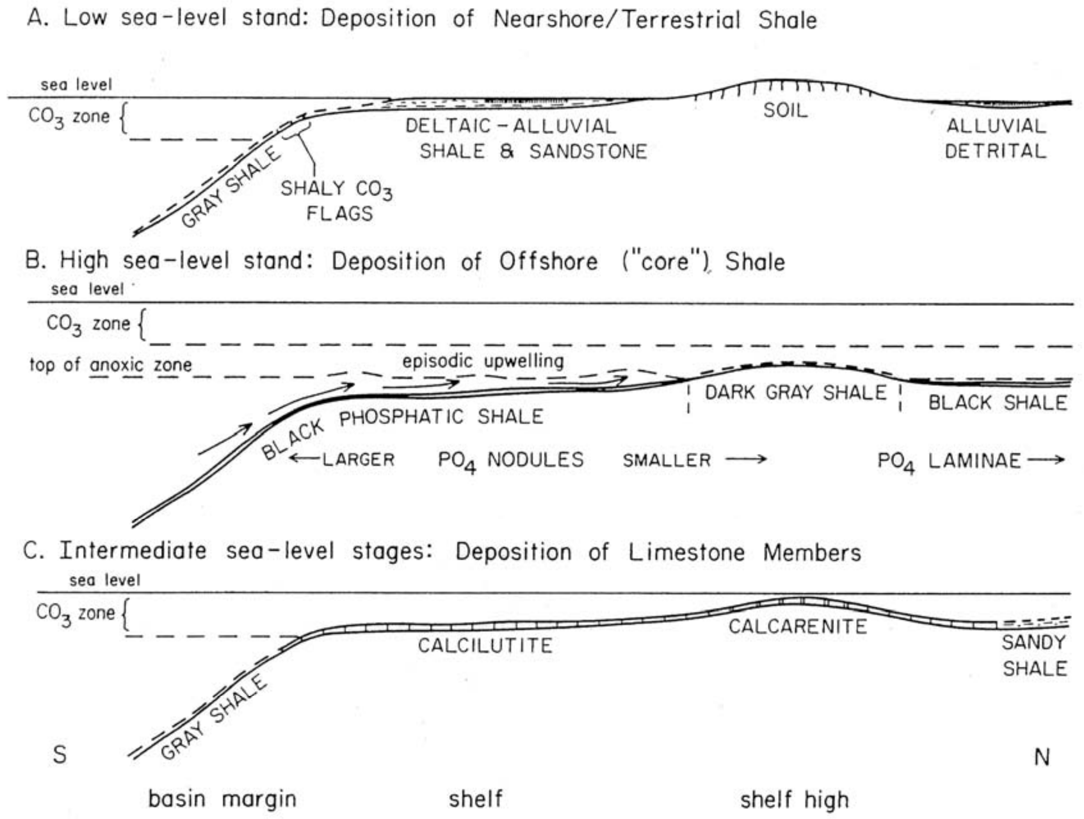


Fig. 4. Model for deposition of dominant rock types present in major Midcontinent cyclothems related to different stages of sea-level stand on Northern Midcontinent Shelf and adjacent basin to south. Subtle topography shown on shelf helps to explain lateral facies variations observed in laterally extensive cyclothemic members, even in offshore ('core') shale (B) when water was deep over entire shelf. No absolute vertical scale is intended; apparent absence of anoxic water layer in basin during lower sea-level stands (A, C) may be an artifact of the distorted vertical dimension used (i.e. anoxic layer withdrew to parts of basin deeper than that exposed along outcrop), or it may relate to weakening of thermocline due to better vertical mixing during lower sea-level stands associated with glacial episodes in Gondwana (modified from Heckel 1984*a*).

Figure 4 - Model for the deposition of Pennsylvanian black shale cyclothems in the Midcontinent (after Heckel, 1991).

In the Pennsylvanian basin of the Midcontinent, in Arkansas, Algeo and Maynard have published a similar black shale deposition model (Fig. 5). A similar model was published by Algeo, Maynard (2004) for the Upper Pennsylvanian shale of the Midcontinent (Arkansas) with a special comment on Phosphate authigenic formation in these environments:

- Modern phosphates form offshore in area of high OM primary productivity, where the flux of sedimentary organic matter, substantially exceed that of clastic detritus. Supersaturation of sediment porewaters with respect to francolite commonly occurs only within a narrow zone in the shallow subsurface where upward diffusing PO_4 and CO_3 released from decaying organic matter mix with downward diffusing Ca++, SO_4^- and F^- from the overlying water column. Precipitation occurs mainly at depths of 5-20 cm below the sediment-water interface and is favored by midly alkaline conditions, such as commonly develop in the NO_3- reducing zone. Reduction of Fe hydroxides in more anoxic conditions at depth, release the P that is provided to the upper layer.

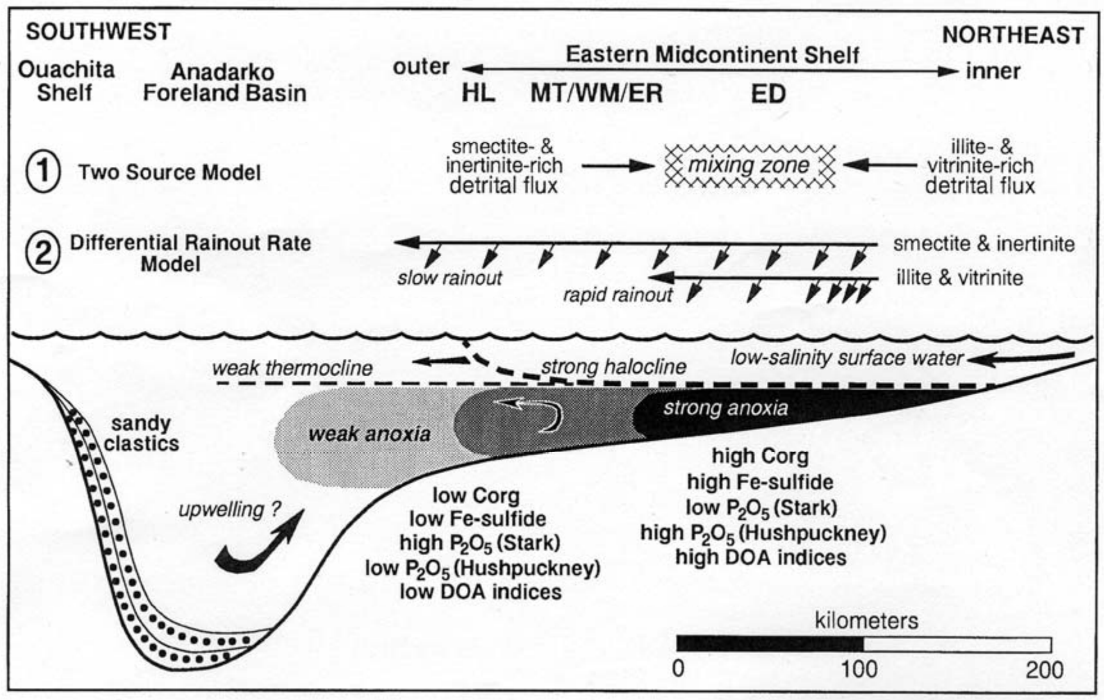


Figure 5 - Model of marginal basin sedimentology for black shale-phosphate association in the Pennsylvanian Midcontinent (after Algeo, Maynard, 1997).

A general increase of the REE, and U content of the black shale is noteworthy in reducing conditions.

In the French Ordovician Black shales of the Pyrénées (Bois JP.,1972; Pouit G., 1976, 1978, 1986), and in the Neoproterozoic black shales of Rwanda, Eu enriched monazite have been explored by the BRGM as a potential REE resource in placers (Laval *et al.*, 1993).

According to Jones and Manning, (1994), the OM percentage, the Mo and P_2O_4 grade of the sediments allow the discrimination between nearshore or offshore environment (Table 1).

Nearshore	Offshore
>20 wt % organic matter (Shaffer and Leininger, 1985); mostly terrestrial (Coveney et al., 1987)	<20 wt% organic matter (Wenger and Baker, 1986) (mostly marine-type)
>500 ppm Mo (Coveney et al., 1987); >100 ppm U & Se. Mainly <300 ppm Mn, but sporadic values >1000 ppm Mn (Coveney and Glascock, 1989)	<500 ppm Mo; <100 ppm U & Se; <300 ppm Mn (Coveney and Glascock, 1989)
<0.3 wt % P_2O_5	>0.3 wt. % P_2O_5
Sparse phosphate nodules	Abundant phosphatic nodules
Abundant whole fish fossils (Zangerl and Richardson, 1963)	Sparse fish fossils, mainly consisting of spines and denticles
Conodonts common	Conodonts very abundant
Silty and sandy quartz	Few sandy mineral grains
Located in predominately siliciclastic sections	Located in predominantly carbonate sections
Minable subjacent coals common (Trask and Palmer, 1986)	Subjacent coals rare
Lateral intergradation with deltaic units (Baird et al., 1985)	Lateral intergradation with gray marine shales
Highly variable $\delta^{34}S$ (Coveney and Shaffer, 1988)	Consistently light $\delta^{34}S$ (Coveney and Shaffer, 1988)
Only known in M. Pennsylvanian	Middle & Upper Pennsylvanian
e.g., Excello Shale; Mecca Quarry Shale; Logan Quarry Shale	e.g., Hushpuckney Shale; V shale; Heebner Shale

Table 1 - Geochemical and sedimentological parameters to discriminate between off shore and nearshore black shale deposits. (Coveney et al.*, 1991).*

The most reliable geochemical indices to use for paleoredox condition definitions in ancient mudstones have been published by Jones and Manning (1994): DOP, U/Th ratio, Authigenic U, V/Cr and Ni/Co ratios (Fig. 6).

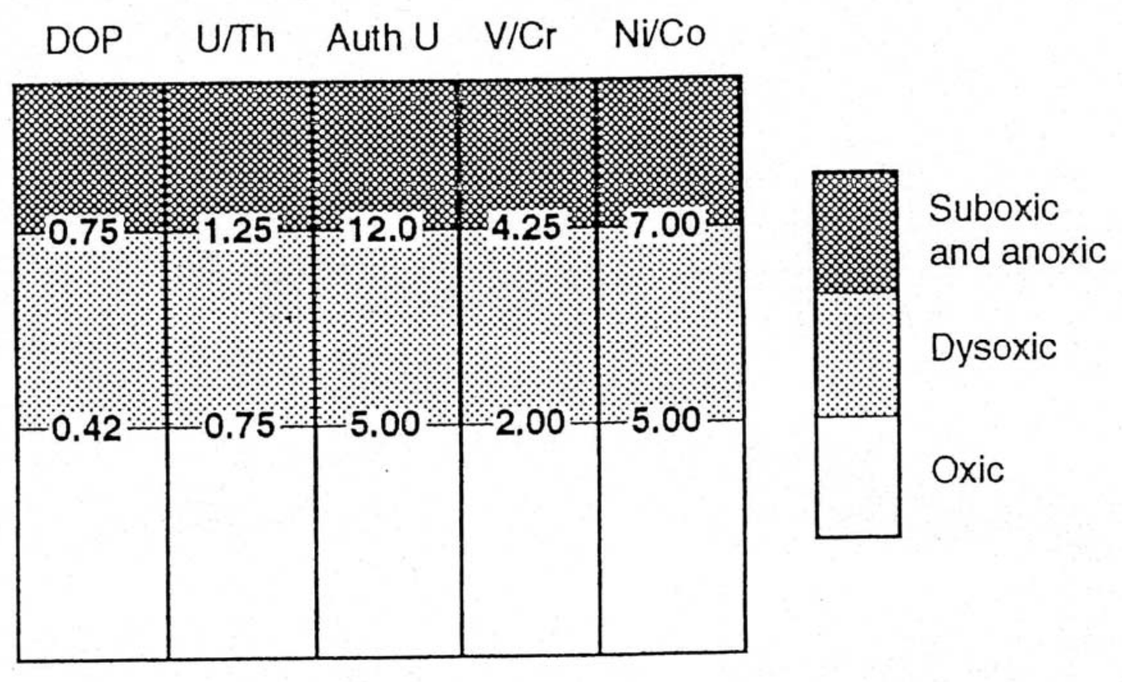


Figure 6 - Tentative correlation chart for the five parameters identified as reliable indices of depositionnal conditions. (according to Jones, Manning, 1994).

An overview of the literature devoted to mineralisations in black shales (Gize and Pasava, 1995) demonstrate that these lithologies are the hosts for a very wide varieties of elements:

- base metals: Cu, Pb, Zn, Ni, Mo, V;
- precious metals: Au, PGE;
- rare metals: W, Sn, U, Ge, Se, Re, Tl, Cd, REE, the later being fixed mainly in diagenetic phosphate nodules (Eu rich monazite);
- raw material: graphite, phosphate, barite.

More commonly, black shales are geochemically characterized by the association: Ba-V-Mo-Ni-Cr –REE association.

Abnormal high concentration of Ni-V in crude oil, asphalts in black shale have been described by various authors (Lewan M.D., Menard J.B., 1982). Both elements are concentrated in the tetrapyrole fraction of OM, mainly inherited from algae deposited in anaerobic conditions.

Similarly, ionic U (VI) may be concentrated by a factor of 10,000 from water in organic matter (mainly fulvic acid). When the sediments are matured by diagenetic processes, U is fixed as uraninite: UO_2 (Meunier J.D., 1991). Bitumen may also be sufficiently enriched in U in continental fluviodeltaic context to produce economic concentrations (see for example the St Hypolyte deposit in lacustrine oil shale, associated with Cu, Pb, Zn sulfides of the Carboniferous margin of the Vosges Mountain (Moreau J., 1980). In the Permian basin of Lodève, an economic U mineralisation has been extracted from autunian black argillite with bituminous layers. These sediments contain black nodules of "carburane" that are pyrobitumen residue enriched in U from percolating early diagenetic oxydized fluids enriched in Uranium (Moreau J., 1980).

Several occurrence of Ge enriched coal or bitumen are reported in the literature, for example in rift coal deposits of Siberia, associated with concurrent volcanic centers (Seredin, Danichelva J., 2001; Höll *et al.*, 2007).

On a regional scale, black shales facies are easily detected by airborne magnetic survey (pyrhotite is magnetic), radiometric survey (the U background is higher, Airo *et al.*, 2004). In follow up ground surveys, EM techniques are also efficient (graphite conductor) and for drill logging neutron gamma spectrometry.

Their mineralogy change according to the age of the deposits: the younger the deposit, the more metallic content bound to the organic components. After compaction and diagenesis, connate waters that are heavily charged in chlorine, boron and organic metallic complexes are expelled from the anoxic sediments and move along basin channelways (fault, porous rocks) and are redeposited at some redox boundaries. If metamorphic grade overpass the oil window, a part of the metallic contents escape with the lighter hydrocarbons. The residue is fixed in sulfide or heavy bitumen that will convert to shungite for example. The ability of humic substances to fix Au, PGE U V metals is strongly reduced if the temperature exceed 100°C (Wood S.A., 1996).

Geothermal circulation may be induced by deep intrusive along the rift axis. The oxygen rich peribasinal waters are driven through evaporitic upper layers (for example the Zechstein evaporite in the Kupferschiefer). Their high salinity allows a dissolution of the underlying red sandstone and black shale metals that are transported along fault and redeposited within smaller size hollow sub-basins or into more porous layers (sandstone, dolomites) caped with waterproof layers. Moreover, organo-metallic complexing enhances the transport of metals in hydrocarbon bearing fluids, and reduction of metallic complexes by organic matter enhances ore deposition (Parnell J., 1988). Geochemistry of peribasinal brines has demonstrated that initial, relatively reducing oil field brine can evolve chemically into a more oxydized fluids (capable of transporting a relatively high amount of copper, lead, zinc and sulphate) by reacting with an anhydrite-hematite rich assemblage and red bed aquifer units (Sverjensky DA., 1987).

1.4. ORE TYPOLOGY

a) Sedex deposits

Sedimentary exhalative deposits (SEDEX) are typically tabular bodies composed predominantly of Pb, Zn, and Ag bound in sphalerite and galena that occur interbedded with iron sulfides and bassinal sedimentary rocks. These mineralisations are deposited on the lake, sea floor near vents from hydrothermal fluids in continental rifts (Fig. 7, Goodfellow W., Lydon J., 1993). Their deposition mechanism bear some similarities with massive sulphide deposits (geothermal brines) but here, the connection with a synchronous submarine volcanic event cannot be established (no volcaniclastic nor lavas directly connected). There is some relationship between MVT and sedex deposits with respect to their timing of deposition, mineral association and geochemical fluid compositions (Goodfellow *et al.*, 1993). Mississipi Valley Pb-Zn (MVT) are unconformity related deposits, most of them being related to paleokarst system in continental setting or near shore context (Verraes G., 1984). Most of the sedex deposits are issued from fluids vented on the sea floor water interface. Of course, their metal and organic content has changed according to the early diagenetic fluid migrations, to tectonic overpressure effects and metamorphic recristallizations.

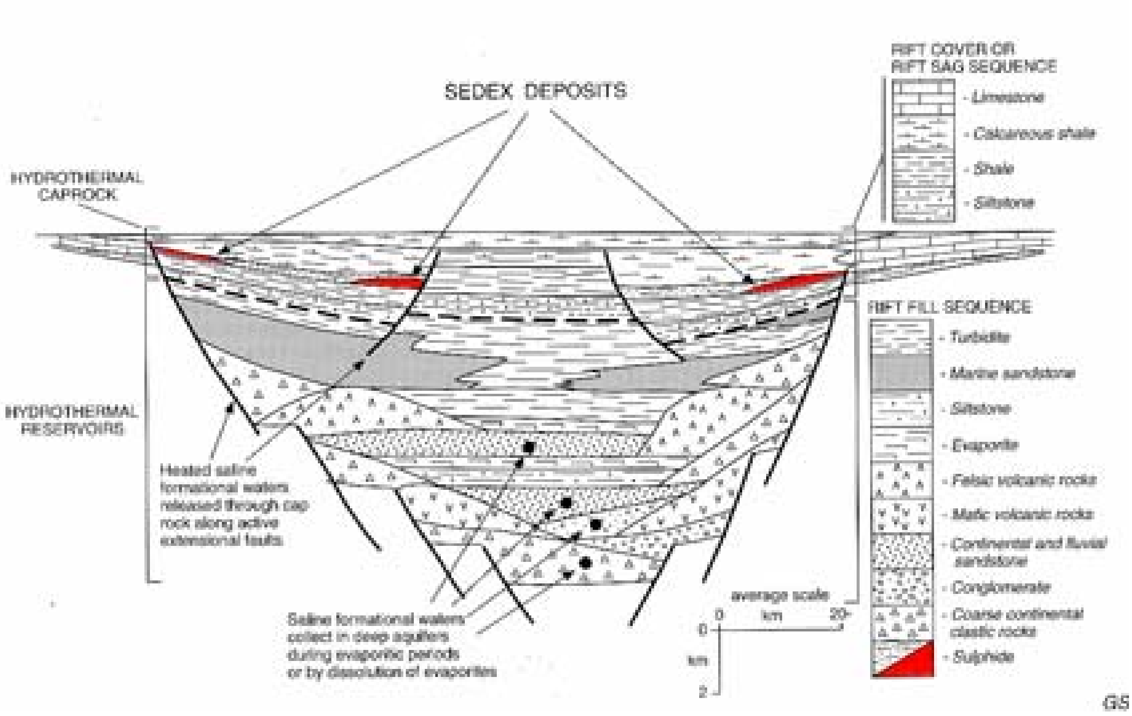


Figure 7 - Schematic model of sedex deposits in an intracontinental rift (from Lydon J.W., 1993).

Hydrothermal sediments commonly associated with sedex deposits are manganese and calcium, magnesium carbonate, silicate-oxyde-carbonate and barite layers.

If we consider the number of deposits on the time stratigraphic column, we see that three major periods of sedex encompass more than 50% of the known deposits (Fig. 8):

- Mesoproterozoic: Australia, India, South Africa;
- Cambro-ordovician-silurian: China, Canada, France;
- Devono-carboniferous: Ireland, Spain, France, USA (Alaska).

Neoproterozoic, and Permo-Triassic are also a very important period for Cu deposits in Africa, Poland, Germany.

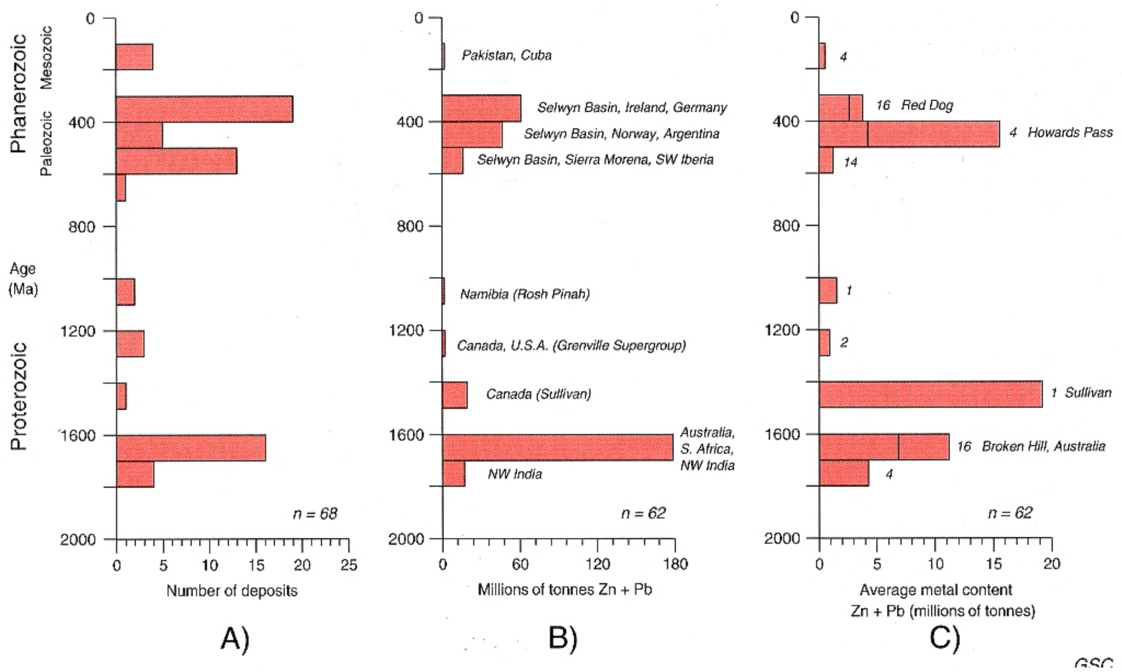


Figure 8 - Total metallic content, tonnage, age distribution of the major sedex deposit districts in the world (after Lydon J. in *Eckstrand* et al.*, 1995).*

b) Kupferschiefer deposits

Stratiform Cu-Co-Ag deposits occur generally in a post tectonic extensional subsidence or continental rifting in anoxic basin developed along a shallow water continental margin. The host lithologies show a transition from an aerial desertic landscape (eolian sandstone) to more humid, marine transgressive phase, starting with dolomite and evaporitic layers. Very often, a subsynchronous submarine mafic volcanism is recorded in the basin but only distal products are associated like Mn cherts. These deposits like in the Zechstein sea in Poland-Mansfeld or like in Shaba in the Neoproterozoic Roan serie have a very wide lateral extent that contrasts with their short vertical stratigraphic control (some cm to 1 m in Poland).

On a regional scale, the metal distribution is not homogeneous, a geochemical pattern appear connected with peribasinal faults that were the channels to more oxydizing, higher temperature fluids. Cu (and precious metal like Au, Pd, Pt) are more proximal to these vents, whereas Zn and Pb, Ag are more distal.

The major sulphide minerals are chalcosite, covelite, chalcopyrite, sphalerite and galena.

There is still a debate between syngenetist and diagenetist because, mineralogical and thermo-geochemical studies have demonstrated that a part of the chalcopyrite in the Lubin ore was secondary after a primary pyritic diagenetic precursor. Chalcosine veinlets crosscut the stratigraphy and are clearly post diagenetic, syntectonic with the alpine orogeny.

In the Shaba district, Co and U, Ge, Pd are by product of the stratabound Cu mineralisations.

c) Distal VMS deposits

In the major volcanic massive sulphide province like the Archean province of Abitibi or the Devono-carboniferous province of Iberia, most of the Cu rich massive sulphide mineralisation are located on top or near the flank of the submarine volcanic ridge. Paleogeographic studies showed that most of these basins had a basin and horst structure, and beside the volcanic ridges, there were small anoxic basin filled with sulphide rich black shales and exhalites. In some basins, lower temperature mineralisations were deposited with Pb-Zn, Ag, Sb, Au, disconnected from the main volcanic vent. We have included these deposits with the Sedex type because both deposits type have many similarities. In the Iberian province, for example, a lot of banded "complex ore" are located in these anoxic basins (Lousal, Massa Valverde, Aljustrel, Sottiel-Migollas, Romanera, Sierrecilla, Tharsis, Filon Norte, Pinedo vara, 1963, Strauss and Gray, 1984; Tornos F., 2006) but their reserves are poorly assessed.

In the world, numerous orogenic gold deposits are associated with quartz veins cross-cutting black schists [e.g. Ballarat, Australia, (in Routhier P., 1963), Sukhoi Log, Russia (Distler *et al.*, 1998, 2001, 2003, 2004), Carlin gold trend (Bagby W.C. and Berger B.R., 1987); Viges in France, (Bonnemaison M. and Braux Ch., 1987); Nyungwe, Rwanda, (Salpeteur I. *et al.*, 1992). Probable origin of this gold enrichment is the geochemical trap played by the organic matter that reacted as a geochemical redox barrier for the Au enriched fluids (Gatellier J.P., 1990).

Gold in black shales is frequently locked as very small inclusions in arsenian pyrites, like in Carlin gold mines, in Nevada (Wells *et al.*, 1973), and this may cause severe problems for its beneficiation.

1.5. ECONOMIC WEIGHT

The continuous raw material price increase for the last 5 years clearly indicates that we are only at the beginning of an economic super-cycle. It corresponds to a long price increase due to a major economic emergency. The scarcity of mining investments during the last ten years and the economic emergence of the two most populated countries; China and India, are responsible for the enormous price increase of most commodities since 2002 (Hocquard, Samama, 2007). Among the base metals, three metals have seen their price multiplied by **more than 6** in the last five years: Ni, Mo and U (Fig. 1). These metals are particularly enriched in organic rich black shales, together with some precious and high technology metals like the PGE, Se and Ge (Höll *et al.*, 2007), whose demand is still very strong. This is why heavy investments are needed to explore these deposits. Some in situ reserves would be reassessed to fit with these new favourable trends of the world metal market. New challenges will be to develop selective extraction techniques and low cost bioleaching processes to recover the rare and precious metals contained in these deposits.

Beside their metallic content, black shale attract an improving interest for their oil content: 62% of the world potentially recoverable resources are located in the US. States of Colorado, North Utah and SW Wyoming in the Eocene Green river formation. The total estimate is 3 trillion tonnes of shale averaging 57 kg of oil by metric ton (worldenergy website)

Concerning their metallic resources we have distributed the black shales hosted mineralisations between the various ore types: Sedex, Kupferschiefer and distal VMS.

a) Sedex

Sedex deposits account for more than 50% of the Zn and 60% of the Pb world reserves (Goddfellow W., Wayne J., 2004). Very large Sedex mineralized districts (supergiant) are known in the lower Silurian Selwyn basin (Canada) with more than 525 Mt reserves and the Cambrian Zunyi district in China hosting 7 mines spread over an area of 1,700Km (Table 3).

The average deposit size from 126 deposits is 35 Mt reserves with 0.97% Cu, 3.28% Pb, 6.76% Zn and 63 g/t Ag. For example: the two giant deposits represented :

- Sullivan: 162 Mt@5.8% Zn and 6% Pb

- Broken Hill: 280 Mt@11% Zn, 10% Pb and 180 g/t Ag

More recently, new Ni, Mo, V and PGE enriched sedex types were discovered in China (Zunyi district, Fig. 17), and in Canada (Nick property, that belong to the Selwyn basin northen extension, (Hulbert L.J., 1995). These are very thin layer (few cm to one meter) enriched in these metals and organic bitumen. A similar geochemical anomaly leading to subeconomic resources is currently evaluated in the lower Proterozoic black schists of the Stokamo district in Finland.

This low grade but extensive Ni deposit contents about 318 Mt of ore averaging 0.27% Ni, 0.15% Cu, 0.02% Co and 0.56% Zn (Loukola-Ruskeeniemi K., 1999).

b) Kupferschiefer

Stratiform or stratabound copper deposits account for approximately 25% of the world's production and reserves. This figure includes not only the Kupferschiefer type but also the red bed type (Kirkham R.V., 1989).

The famous Polish-German late Permian Kupferschiefer district of Mansfeld-Lubin, located on the continental margin of a very wide evaporitic sea (Zechstein, fig. 9), represents a potential geologic reserve of:

1,422 Mt of ore averaging 1.9% Cu; **51 g/t Ag** and additional precious metals: Au, PGE.

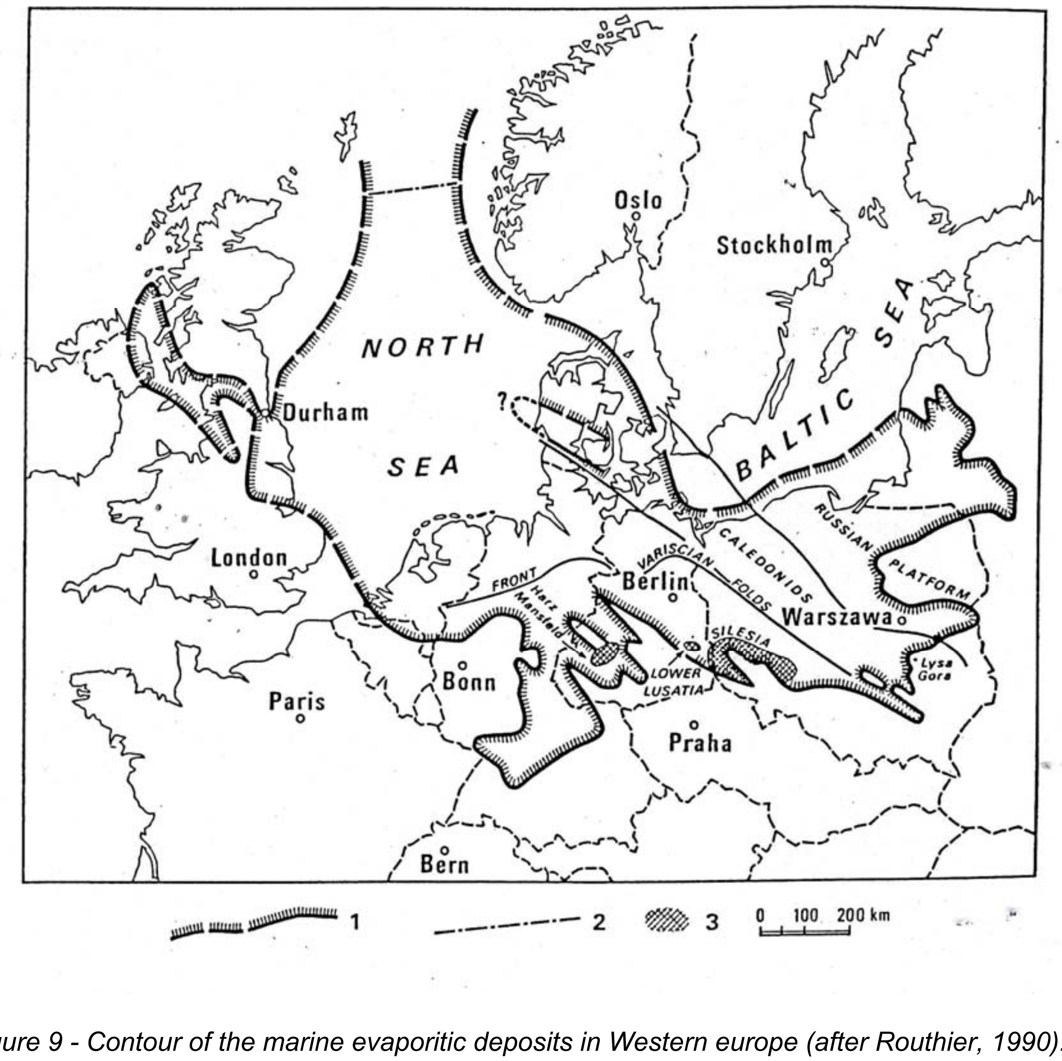


Figure 9 - Contour of the marine evaporitic deposits in Western europe (after Routhier, 1990).

Only for the Neoproterozoic Zambian-Congolese copper belt, the reserves amount more than **3,700 Mt with a Cu grade over 2%** and Co 0.1%. In these districts, most of the mines focus on the richest ore inherited from paleoweathering under tropical climates (covellite, bornite enriched ore, malachite in dolomitic paleokarsts).

c) Distal sedex

The amount of potential reserves of polymetallic ores in the VMS districts is very difficult to estimate.

Indeed, in the Iberian province for instance, the majority of the old mines were firstly evaluated for pyrite (to produce sulphuric acid) and after for Cu-Au extraction. Due to the beneficiation problem, most of the polymetallic ore reserves were not assessed. In the Rio Tinto deposits, a 12 Mt of complex ore was defined with 1.6% Cu, 1% Pb, 2% Zn. In Aznalcollar-la Zarza mines a total of 47 Mt of complex ore averaging 0.58% Cu, 3.3% Zn, 1.77% Pb and 67 g/t Ag was delineated. The extraction was stopped because of the low price and high beneficiation cost of the flotation process that need a very fine grinding to less than 20 µm.

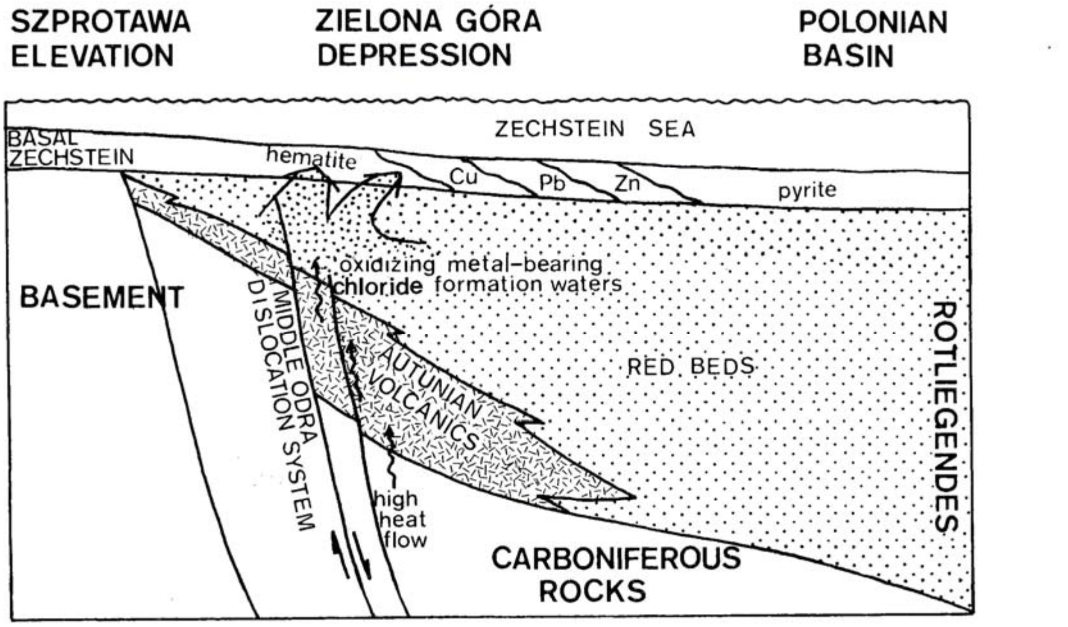
As a raw estimate, the total low grade polymetallic ore that could be processed by bioleaching in this province **overpass 500 Mt.**

1.6. GENETIC MODELS

For the kupferschiefer deposits of Poland an early syngenetic deposition of the metals by groundwaters enriched in metals during their transfer from the continent to the Bundsandstein sandstones was favoured (Wedepohl, 1980; Orbec and Serkies, 1968). In this model, the organic mudstone played the role of a redox trap for the metals.

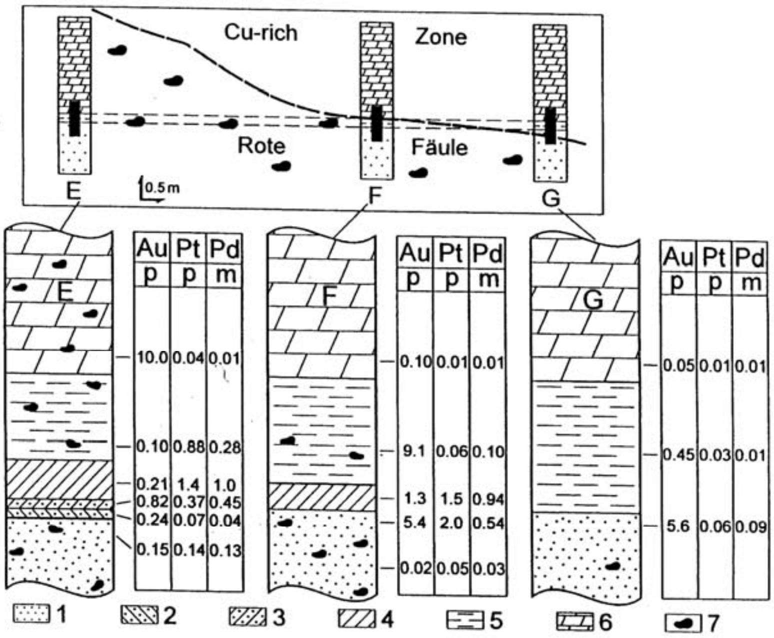
A later theory is based of the observations of unconformable mineralisation enriched in Cu and precious metals in connection with the Rote Faule and grading laterally to the stratabound Cu and Zn, Pb black shales (Oszczepalski S., 1999, Fig. 10). Disseminated Cu mineralisation invades not only the basal sandstone, but also the overlying dolomite, along these faults. A precious metal (Au, Pd) enriched halo is located near the fault black shale contact (Fig. 11).

Moreover, chalcosite is reconcentrated in small veinlets cross cutting the black shales and affected by a younger structural event. The diagenetic hypothesis considers that continental waters enriched in metals by supergene weathering of the hercynian basement, percolated downward along peribassinal faults and were heated at depth and were injected upward through the porous lithologies and precipitated their metallic content on the mud – sea water interface. The metallic enrichment of these waters is also related to partial dissolution of the evaporites in lateral basins. Bacterial or thermochemical sulphate reduction (TSR) of sulphate played also an important role in the H_2S production at that stage (Kucha and Przybylowicz, 1999; Warren J., 2006).



Schematic model of the formation of the Kupferschiefer mineralization in southwestern Poland

Figure 10 - Schematic model of the formation of the Kupferschiefer mineralisation in southwestern Poland (after Oszczepalski S., 1989).



Cross-section through the contact between Cu-rich and Rote-Fäule zones, Polkowice mine: *1* = white sandstone; *2* = carbonate-rich red sandstone; *3* = carbonate-rich brownish sandstone; *4* = red shale; *5* = black shale; *6* = dolomite; *7* = red spots.

Figure 11 - Cross section through the contact between Cu rich and the Rote Faule zone, Polkowice mine (Piestrzinski A. et al.*, 1999) showing the enriched Au, Pt, Pd halo.*

According to Sverjensky (1987) evaporite are crucial to the development of the oxygen fugacity conditions required to leach Cu from red bed sandstone layers in the rift sequence and transport the metal upward to fix it in the redox sulphide rich graphitic schists. More recently, Goodfellow and Lydon (2004) proposed two different models for the Canadian Sedex deposits (Fig. 12):

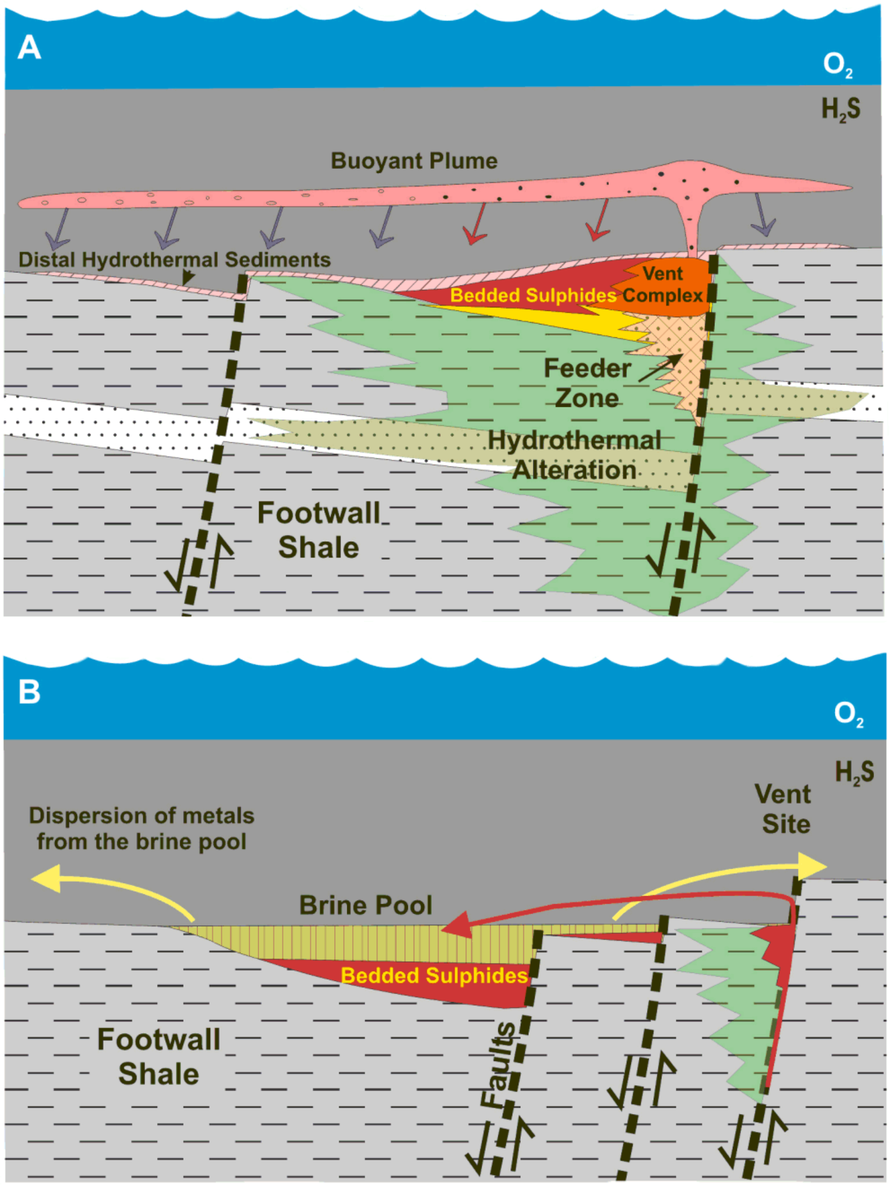


Figure 12 - Genetic models for Sedex deposits: A: vent-proximal deposits formed from buoyant hydrothermal plume. B: vent-distal deposit formed from a bottom-hugging brine.

- a model for proximal deposits (Fig. 12A) where two distincts type of mineralizations are deposited: Cu, Zn, Pb sulphide laterally from the vent complex (similar to the Kupferschiefer zonality) and a more distal base metal enriched sediments whose metals are inherited from a wide buoyant hydrothermal plume developed laterally near the sea bottom, under the anoxic boundary;

- a similar system developed in the bottom en echelon basin (Fig.12B), related to fault activity where denser brine deposited the metals with lowering of the temperature. In this case, there is no buoyant plume.

In the case of the Lower Silurian Nick sulphide mineralisation, it is assumed that hot hydrothermal fluids (140°C according to the sulfide equilibrium), percolate through the organic Ni, Mo, V rich mud near the shore and were transported deeper below the thermocline to precipitate the sulphide in anoxic mud enriched in phosphate (a phosphatic nodule layer is associated see Fig. 5). Phosphate are produced in the mixing zone between shallow and deep marginal conditions where upwelling currents are active (see the model of Algeo, Maynard, 1997, Fig.4).

According to G. Pouit (1996), the present day deposition of sulfides rich mud (averaging 2% Zn, 0.4% Cu and 40g/t Ag in the Atlantis deep sub-basin in the Red sea is a reliable model of fossil sedex deposits (or distal VMS).

2. Major districts enclosing low grade sulphide resources in black shales

2.1. FOREWORD

Since more than fifty years, BRGM has been working on black shales occurrences in France, Africa, Saudi Arabia, India to evaluate their economic potential (Table 2). During currently oversea operations particularly in West Africa, new data on black shales hosted mineralisation have been collected.

Permian and Carboniferous rifts are also the location for continental organic matter deposition leading to bitumen, coal deposits.

In most of the middle tropical countries however, deep ferralitic alteration has concealed the black color of the shales and very often they are not recorded as black shales but as violine or whitish pinkish shales because of the strong oxydation of the associated iron sulfide. Airborne, stratabound magnetic linear anomalies may help to delineate these horizons that often contains disseminated magnetite or pyrhotite and Ba, V, Cr, Mo regional anomalies are specific markers.

Black shale have been recognized in Algeria, Mauritania, Mali, Ivory Coast, Cameroon, Ghana etc… from rocks of Paleoproterozoic ages of the Leo Man shield, to younger folded Cambrian and neogene margins of these cratons (see Table 2).

Various data bases do exist concerning Sedex or copper shale deposits in the world (USGS, CSIRO,..). However, it is not always possible to evaluate the existing reserves knowing that some deposits were abandoned due to technical problems (like an underground water flooding), and for the biggest mines, most published figures give a global resources including the past exploited resources and the probable or inferred resources. Moreover, the recent increase of most of the base and precious metals, must induce a general reassessment of the cut of grade (in a lower sense) according to the new economic constraints. **The inventory of low grade but economically interesting mining dumps in these major mining districts remains to be done**. Very often, in old mine, none analysis for precious or rare metals were done so the opportunity of discovering new enriched areas is still open. For example, new PGM (sperrylite, stibiopalladinite, native Pd) have been recently discovered in the V, Cr enriched Silurian black shale of the Spanish Pyrénées (Canet C. *et al.*, 2003), however PGE have never been analysed in similar context of the Cambro-ordovician and particularly, in the Ni, V, Cr, Zn anomalous of the Canaveilles serie in the French Pyrénées (Moyroud, Salpeteur, 1996).

Country	Age	Geodynamic	Lithology	Base metals	Rare/precious metals
RDC(Moto area)	Archean	Rift-sedex	BS,BIF	Fe	Au,
GHANA(Obuasi area)	Paleoproteroz.	Rift basin	BS,Turbidite	Fe	Au,
SAUDI ARABIA	Neoproteroz.				
Ar Rjum	Neoproteroz.	Shallow Continental margin, back arc	BS, dolomite, volcanic	Zn,Pb,	Ag,Au
Shaib Lamisah	Neoproteroz.	Rift	BS, turbidite	Zn,Pb,	Au,
Mardah	Neoproteroz.	Deep Basin, suture	BS, ophiolite	Ni	?
Rwanda-Burundi; RDC(Kivu)	Neoproteroz.	Continental margin	turbidite, BS,sandstone, Mn exhalite, volcanics, Phosphate	Fe,S,P	W,Au,REE

Table 2 - Some examples of black shale hosted mineralisations in Africa and Saudi Arabia.

Country	Age	Geodynamic	Lithology	Base metals	Rare/precious metals
Mauritania (Taoudeni) Mali	Neoprot-Cambrian	Intracratonic basin -rift	eolian sandstone, dolomite, BS,claystone, felsi volcanic	Cu (Pb,Zn)	?
Marocco (Tizirit)	Cambrian	Continental margin (shallow)	Dolomite, BS	Cu	?
Algeria	Silurian	shallow platform	black shale	U	
	Lower Frasnian	Shallow platform	Black claystone	?	
	Middle Cretaceous	Continental margin (shallow)	Black carbonate	Pb,Zn,Ba, Mo, pyrite	
Jordan (Wadi Araba)	Cambrian	Continental margin (shallow)	Dolomite, BS	Cu,Mn	?
Algeria(Mesloula)	MiddleCretaceous	shallow basin	Black marl,Carbonate	Pb,Zn,Ba,Sr	
Algeria (Guergour)	Cretaceous(inf./sup)	unconformity surface	carbonaceous black shale	Zn>Pb	?
Tunisia (Bou Grine)	Middle Cretaceous	Rift-sebkha	Evaporite, salt dome, OM rich marl	Zn,Pb	Cd,Ge

Table 2 (continuation) - Some examples of black shale hosted mineralisations in Africa and Saudi Arabia.

The annexed Table 3 describes 33 mines having a good potential for that purpose. They have been selected to give a large panel of the 3 major sedex deposit types in the world and located in various stratigraphic settings from Archean to Tertiary.

2.2. MAJOR DISTRICT FOR SEDEX BLACK SHALE HOSTED DEPOSITS IN THE WORLD (TABLE 3)

2.2.1. The Paleoproterozoic Kainu schists in Finland (from Loukola-Ruskeeniemi K., 2006)

Talvivaara is located in the Kainuu schist belt which consists predominantly of metasediments like micaschists, quartzites, dolomites and metamorphosed black shales and was formed 2.2 to 1.9 billion years ago. The belt is narrow and roughly S-shaped, the length of the belt is 200 km in north-south direction and the width is 40km in east-west direction. Black shale formation can be followed for hundreds of kilometres (Fig. 13). This belt occurs as a synform inside a more metamorphic archean terrain. The later contain the major Outokompu (Cu, Zn, deposit), the Skellefte Cu, Zn deposit and the Vihanti Zn, Ni deposit that are VMS type deposits associated wilth ophiolitic serpentinites and pyrite talcschists.

Rocks in the Kainuu schist belt have undergone several tectonic deformation phases. Regional metamorphism was of medium grade, amphibolite facies, in the area of Talvivaara. In the northern part of the belt regional metamorphism was not as high: the rocks have undergone greenschist facies metamorphism.

Black shale formation in Talvivaara is 15 km long, 1-2 km wide and up to 400 meters thick (Loukola-Ruskeeniemi and Heino 1996). Due to tectonic processes the formation of metamorphosed black shales has been thickened. Talvivaara deposit is outcropping and topographically elevated.

Genesis of black schists in Talvivaara

The metamorphosed black shales of Talvivaara were originated as sulphur- and organic rich mud deposited on the seafloor, which is evidenced by high sulphur and graphitic carbon concentrations (median values are 7.5% carbon and 9.2% sulphur for the metamorphosed black shales). The $\delta^{13}C$ values are within the range of C-isotope values of organic C in sedimentary rocks. The depletion in the metamorphosed black shales of Talvivaara is a typical signature of marine conditions. The degree of pyritisation values indicates deposition under anoxic conditions.

Deposit or prospect name	Country	Area	District	Stratigraphic host	Lithology	Mineralogy (2)		Reserves [1]	Grade			Environmental constraint	Reference
Europa						Main	Accessory		Major element	Other valuable	Economic status		
Lubin -Polkowice	Poland	Fore-sudetic monocline	Lubin-Glogow	Late Permian	Sandstones, black shale, dolomite, evaporites	Chalcosite, bornite, Chp, covellite, digenite, ZnS, PbS,	tennatite, Ag, stromeyerite, cobaltite	1,422Mt	Cu 1.9%; Ag: 51 g./t	**Au**	**3 mines operating**		Bechtel *et al.* (2002), Oszczepalski S. (1989)
Talvivaara	Finland	Kainu-Outokompu	Fennoscandian shield	Paleoproterozoic	Black schist, talc carbonate rocks, calc-silicate rocks, amphibolite	Py, Po, pentlandite		318Mt	**Ni: 0.27%; Cu: 0.15%; Co: 0.02%; Zn: 0.56%**		**Pilot test operation**		Loukola Ruskeeniemi K. (1999)
Bodennec	France	Brittany	Chateaulin bassin	Gedinian/Frasnian	Black shales and quartzites over metavolcanics	Chp, ZnS, PbS, Py, Po		2.11Mt	1.16% Cu	2.9% Zn; 0.7% Pb; 55.8ppm Ag	BRGM Claim, Access to -60m level by a 400m decline	Agricultural field	Stolojan N. et Viland J.C. (1991)
Porte aux Moines	France	Brittany	Chateaulin bassin	Gedinian/Frasnian	Felsic metavolcanics (footwall) and black shales, pelites	Py>ZnS, Chp, PbS,	Po, Asp, Sb, Sulphosalt	1.86Mt	0.76% Cu; 7.8% Zn;1.7% Pb	96.6g/t Ag	BRGM claim, Access to -150m level by a decline, beneficiation test positive (70% recovery rate), prefaisibilty study	Agricultural field	Stolojan N. et Viland J.C. (1991)
Rouez	France	Brittany	Sarthe	Silurian/Devonian	Chloritic pelites, black pelites with disséminated pyrite	Py, Po, Sid, ZnS	Chp	50-70Mt	0.58% Cu; 0.28% Pb; 1.5% Zn	Au?	Access to the polymetallic ore by a 800m decline to -150m. Beneficiation tests; Gold extracted from the iron cap by SNEAP-Cheni joint venture	Agricultural field	Stolojan N. et Viland J.C. (1991)
Chessy	France	Beaujolais	Brevenne	Devonian/Carboniferous	Felsic metavolcanics (footwall) siltites,	Py, Chp, ZnS, $BaSO_4$		5.4Mt	2.3% Cu; 9% Zn; 14% Ba	0.35% Pb; 22g/t Ag	Access to the polymetallic ore by a 1,274m decline to -164m. Beneficiation tests; Claim owned by ? (BRGM-…)	wineyards	Stolojan N. et Viland J.C. (1991)
Le Bleymard	France	Lozère	Nord Cévennes	Middle Jurassic	Carbonate, dolomite (Bajocian, bathonian), breccias	ZnS, PbS, Py, Marc	Zn Oxydes	?	2-4% Pb, 6-10% Zn	Ge	45Kt Zn and 20Kt Pb already extracted (1900-1931) Abandoned		Stolojan N. et Viland J.C. (1991)
Le Soulier	France	Gard	S-E Cévennes	Liassic-triassic unconformity	Black marls, dolomites,	Massive pyrite, Zn, oxyde (calamine), sulfide		1.5-2Mt	4-8% Pb+Zn		The richest oxydized part has been extracted by CRAM-Vieille Montagne (1960). The primary sulfide ore content some Zn enricched layers		Stolojan N. et Viland J.C. (1991)
Pierrefite-Estaing-Chèze	France	Hautes pyrénées	Pyrénées	Ordovician	Black shales over metavolcanics (felsic and mafic)	ZnS, PbS, Py, Po, Chp	Sulfosalt (Sb, Ni, Co), Ge, Ga, Sn	nx 100Kt (?)	10% Pb+Zn, Ag (60g./t)	Ge, Ga, Co, Ni	2,6Mt already extracted between 1940 and 1969 by SMMP. Many additional reserves possibles (Banciole, Bois de la Tasque…Arrens)	Mountainous area, natural reserve (?)	Stolojan N. et Viland J.C. (1991), Bois JP., (1973); Pouit G. (1976)
Bentaillou	France	Hautes pyrénées	Pyrénées	Upper Ordovician	Alternating carbonates and sulfide bearing black siltite	ZnS > PbS, Py, Po	Chp, Misp, siderite, Mag,	0.8Mt	7% Zn	Ag	Abandoned mine but new addit drilled in 63 at 1740 and 1650 level	Mountainous area, natural reserve (?)	Stolojan N. et Viland J.C. (1991)
Carboire	France	Hautes pyrénées	Pyrénées	Lower Devonian	Carbonaceous schist, black albitite	ZnS, PbS, Py, Po	Chp	1.6Mt	6.9% Zn,0.9% Pb	Ge rich	Abandoned mine in 1905, but new addit and drill holes allow a reassessment of the reserves in 1976	Mountainous area, natural reserve (?)	Stolojan N. et Viland J.C. (1991)
Arrens	France	Hautes pyrénées	Pyrénées	Lower-Middle Devonian	Carbonate, chert with sulfides, baryte, black schist	ZnS, PbS, Py, Po		2-4Mt	5-10% Pb+Zn		Small abandoned mine (1914) reassessed in 1924-1931 then 58-60 (SMMP) and lastly by Cominco (1984)	Mountainous area, natural reserve (?)	Stolojan N. et Viland J.C. (1991)
Stratabound Zn-Pb-Ge-P St Salvy	France	Southern Massif central		Cambrian	Quartzitic phosphate, black graphitic (C 0,2-2%) schist	ZnS, PbS, Siderite, fluorapatite		? not evaluated	3-8% Zn	Ge, Cd, Ag	Ferrières, Cambounès prospects studied by Beziat P. (1977)		Brula P. (1984), Barbanson L., Geldron A. (1983) Chron.Rech.Min. N°470, p. 33-42
Meggen	Germany	Rhenish massif		Upper givetian (Middle dév.)	Dark grey silty pelagic shales with baryte (laterally)	K-Al rich illite, ZnS, PbS, Py, marcassite, $BaSO_4$,	Boulangerite, chp, tetrahedrite	7.7Mt	5,2% Zn	Ni: 0.0172%, no Au reported. 190ppm Tl; 310ppm Cd, Ge:10ppm	Abandoned (?)		Walther (1986), Krebs W. (1981), Höll *et al.* (2007)
Rammelsberg	Germany	West Harz rise		Middle devonian	Laminated dark grey shale and pyritic ankeritic dolomite	Py, Chp, ZnS, PbS, $BaSO_4$	pyrrhotite, arsenopyrite, magnetite, tetrahedrite, electrum	>28Mt	3% Zn,1.5% Cu, 1.4% Pb (Kniest facies)	Au: 1.2ppm; 500ppm Cd; 800ppm Sb; Ge: 3ppm	Closed		Large D., Walcher E. (1999) Muchez *et al.*, 2006)
Ben Eagach	UK	Scotland		Neoproterozoic(Dalradian)	Graphitic micaschist, carbonate schist, metabasalt	Py, ZnS, Po, Mte	fuchsite, celsianite, cymerite	?	8% Zn, 4% Pb	$BaSO_4$	Exploration stage		Coats *et al.* (1980)
Southern Iberian Province	Spain-Portugal	Andalucia-Beja	Southern Iberian basin	Devono-carboniferous	Volcaniclastic, black shale, jasper	Py, ZnS, PbS	sulphosalt, Au, Ag	> 300Mt	2.5-5% Zn; 1-2% Pb; Cu 0.4-1%	Au : 0.5-1g/t; Ag 40-60g/t	Abandoned due to beneficiation problem		Strauss and Gray (1984)
CANADA													
XY Deposit	Canada	Selwyn basin		Lower Silurian	Black chert, pyrite, carbonate, baryte	ZnS, PbS, Py	Chp, Tetrahedrite, molybdenite, pyrrhotite, polydimite, millerite	>525Mt	5% Zn, 2% Pb, 85 ppm Ag		Currently developped		Goodfellow W.G., Jonasson I.R. (1983)
Nick deposit	Canada	Yukon		Devonian	Black shale, phosphatic chert member, ball limestone	py, vaesite, ZnS		0.9Mt Ni metal	5.3% Ni; 0.73% Zn	770 ppb Au+PGE; 61ppmRe	Exploration stage		Hulbert *et al.* (1992)
Sullivan	Canada	British columbia		Middle Proterozoic	Carbonaceous mudstone,quartzwacke, pyrthotite laminated mudstone	Po, Py, ZnS, PbS	Asp, Chp, SnO_2, $CAWO_4$ in veins	1.8Mt (2000)	6.5% Zn; 3.2% Pb	Sn, Cu, Ag, Sb, Cd, Bi	Exhausted but low grade ore reserves still important		minfile.gov.bc

Deposit or prospect name	Country	Area	District	Stratigraphic host	Lithology	Mineralogy (2)		Reserves (1)	Grade			Environmental constraint	Reference
						Main	Accessory		Major element	Other valuable	Economic status		
USA													
Red Dog	Alaska	Western brooks range		Carboniferous	Black siliceous shale, chert	ZnS, Py, Marcassite, PbS	chp, Po in ZnS; boulangerite	77Mt	17% Zn; 5% Pb and 82g/t Ag	Ge: 60ppm; $BaSO_4$	Operating		Moore D.W. *et al.* (1986); Höll *et al.* (2007)
Creta Mine	Oklahoma,Texas			Permian	Black shale, sandstone, gypsum evaporite	Chp, Chalcosite, digenite, anilite, djurleite	Ag (stromeyerite)	??	2-4% Cu	Ag	Creta mine exploited, Mangum deposit lower grade (1% Cu)		Johnson K.S. (1976); Huyk, Chorey (1991)
SOUTH AMERICA													
Mina Aguilar	Argentina	Jujuy Province		Ordovician	Quartzite, black schist	ZnS, PbS, Py		6Mt	6.8% Zn; 3.4% Pb; 50ppm Ag		Operating		negocios.cfired.org.ar
Mina Esperanza	Argentina	Jujuy Province		Ordovician	Quartzite, black schist	ZnS, PbS, Py		10Mt	7.8% Zn;2.3% Pb; 50ppm Ag		Stopped		negocios.cfired.org.ar
Juramento deposit	Argentina	Salta Province			Carbonaceous carbonate, evaporite	Chp, Bornite, py, tennantite tetrahedrite, PbS, ZnS		11Mt	0.4% Cu	19ppm Ag	Prospect		Durieux C.G. (2000)
AUSTRALIA													
Nifty Mine	Australia	Patterson province	Yeneena basin	Neoproterozoic	Silicified black shale	chp, Chalcosite, native Cu, cuprite, malachite, azurite		148Mt	1.3% Cu		Prospect		Anderson *et al.* (2001)
Mount Isa	Australia	Carpentaria-Mount Isa province		Paleoproterozoic	Shale, carbonaceous dolomite	Py, ZnS, PbS		84.5Mt	4.1% Zn; 3.4% Pb; 82g/t Ag (open pit 2005)		New deposit currently mined: Black Star with 23.9Mt @5,1% Zn; 3.1% Pb and 60g/tAg		Tonkin D.G., Creelman R.A. (1990)
						Chp		69.7Mt	2% Cu				Perkins W.G. (1990)
Mt Gunson	Australia	Stuart shelf	Adelaide fold belt	Neoproterozoic	Black shale, sandstone	Chp, chalcosine, bornite			1.9% Cu		7.4Mt already extracted		
Browns deposit	Australia		Northern Territory	Paleoproterozoic	Black carbonaceous pelites	PbS, ZnS, Chp, Py, Siegenite, Digenite, Asp, gersdorfitte, Pb phosphate	Co, Ag	39Mt	0.44% Cu, 1.28% Pb, 0.11% Co, 0.09% Ni		Subeconomic; Browns East similar grade and tonnage		Mc Cready A.J., Stumpfl E.F., Lally J.H., Ahmad M., Gee R.D. (2004)
ASIA													
Shalkya	Kazatskan			Late devonian, Early carboniferous	Shale, siltite, carbonaceous dolomite	ZnS, PbS, Py		225Mt	3.4% Zn; 0.94% Pb		Not extracted		Hocquard Ch. (2007)
Zawar-Mochia-Balaria	India	Rajasthan	Aravalli belt	Neoproterozoic	Dolomite, dolomitic quartzite, pelites, graphitic schists	ZnS, PbS, Py, Po, Asp		40Mt	4.5% Zn; 1.9% Pb	Ag	4 producing mines		Roy A.B. (1995); Res. J. (1992)
Zunyi	China	Guizhou, Hunan, Jianxi, Zhejiang		Cambrian	Conglomeratic, to sand sized sandstones, laminated silt and claystones	Py, As pyrite, Vaesite, Millerite, jordisite		several Mt	4% MO; 4% Ni; 2% Zn; 0,7ppm Au	Se (2,700ppm) Pt 0.3ppm, Pd 0.4ppm	7 mines currently operating over a 1,600Km long belt		Lott *et al.* (1999); Coveney R.M. *et al.* (1991)
Changba	China	Gansu Province	Qinling orogenic belt	Middle devonian	Biotite quartz schist, marble,banded baritite, Coal beds	ZnS, Py, PbS, Asp, Po, Boulangerite, Chp		142Mt	7.34% Zn; 1.31% Pb		140 orebodies		Guoliand *et al.* (2004)
Jinding	China	Western Yunnan	Lamping Simao Basin	Cretaceous-Tertiary	Sandstones, breccias, mudstone	ZnS, PbS, Py, Chp, Wurtzite	Argentite, Ag tetrahedrite	200Mt	6% Zn; 1.23 % Pb	Tl, Cd, Ag			Chunji Xue
AFRICA													
Konkola, Mulufira, Nchanga	Zambia	Musohi, Konkola, Nchanga..	Katanga	Neoproterozoic	Conglomerate, dolomite, Black shale	Chp, Bornite, chalcosite, pyrite		>800Mt	2.8% Cu; 0.10% Co	U, Pd, Re…	more than 10 mines		Mendelsohn F. (1989)
Kolwezi, Tenke, Kambove	Shaba		Katanga	Neoproterozoic	Siliceous dolomite, conglomerate, grey dolomitic shale	Chp, Bornite, chalcosite, pyrite		>2,900Mt	2% Cu	Co, U, Ge	more than 15 mines		Kirkham R.V. (1989)
Ross Pinah	South Africa	SW Namibia		Neoproterozoic	Mudstone, black shale, dolomite	Zns, PbS, Cp, Bornite, tennantite, stromeyerite, Au	Au	50Mt	8% Zn; 2.5% Pb				Goodfellow, Lydon (2001)
OCEANIA													
Matahambre Mine	Cuba	Pinar del Rio		Late Jurassic	Black shale, sandstone	ZnS, PbS	Py, Chp, Po, Ag telluride, selenide	1.8Mt	Cu, Pb, Zn (?)	Ag, Se, Bi	More than 15Mt already extracted during 15 years.		Perez-Vazquez R.G., Melgarejo J.C. (1998)

(1) Reserves	Total (when available) Measured+ indicated
(2) Mineralogy	Py: pyrite; ZnS: sphalerite; PbS:galena; Asp: Arsenopyrite; Po: pyrhotite; Chp: chalcopyrite; Sid: siderite; Mte: Magnetite

VMS type

Kupferschiefer type

Sedex type

Table 3 - Major base and rare metal districts hosting medium grade deposits favourable for future bioleaching processes.

M.-L. Airo, K. Loukola-Ruskeeniemi / Ore Geology Reviews 24 (2004) 67–84 69

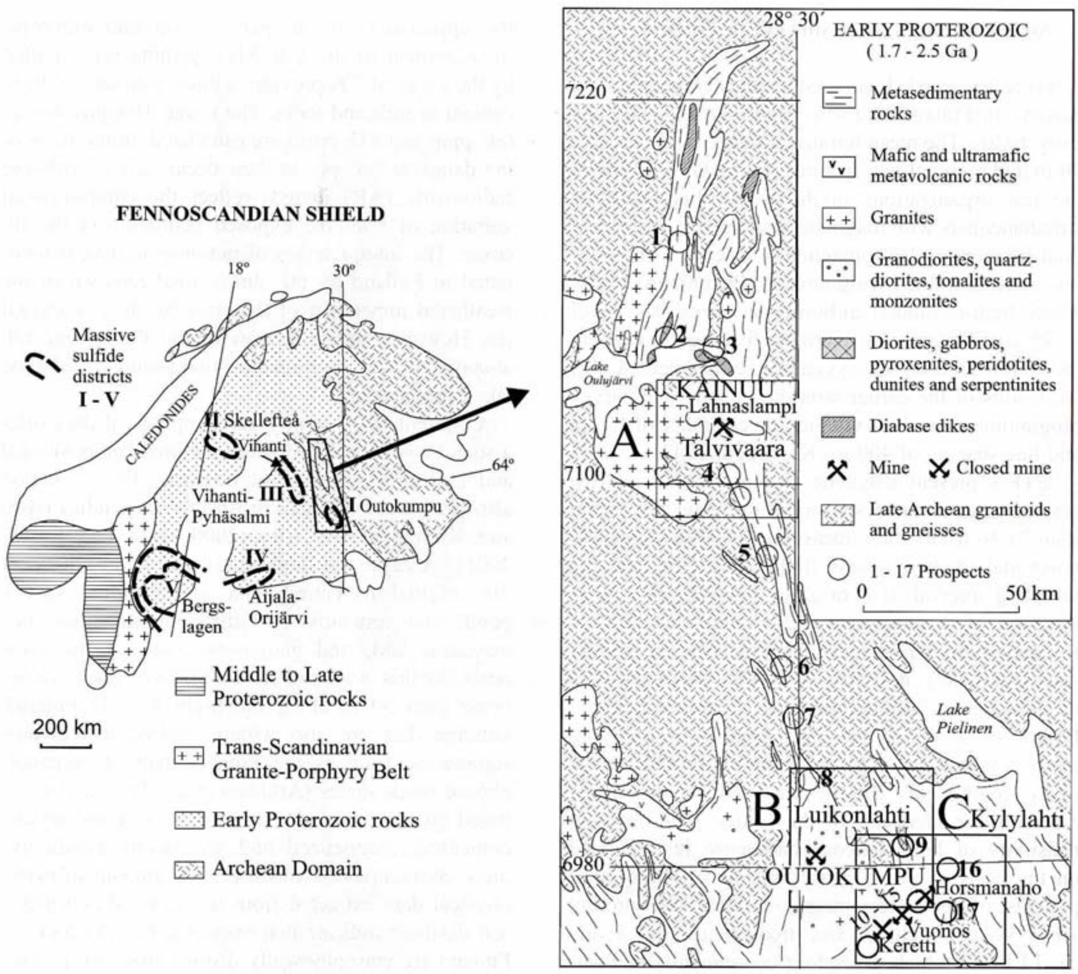


Fig. 1. Generalized geological map of the Kainuu–Outokumpu area in the Fennoscandian shield. Prospects and mines sampled during the project: 1 = Puolanka, 2 = Melalahti, 3 = Jormua, Lahnaslampi = Lahnaslampi talc mine, 4 = Talvivaara black-shale-hosted Ni–Cu–Zn occurrence (northern circle: Kolmisoppi area, map sheet 3433; southern circle: Kuusilampi area, map sheet 3344), 5 = Alanen, 6 = Pappilanmäki, 7 = Ruukinsalo, 8 = Losomäki, Luikonlahti = Luikonlahti Cu–Zn–Co mine, 9 = Miihkali, 10 = Viurusuo, 11 = Keretti Cu–Co–Zn mine, 12 = Kaasila, 13 = Kalaton, 14 = Vuonos Cu–Zn–Co mine, 15 = Sukkulansalo, Horsmanaho = Horsmanaho talc mine, 16 = Kylylahti, 17 = Sola. In western Finland: Vihanti = Vihanti Zn–Cu–Pb deposit. Detailed study areas are outlined: (A) Lahnaslampi–Talvivaara, (B) Luikonlahti–Kokka, (C) Outokumpu–Kylylahti.

Figure 13 - Geologic setting of the Kainu and Outokumpu areas within the Fennoscandian shield (after K.Loukola-Ruskeeniemi, 1996).

The precursors to the Talvivaara black shales were deposited in anoxic conditions in a sea basin associated with hydrothermal activity. The Ni-rich and Mn-rich horizons with black calc-silicate rock intercalations probably result in part from precipitation of upwelling hydrothermal solutions through the sediments, analogously with the processes encountered, for example, in the recent Galapagos mounds hydrothermal field.

The black schist are anomalous in Ni, Zn with an average grade of 0.26% Ni; 0.14% Cu and 0.53% Zn (K.Loukoula-Ruskienemi,1999). The precious metal content is very low. The anomalous black schists are 330m thick (cut of: 0.8% total BMS). The total potential resource **overpass 300 Mt** (Table 3).

Ni is partially hosted in disseminated pyrite and pyrhotite, pentlandite. The average TOC (graphite) content of the black shale is 7-7.7% and some facies are Mn enriched (>0.8%). Elevated δS^{34} values, and positive Eu anomalies and Mn are indicative of an early hydrothermal influx in the original black mud.

2.2.2. The Early Silurian Selwyn basin hosting Pb-Zn and Ni-Mo enriched black shales

The Selwyn basin (Fig.14) is located on the margin of North West American continent. It has been interpreted as an Early Silurian epicratonic marine basin that formed due to subsidence accompanying rifting of the continental margin of North America (Goodfellow and Jonasson, 1983). Within the Selwyn basin, stratiform Pb-Zn mineralization formed during three major periods:

- early Cambrian deposits of the Anvil district;
- early Silurian deposits: XY, Anniv, of the Howard pass deposits;
- middle to Late Devonian: in Yukon: Tom, Jason, Pete and NE British Columbia: Cirque, Driftpile, Elf…

The Howard pass XY deposit is a sheet like stratiform deposit ranging up to 50m thick and extending several kilometers along strike. The XY deposit is hosted in carbonaceous mudstone and chert that are more pyritic and dolomitic than coeval rocks situated remote from mineralisation. The increase in pyrite is also accompanied by an increase content of several trace elements in pyrite: Ni, Co, As, Sb, Se. Near the deposit a footwall halo is marked by a K_2O increase related to K enriched Ba felsdspars whereas in the hanging wall, a decrease in the phosphate layer thickness is observed and a correlative decrease of the apatite content away from the deposit. The sulphide enriched horizon is interbedded between two chert layers showing a maximum in organic content (>8%) and a decrease in δS^{34} (Fig. 15).

The total inferred metal resources of the XY deposit is **525 Mt with 5% Zn, 2% Pb and 85g/t** Ag. The major host sulfide minerals are framboidal pyrite, sphalerite and galena. Minor minerals are tetrahedrite, polydimite, millerite, gersdorfite, molybdenite. Galena and sphalerite are extremely fine grained and concentrated either in fine laminae either in stripped cleavages.

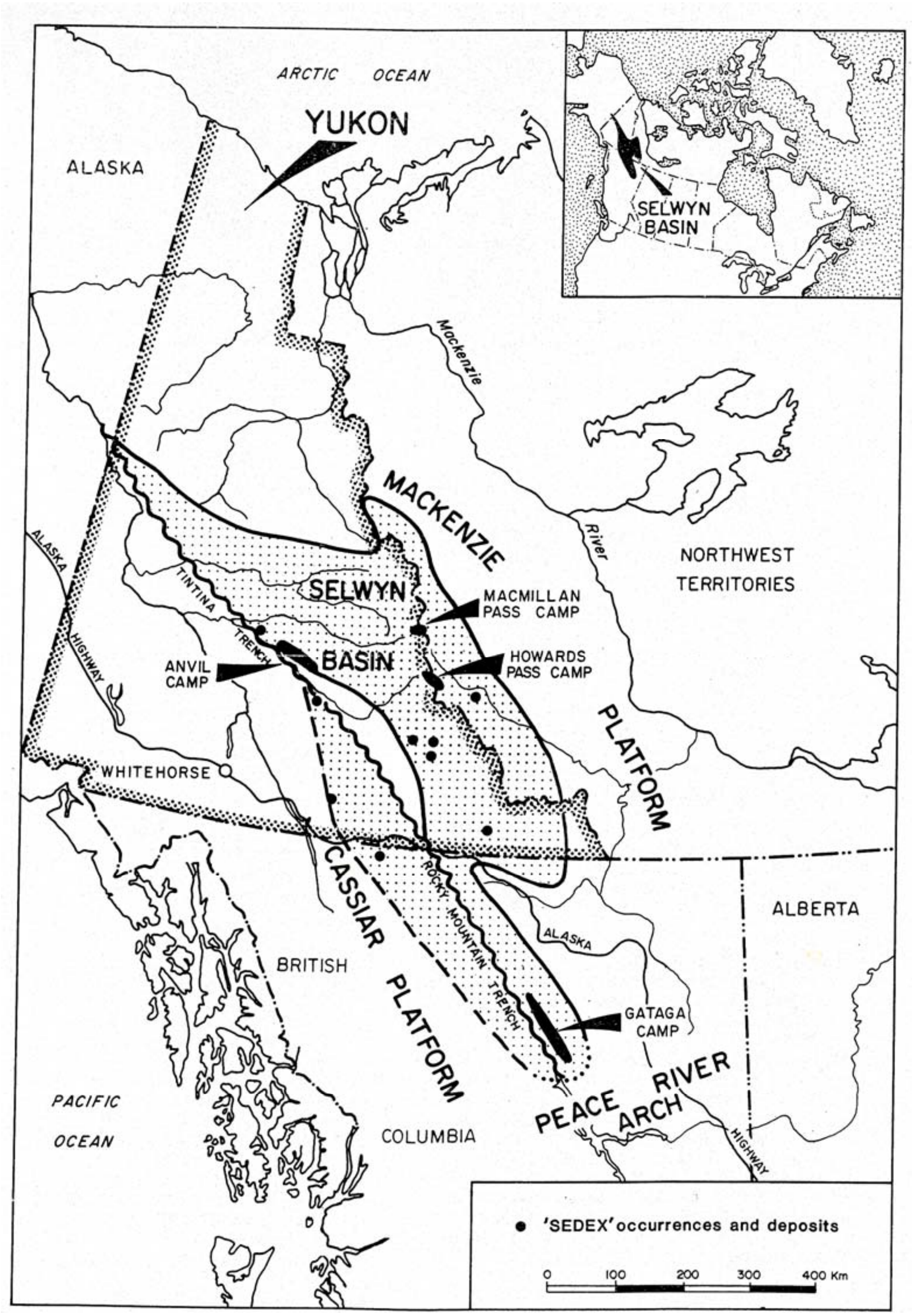


Figure 14 - Location of the Selwyn basin between the Mackenzie and the platform (Yukon-British Columbia).

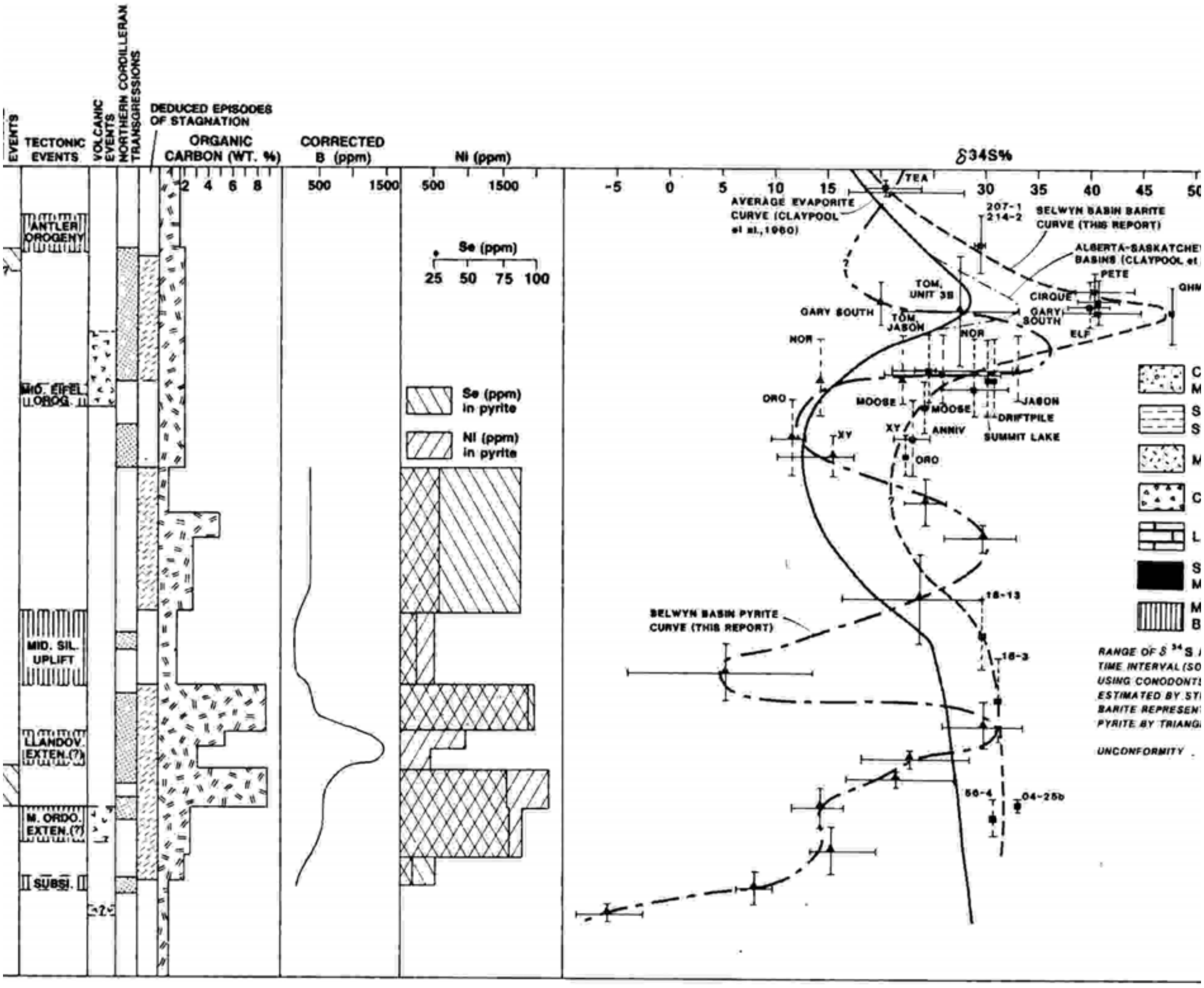


Figure 15 - δS^{34} age curve and pyrite plotted on a composite stratigraphic section of Selwyn basin. B, in illite and Se, Ni in pyrite are also plotted (from Goodfellow, Jonasson, 1983).

During the deposition of the XY deposit, the water column was stratified with anoxic and sulfidic bottom water. After, during the middle Silurian, the water column was ventilated due to shallowing and barite precipitated over most of the Selwyn basin. Isotopic fractionation temperature indicates that the deposit formed at relatively low temperature (<220°C), from metalliferous chloride-bicarbonate brines was discharged at the surface along extensional faults.

The Devonian Ni-Zn Nick deposit in a northern extension of the Selwyn basin

In a marginal marine anoxic basin, a stratabound Ni-Zn mineralisation was deposited along the Mackenzie platform in Yukon (L.J. Hulbert, 1995). The mineralized horizon is located between a calcareous graptolitic shale, a limestone ball member and a phosphatic bed predating a turbiditic siliceous shale and located in two synclines. The layer is 3 cm thick on average and extents more than 80 km^2 (Fig. 16).

The average grade is: 5.3% Ni; 0.73% Zn, 0.25% Mo and 776 ppb Au+PGE. The U content is between 15 and 100 ppm, with elevated grade of As (0.35%) and Re (15 to 61 ppm). The major host sulphides are: pyrite, vaesite (NiS_2), melnikovite, sphalerite, and wurtzite.

The Ni total content would be in the range of 9 x 10^5 tons. Bitumen rich veinlets associated with the ore beds, indicate a strong organic contribution in the metallic transport of the metals.

This deposit presents some analogies with the Cambrian Chinese Ni deposits (see below).

2.2.3. The Cambrian Ni-Mo Zunyi deposits of the Yangtze platform

Bedded Ni-Mo ores occur in a 1,600 km long belt (Fig. 17) within Cambrian metalliferous black shales of the Niutitang and Quihongzhusi formations that unconformably overlies Sinian (Late Proterozoic) dolostone (Lott *et al.*, 1999).

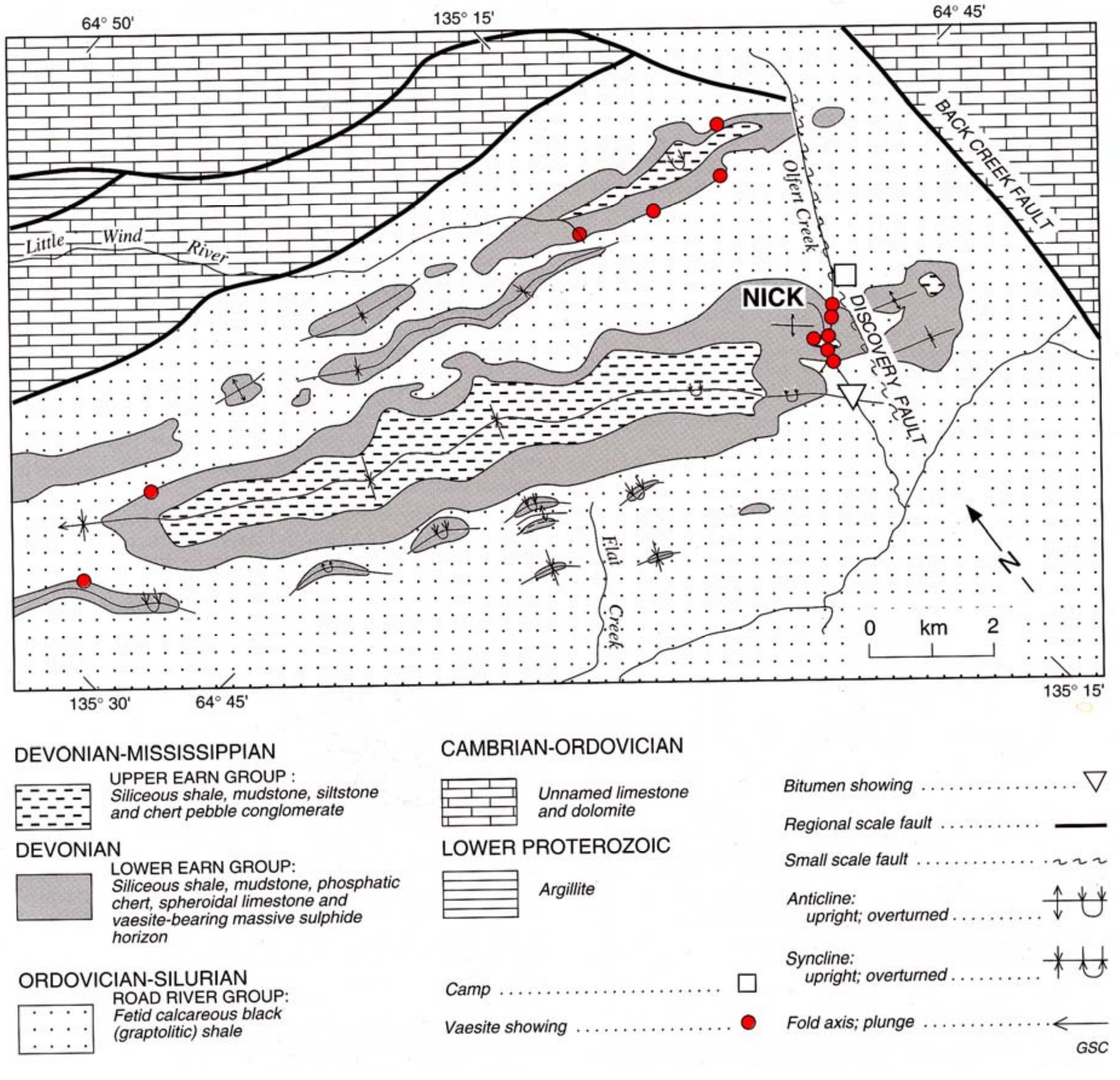


Figure 16 - Geological map of the Nick basin showing the Ni mineralisation occurrences (in red, after Hulbert et al.*, 1992).*

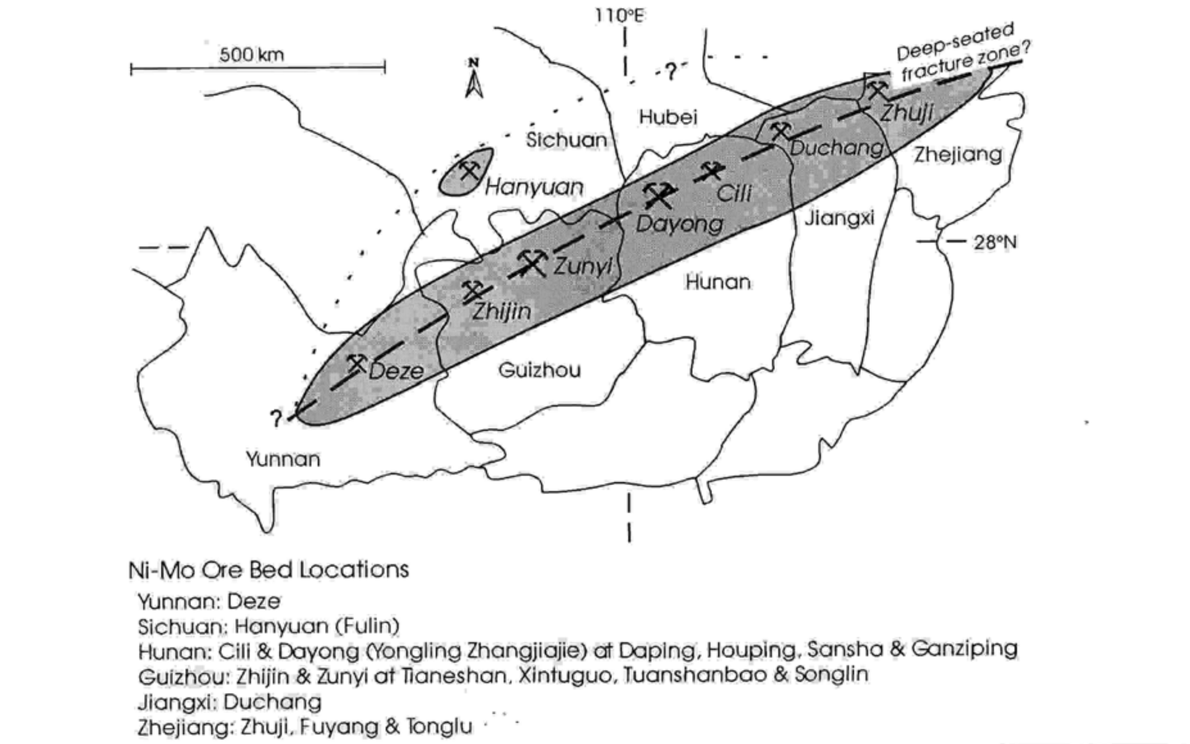


Figure 17 - Location sketchmap of the major Ni-Mo occurrences in southern China.

The structural trend of most of the Ni-Mo occurrences suggest some structural control beside the main paleogeographic sedimentological controls: paleo-shoreline and sub-basin redox conditions. The Ni-Mo ores are not the only mined occurrence in the Southern Chinese Cambrian basin: vanadiferous black shales, uranium and barite ore, thick high grade phosphorites are also extracted.

The Ni-Mo ores consist typically, of a heterogenous mixture of nodules and clasts of Fe, Mo, Ni sulfides, stone coal (alginite), phosphorite and chert. At some locations the beds are laminated (Fig. 18).

The main ore sulfides are jordisite (a mixt phase between MoS_2 and C), Ni bearing vaesite, bravoite. Minor minerals include arsenopyrite, chalcopyrite, covellite, sphalerite, millerite, polydimite, gersdorffite, sylvanite, pentlandite, tennantite, violarite and native gold.

The average grade of these deposits is: Mo: 4% to 7%; Zn: 2%; Ni: 2%; As 2,5% and 1 to 2 g/t Au+PGE and 450 ppm U and V and 0.2% Se (Lott, *et al.*, 1999; Orberger B. *et al.*, 2007). The ore layer content also 19% S and 13% C the later being recovered for energy production. No reserves data have been published to date.

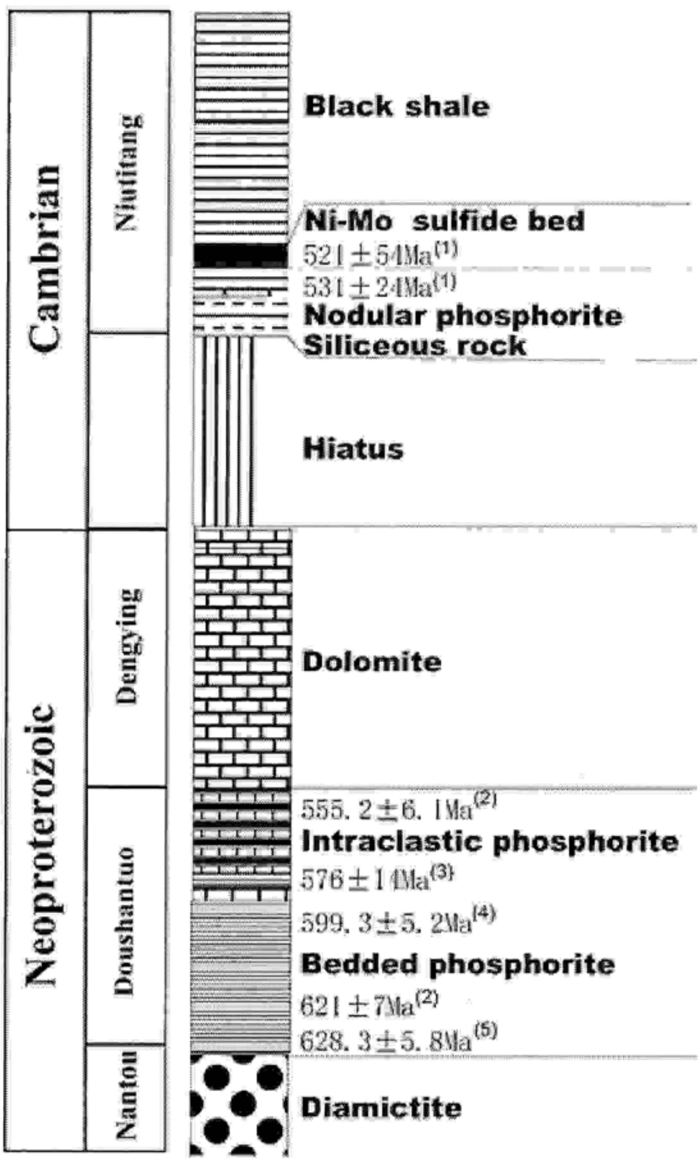


Figure 18 - Cambrian stratigraphy of the Guizhou and Hunan province showing the Ni-Mo horizon (after Jiang J.H. et al.*, 2006).*

More recently, Y/Mo ratios and comparison of the REE spectrum of these mineralized black shales with their normal counterpart indicate that an hydrothermal contribution to the anoxic basin with a bacterial reduction of the sulfides (positive Eu anomaly and low Y/Ho ratio according to Jiang S.Y. *et al.,* 2006) was required to produce these very anomalous shales.

2.2.4 The Paleoproterozoic Carpentaria Mount Isa belt (Australia)

The Paleoproterozoic Carpentaria Mount Isa belt is estimated to contain about 11% of the world known lead and zinc resources, 5% of its silver resources and 1% of its copper resources (Queensland development website, 2007). Two major basins: the Proterozoic Mount Isa Inlier and the Mc Arthur basin to the south host super giant world stratiform Ag-Pb-Zn deposits: Mc Arthur river, Century, Mt Isa, Hilton, George Fisher and one supergiant stratabound Ag-Pb-Zn deposit: Cannington (Fig. 19).

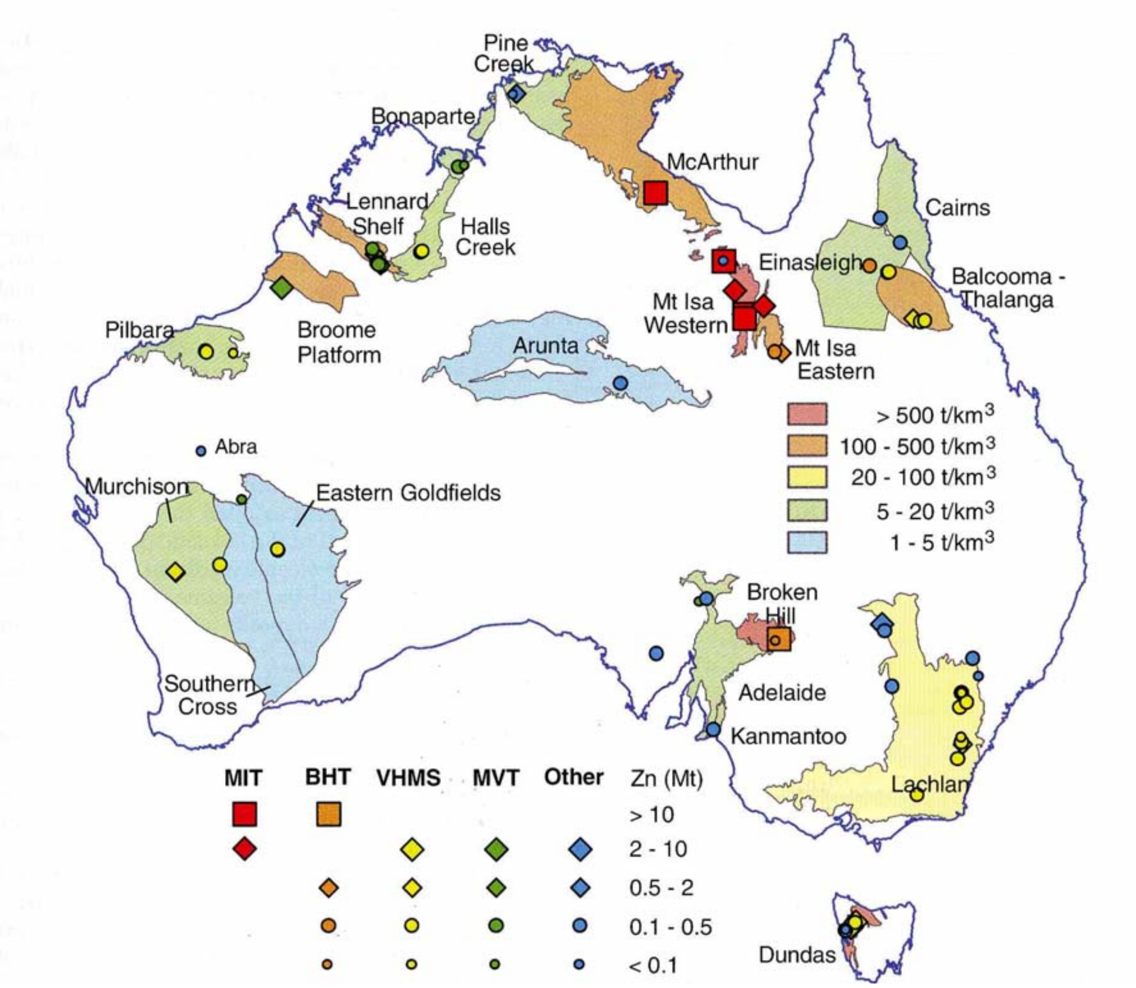


Figure 19 - Major mineralized districts of Australia (after Huston et al.*, 2007).*

The majority of these stratiform deposits exhibit similar geological and geochemical features (Large *et al.*, 2005):

- location close to regional normal and strike slip fault;
- organic rich black shales and siltstone host rocks;
- laminated, bed parallel synsedimentary sulphide minerals;
- stacked ore lenses separated by pyritic and Fe-Mn carbonate-bearing siltstone;
- lateral zonation exhibiting an increasing Zn/Pb ratio away from the feeder fault;
- an extensive stratabound halo of iron and manganese rich alteration in the sedimentary surrounding along strike from ore;
- broad range of δS^{34} for sulphide minerals, (0-20 per mil) with wider spread for pyrite than BMS[1];
- lead isotope ratios indicating a derivation of lead from intra bassinal sources.

These factors indicate that stratiform Zn-Pb-Ag ores were formed approximately contemporaneously with sedimentation and diagenesis. The Mount Isa–Mc Arthur deposits have been dated around 1690-1670 Ma (Plumb K.A. *et al.*, 1990) (Fig. 20, 21).

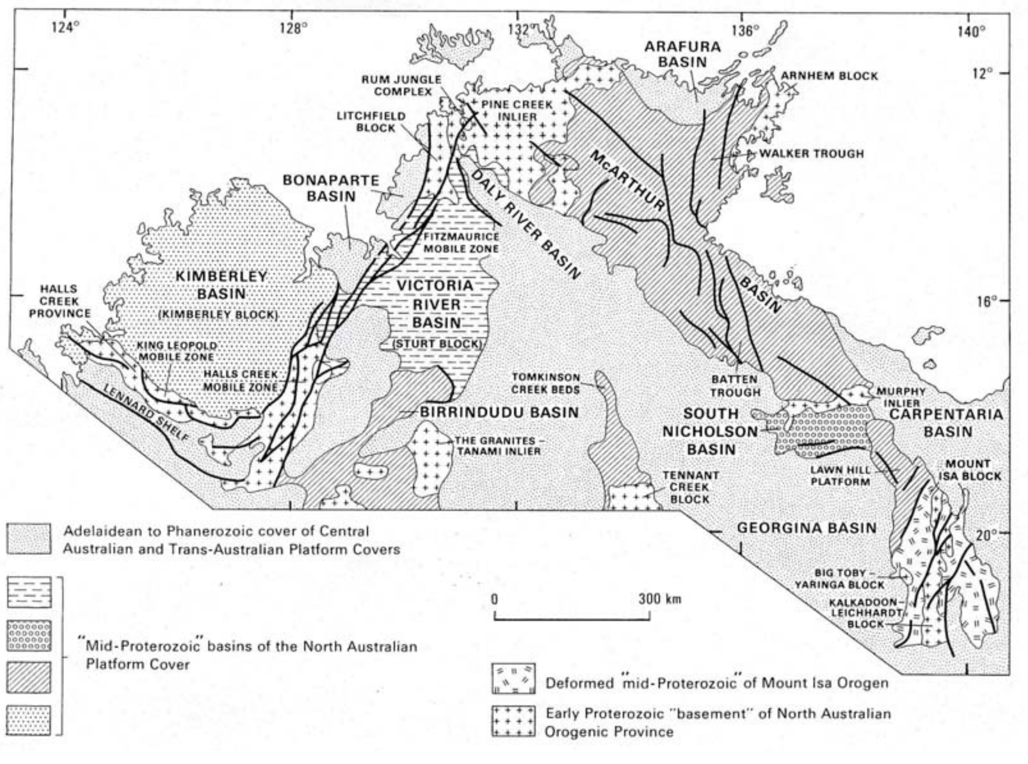


Figure 20 - Main tectonic features for the Mid-Proterozoic covers of Northern Australia (after Plumb K.A. et al.*, 1990).*

[1] BMS = Base Metal Sulfides.

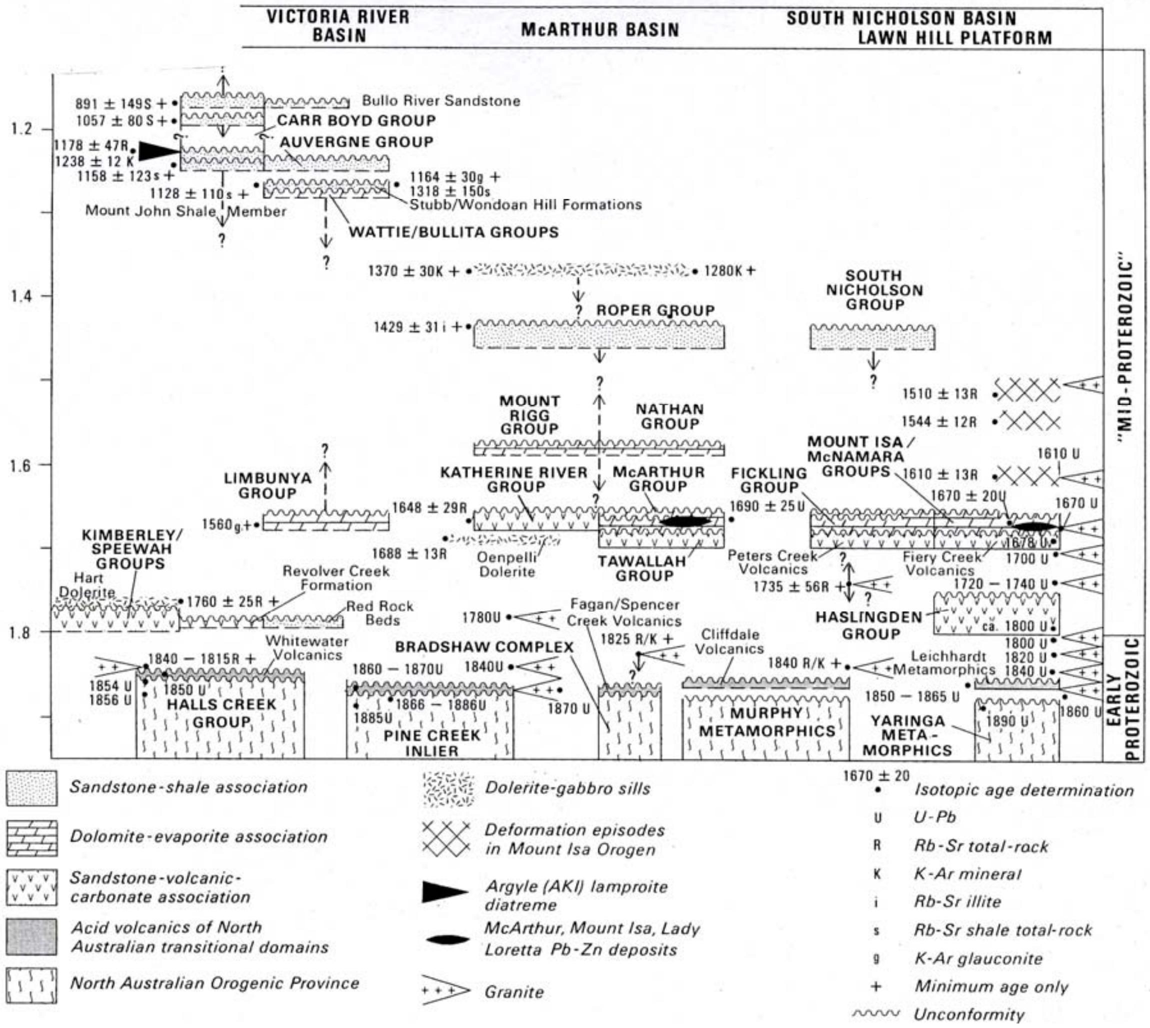


Figure 21 - Time relation for the mid Proterozoic covers of Northern Australia.

The giant deposit of Mount Isa, amounted 84,5 Mt with an average grade of 7% Zn; 6% Pb; 0.1% Cu and 180 g/t Ag (Huston *et al.,* 2007, Table 3). Infact the total resources before mining started in 1923 was more than 150 Mt. The deposit is formed by several millimeters to meters thick sulphide rich laminites with pyrite, pyrhotite, galena and sphalerite, mostly fine grained. Silver is mostly hosted in freibergite near galena. More than 30 orebodies have been delineated in the mine area.

Laterally to the Pb-Zn laminated ore, a Cu orebody was delineated later (Fig. 22), associated with the silica-dolomite rocks. A first ore was mined in the supergene enriched zone: 2.2 Mt with 3.9% Cu.

Further drilling delineated a resource of 69,7 Mt of primary Cu mineralisation averaging 2% Cu (Fig. 22).

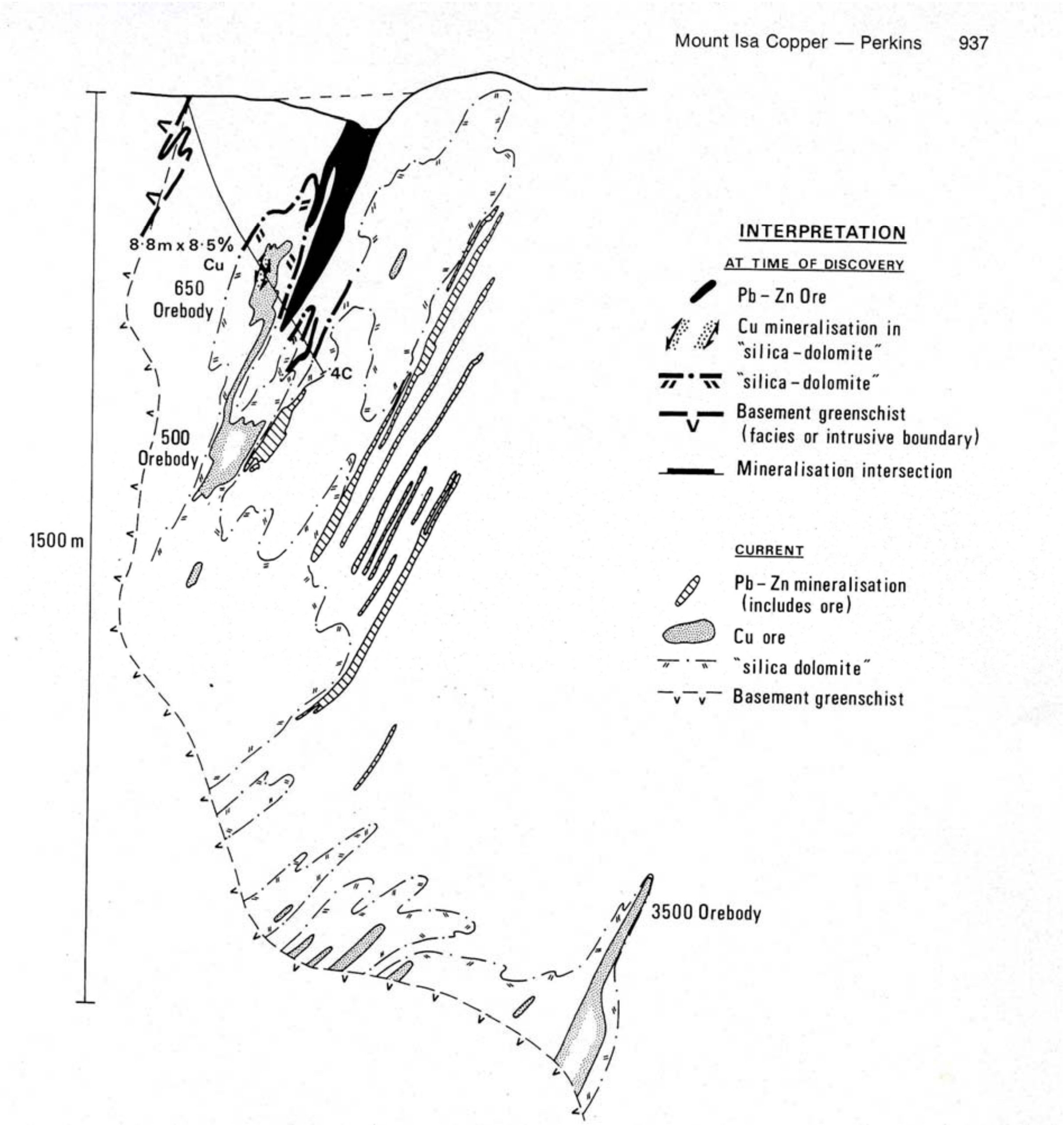


Figure 22 - Vertical section showing the Cu enriched ore beside the Mount Isa Pb-Zn banded ore. (from Perkins W.G., 1990).

Mc Arthur river is of similar age and equivalent size: the HYC deposit amounted 190 Mt averaging 4.1% Pb, 9.5% Zn, 0.2% Cu and 44 g/t Ag. All deposits of this area are hosted in pyritic, carbonaceous and dolomitic black shales. Two phases sources of sulfides were present: fine syngenetic pyrite formed by microbial sulfate reduction and later lead zinc sulfides formed from magmatic or evaporite derived basinal brines via channelways within the Emu fault zone (Plumb *et al.,* 1990).

Cu Kupferschiefer type deposits

The Neoproterozoic Yeneena basin, in the Patterson Province of NW Australia, disseminated Cu stratabound mineralisation have been discovered recently. The Nifty mine represents an global resource of 148 Mt@1.3% Cu (Anderson *et al.*, 2001). The mineralisation is composed of chalcosite, chalcopyrite and their supergene minerals: native Cu, malachite, azurite in silicified black shales.

The Mt Gunson Cu mine formerly exploited, is located in the same district.

The Browns deposit, is a polymetallic Cu-Pb-Co-Ni deposit discovered in the Paleoproterozoic belt of the Northern territory.

Numerous stratabound deposits have been mined in this country.

2.2.5. The Neoproterozoic Congolese-zambian copper belt

The Congolese Zambian copper belt (Lufilian belt) is one of the richest in the world and extend over more than 160 km with a 30 km width. It represents about 30% of the world stratabound copper reserves. The total resources of the copper belt in DRC and Zambia are estimated at more than **150 Mt Cu metal and 8 Mt Co metal** (Dewaele *et al.*, 2006). It was discovered at the end of the colonial period (1885) and its economic importance influenced the border drawing between the former tutelage Belgian and English powers. Since that period, more than 15 Cu-Co deposits have been discovered, most of them having a supergene enriched caping whose grade are very high in some areas (Fig. 23).

Most of the Cu-Co stratabound mineralisations are enclosed in Neoproterozoic shales and dolomite dated between 1,100 Ma and 900 Ma. A correlation exists between the “Mine series” in RDC and the Roan serie in Zambia.

Most of these copper mineralizations occurs at the transition between a continental margin and a platform serie invaded by a restricted marine, shallow water with evaporites and black shales. Intertidal reef dolomite are located at the base of the Mine serie or interlayered with anhydrite bearing ore shales in the sedimentary cover overlying the Kibaran shield.

The Katanga Supergroup consists of a 5-10 km post-orogenic thick sequences dated post 880 Ma, and that was deformed by the Pan-African orogeny at 560-550 Ma.

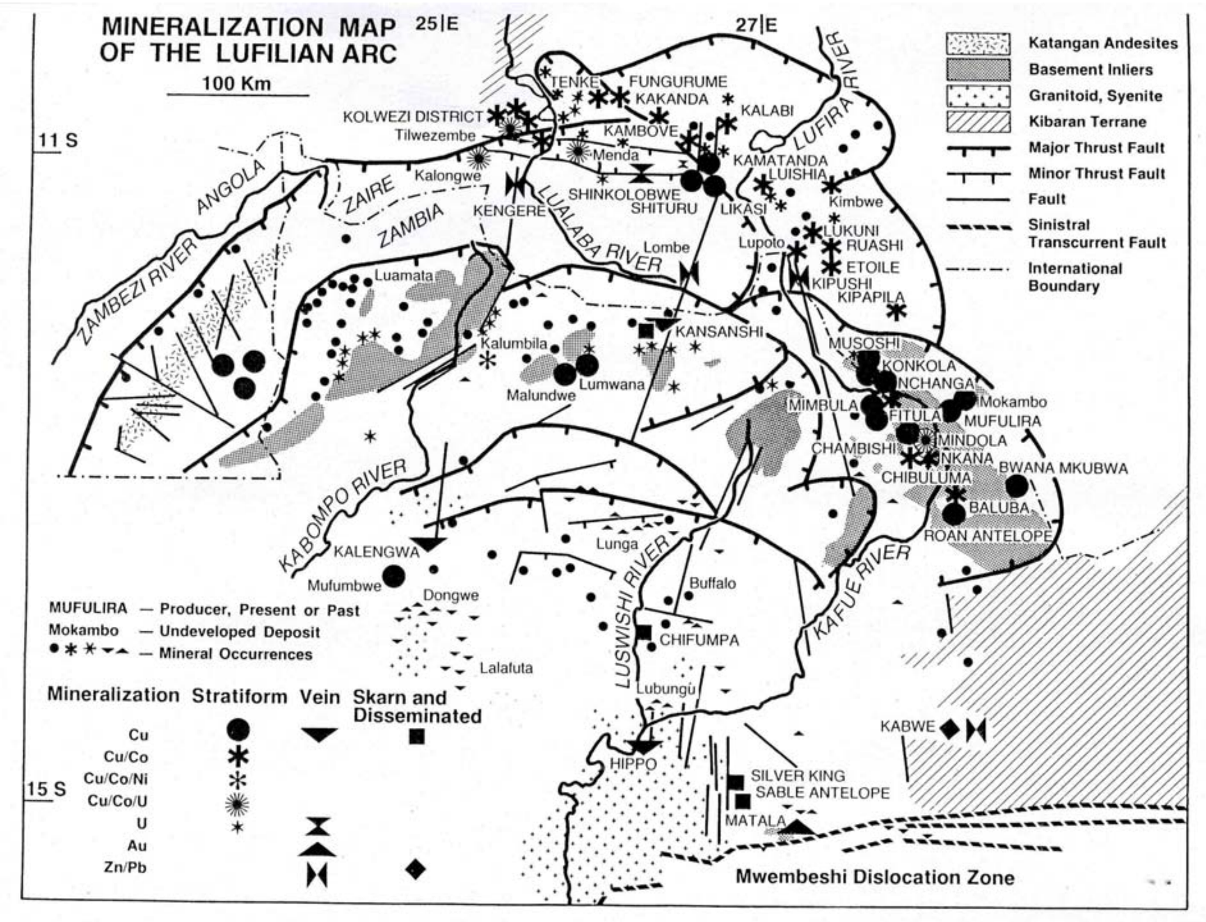


Figure 23 - Location of the major Cu–Co stratabound mineralisation in the Lufilian fold belt of RDC and Zambia.

Three types of Cu mineralizations are recorded in this area: stratabound, early diagenetic base metal sulfides, supergene enriched deposits and vein type deposits. MVT breccia type mineralisation are also described in the dolomite (see for example Kipushi mine).

The genesis of the stratabound deposits is related to the paleosalinity in a lagoonal environment and where biogenic activity (reducing bacteria) and algal mats provided the necessary carbon and H_2S. In Shaba, a first Cu mineralisation was deposited in a transgressive marine lagoon, followed by an offshore barren reef and then by the upper mineralisation deposited in a fore-reef shale which grade laterally in a carbonaceous pyritic shale (Garlik W.G., 1989).

The Cu mineralisation are hosted in various lithologies: eolian sandstone and fluviatile conglomerates (red bed reduced type), in disseminated in black shales and dolomite.

Supergene enrichment of the stratabound mineralisation produced three main secondary facies: Cu oxides (cuprite), Cu carbonates (malachite) and Cu silicates (e.g. chrysocolla).

The ore shales are a silt sized micaceous black calcareous argillite containing quartz, feldspar and Cu-Fe sulfides. In some places, the shales contain more than 2% organic matter. The ore shales are typically 20 m thick, whereas, the Cu orebodies are 10 m thick.

The main ore minerals are chalcosite, bornite, chalcopyrite, pyrite, pyrhotite and carollite. The amount of sulphide in the ore is remarkably constant: 7%.

The ore zone is generally 2 km wide and beyond, iron sulphide predominates in the carbonaceous zone 8-12 km wide. Microthermometric studies indicate T° between 80 and 195°C and a salinity between 8.4 and 18.4 eq. NaCl for the fluids that deposited the diagenetic ore (Dewaele *et al.*, 2006). Higher T° are recorded by syn deformational quartz veins related to the Lufilian compressional deformation and metamorphism.

An example of the remaining reserves (Cu, Co) of some deposits is given in Table 4.

The Tchanga deposit is one of the biggest with **268 Mt of total reserves grading 3.16% Cu** (Fig. 24).

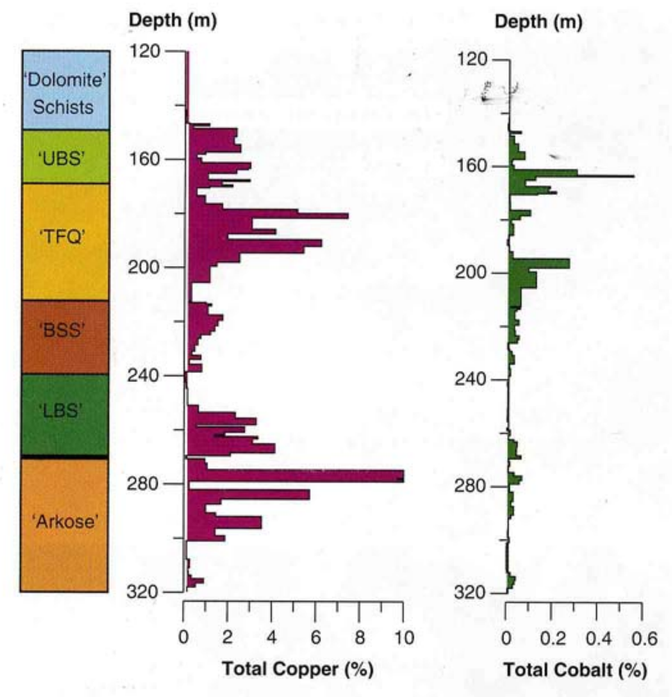


Figure 24 - Colour stratigraphic log of the Zambian copper belt showing the two mineralized episodes (1 and 2).

Reserves[1] and grades for major Zambian Copperbelt type Ore Shale deposits

Mine/deposit	1974				1982		
	Gross tonnes[2] (Mt)	Grade of Cu (%)	Tonnes remaining[3] (Mt)	Grade of Cu (%)	Tonnes remaining (Mt)	Grade	
						Cu (%)	Co (%)
Musoshi	220	2.1	220	2.1	200	2.1	?
Konkola (Bancroft) (Includes Karila Bomwe)	161	3.65	126	3.56	207	3.72	0.05 [4]
Nchanga	374	4.11	254	3.45	268	3.16	[5]
Chambishi	55	2.92	43	2.93	29	2.81	—
Chambishi Southeast	—	—	—	—	55+	2.4	[6]
Nkana (Includes Mindola)	312	2.81	122	2.51	110	2.33	0.13
Baluba	112	2.41			58	2.52	0.16
			142	2.58			
Luanshya (Roan Antelope)	254	2.86			51	2.44	—
Totals and averages	1488	3.11	907	2.85	978	2.73	—

Table 4 - Example of tonnage and grade of Cu-Co deposits in Zambia.

The economy of the recovered metals relies also on some important rare metals associated like Ge (Ge rich ore reaching 0.8% Ge, Kipushi mine, Holl *et al.*, 2007), Pd oxide (e.g. in Ruwe mine, Jedwab *et al.*, 1993) and Pd, Cu selenide (Oosterboschite in Musonoi¨mine).

2.2.6. The Lower Permian Polish German Kupferschiefer

During the post-hercynian extensional phase, several sub-basins were developed in the Middle-northern part of Europe. After a long period of continental weathering under tropical climate and erosion, the Variscan mountains were reduced to a peneplain and eolian transport led to red sandstone accumulation on the margin of the continent. Then several marine transgressive phases from the Northern Boreal ocean, invaded the structural lowland creating the Zechstein sea (Upper permien, Fig. 25). This shallow epicontinental inland sea extended over more than 1,600 km E-W, from Poland to the British Islands, and 900 km North-South from Holland to Norway (Fig. 25). Five major sedimentary cycles are recorded in the Zechstein sea (Z1 to Z5) depositing more than 2,500 m of sediments in 5 Ma. Each cycle includes continental, clastic turbidites, black shales, dolomitic carbonates, anhydrite, halite and finally K, Mg rich salts that indicate a regressive evolution ending with more restricted water and evaporites (F. Orzag-Sperber, 2001). These evaporatic sequences are the traps of the major oil and gas deposits of the North Sea.

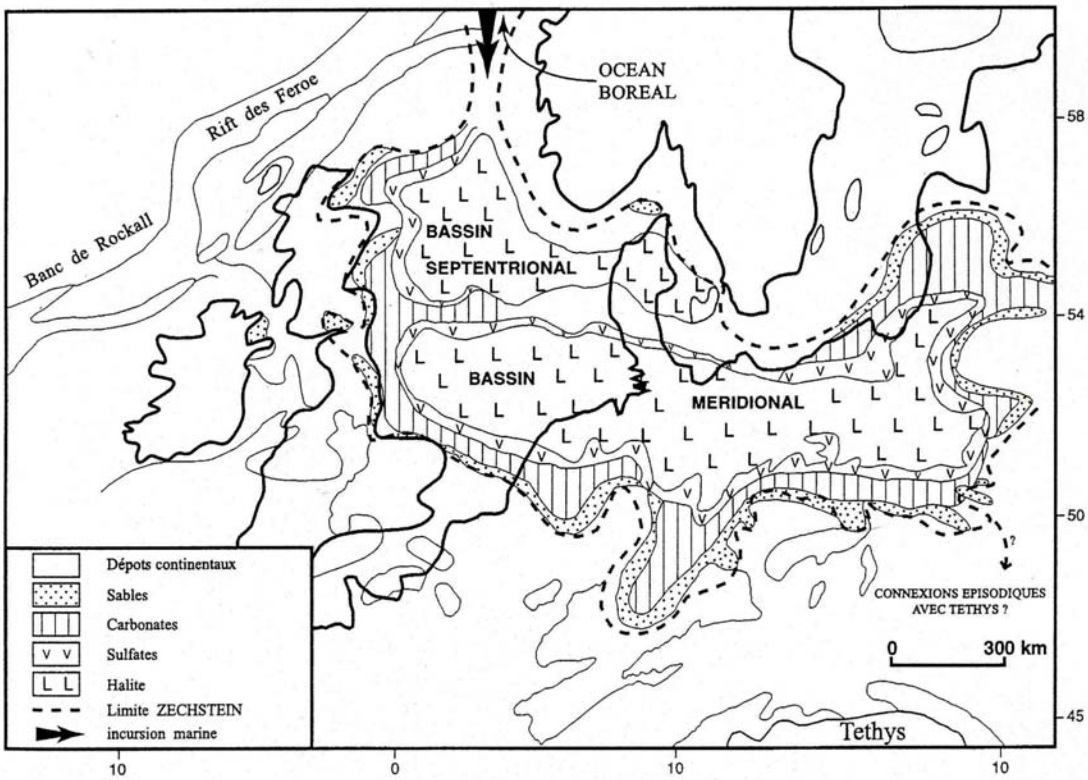


Figure 25 - Major facies deposited along the Upper Permian Zechstein sea (from Ziegler,1982).

The major Cu-Zn deposit of the Kupferschiefer are restricted to the base of the Z 1 cycle, in two major sub-basins: the Mansfeld basin in Eastern Germany and the Lubin–Sierozowice basin in Southern Poland.

In the Rheno-Hercynian zone, six polymetallic rich districts were discovered from South to North (Fig. 26): the Richeldorf Cu mine (1, Fig. 26), the Mansfeld-Sangerhausen district (2), the Basse Lusatia district (3), the North sudetic Through (4-5, Nowy Kosciol and Lena former mines), and the Fore Sudetic Monocline (6) with 4 mines: Sieroszowice, Rudna, Polkowice, Lubin.

Economic value (after Kirkham, 1989)

The Mansfeld district is now closed, but it represented more than 75 Mt of ore (reserves and past production) at an average Cu grade of 2.9% Cu with 150 g/t Ag with minor Pb, Ni, Au.

The abandoned Konrad–Lena district of Southern Poland had a total resource of 181 Mt with an average Cu grade of 0,7% Cu.

The Lubin district (Fig. 27) hosts the major Cu reserves with more than **2,600 Mt with an average Cu grade of 2%** and 30-80 g/t Ag. Three underground mines (-600 m to -1,200 m) are still operating: Rudna, Polkowice and Lubin. The ore thickness varies between 0.4 and 26 m.

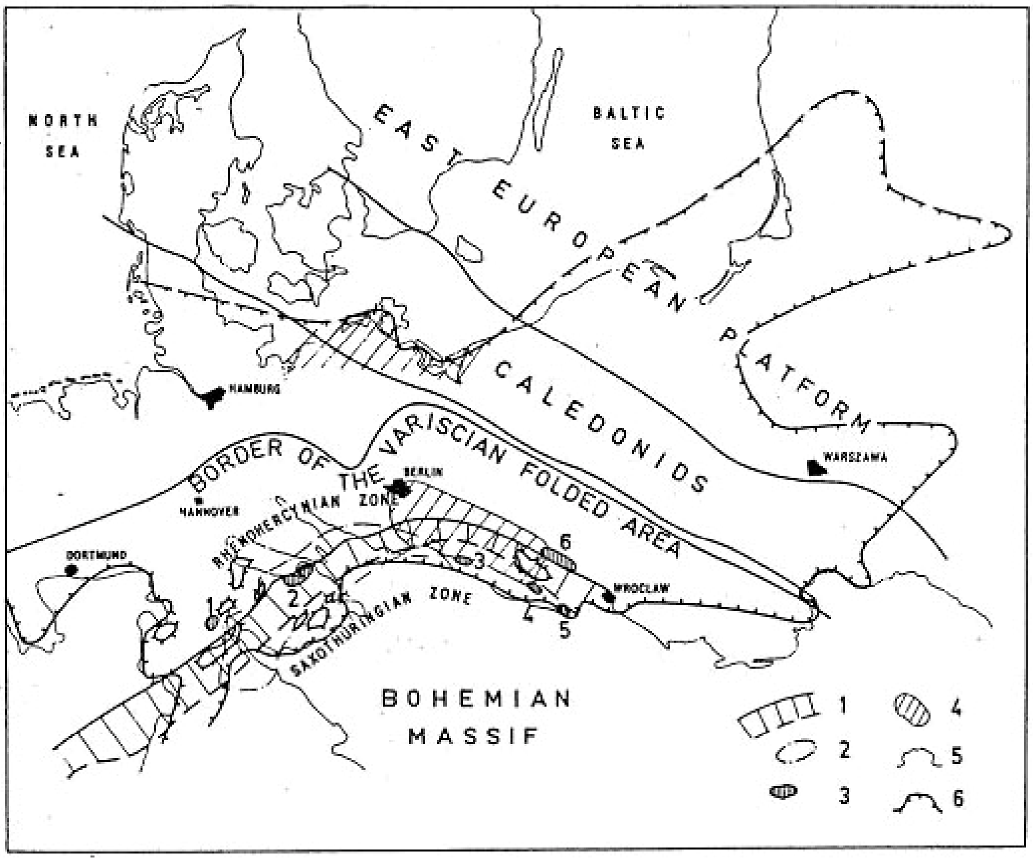
In 2003, the three operating mines **produced 569,000 t Cu, 17,550 t Pb and 1,561 t Ag, 1,955 t of Ni sulphate and 296 kg Au**.

20% of the Cu mineralisation occur in the black shale horizon, 50% in the underlying sandstone and 30% in the overlying dolomite (Fig. 28).

The major syngenetic sulphides of the black shales are pyrite, chalcosine, bornite and chalcopyrite deposited in laminated shales. Later fissural chalcosite, carbonate are related to diagenetic remobilisation and a later stage is connected with the alpine folding and recristallisation.

The peribasinal rote Faule are the main channels for the hypersaline mineralizing fluids. Laterally they deposited the Cu, Pb, Zn and Fe sulphides with decreasing fluid T° (Fig. 10).

The Cu-Fe-Pb-Zn-S shale hosted ores are the most intensely mineralized and the Au-Ag-PGE ores (0.1-9 g/t for Au and 0.01-9 g/t for Pt and 0.01-1 g/t for Pd) occur at the redox interface between the Rote Faule oxidized zone (hematitic) and the unoxydized, mineralized shales.



Extension of the Kupferschiefer in Central and East Europe; on the southern margin of the basin

1. *Crystalline area of the Saxothuringian basement;*
2. *Area of the Saale-through;*
3. *Copper ore deposits :*
   1, Richeldorf
   2, Mansfeld-Sangerhausen
   3, Lower Lusatia
   4 et 5, North Sudetic syncline
   6, Presudetic Monocline
4. *Large areas with "Rote Fäule" facies;*
5. *Outcrops of the variscan folded basement;*
6. *Area of the Kupferschiefer.*

From J. RENTZSCH (*1974*), *fig. 1*

Figure 26 - Major structural units of the Kupferschiefer and location of the Cu districts (after J. Rentzsch, 1974).

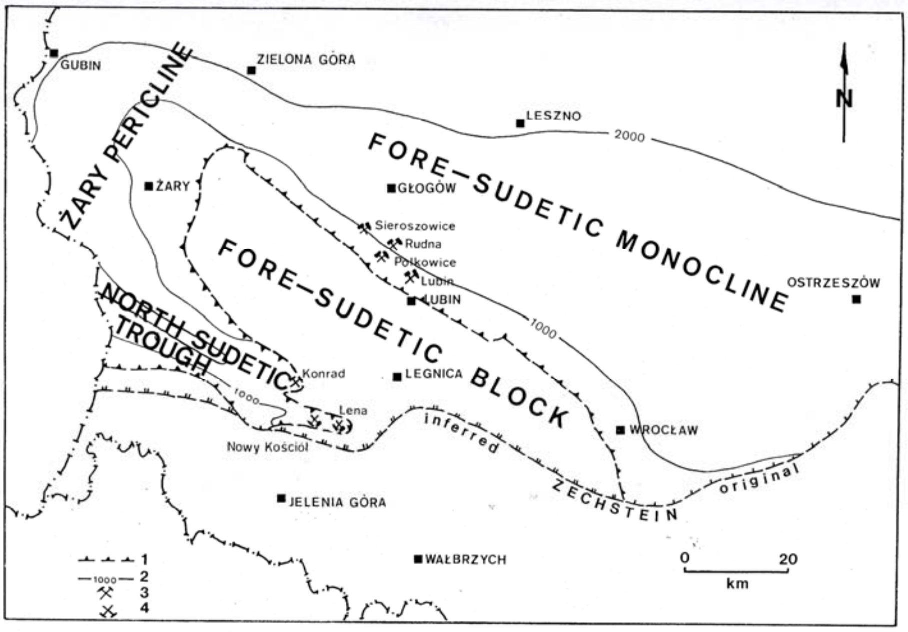


Figure 27 - Sketchmap of the Polish Kupferschiefer with Cu mines location (from Oszczepalski S., 1989).

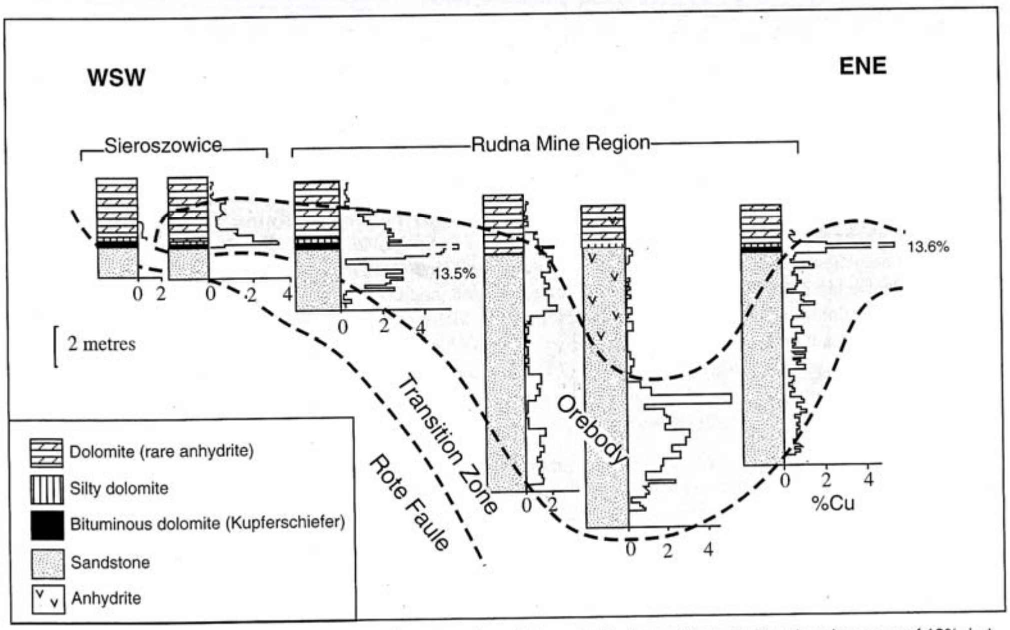


Figure 8.7. Distribution of Cu in the ore zone, it shows higher Cu enrichment in Kupferschiefer with Cu values in excess of 13%, but the greater thickness/volume of ore resides in the sandstone beneath an evaporite seal (after Wodzicki and Piestrzynski, 1994).

Figure 28 - Distribution of copper in the ore zone. It shows higher Cu grade in the Kupferschiefer (with 13% Max.) but the greater thickness/volume of ore resides in the sandstone beneath an evaporite seal.

Various indexes indicate a vertically temperature decrease in the Kupferschiefer:

- $\delta^{13}S$ of the organic matter decreases upward, and the Cu rich basal part is enriched in heavy sulphide ($\delta^{34}S$) concurrent with lower HI (Hydrogen index) values. The later parameters indicate that the inherent organic matter was used for thermal sulphate reduction and production of HS- (Fig. 27, 28).

Thus early precipitation of sulphide was related to bacterial sulfate reduction (BSR). During diagenesis Cu^{++} substitutes partly Fe to produce chalcopyrite and bornite. The higher sulphide content to produce the richest layer was provided by thermal sulphate reduction (TSR) of the earlier formed anhydrite and secondary carbonate were formed (Bechtel. A. *et al.*, 2001).

Vitrinite reflectance (PR) of the organic matter confirmed maximum paleotemperatures of 100-120°C leading to residual pyrobitumen in the dolomite.

The underlying volcaniclastic rocks of the Rotliegendes (Early Permian) are considered by most authors as the main source of the metals. A submarine volcanic event is recorded at the same epoch but very far from this area (near the UK border). Continental weathering of the mineralized hercynian shield has probably also contributed to the enrichment of peribasinal brines.

2.3. EXAMPLES OF BLACK SHALE HOSTED MINERALISATIONS IN FRANCE (INCLUDING SOME LIGNITE, CARBON RICH MARLS)

These facies are ubiquitous through the whole time stratigraphy spanning from the Precambrian to the Cenozoic era (see table 5).

France	Age	Geodynamic	Lithology	Base metal	Rare/precious metal
Pyrenées-Montagne Noire	Cambrian	Back arc basin	BS, Dolomite Phosphate	Fe, Pb, Zn, P	Ge, Cd
Eastern Pyrenées, Montagne noire (S)	Cambrian	Active margin	Turbidite, BS volcanics	Pb, Zn, Fe, Cu, Ni, Co, Sb	Au, W
Pyrenées	Ordovician	Continental, margin	BS, flysch	Pb-Zn	Ge,Cd
Massif central (border)	Triassic	Continental, margin (lagoon)	BS, marl, evaporite, conglom.	Pb, Zn, F, Ba Sb	U
Dauphiné basin	Cretaceous	Intracontinental Rift	Blue marl, phosphate	Ni, CU, Ba, Pb	U, REE

Table 5 - Some examples of base metal enriched black shale in France.

The Cambrian period represents a wide mineralized area in the southern part of France with stratabound Zn-Pb-(Ge) disseminated sufide mineralisations located in various black lithologies: black shales of the St Salvy area (Montagne Noire), phosphatic black shales, slightly anomalous in Cu, Zn, U and REE in the Peux area, black dolomitic carbonates anomalous in Ba, P, Co, Ni, Pb, Zn of the Montagne noire tectonic thrusted slices, a black schist anomalous in Au, Cu, Pb, Zn, As, Sb in the Cévennes area (Orgeval *et al.*, 1997), locally associated with sideritic lenses. In the Peux area, a REE study (Laval *et al.*, 1990) showed that some Eu anomalies in a relatively low REE background in black shales could indicate either a $BaSO_4$ influence, either a paleo-hydrothermal event (paleo vent or VMS) in these Cambrian strata.

In the Eastern part of the Pyrenees, similar lithologies host Zn, Pb, Cd, Ba, F mineralisations in dolomitic shales with locallly, albitic metavolcanics. If various authors agree on the stratabound character of these mineralisations (Bois J.P., 1973; Pouit G., 1976) some argue about a distal volcanic contribution according to the commonly observed interlayered metavolcanics (sedex type of Pouit G., 1989). Several younger hydrothermal overprint related to the hercynian folding and late granitic intrusives are also common in these areas but, the regional distribution of the Pb-Zn anomalies delineated after the National geochemical survey gives a strong support to an early stratabound heritage in these areas (Pouit G., 1993; Orgeval J.J. *et al.*,1997; Moyroud *et al.*, 1993).

The Ordovician period records also Pb-Zn Ba mineralisation that have been exploited in the Pyrenees (Pierrefite-Nestalas and Bentaillou). These are also hosted in black shales associated with shallow turbidites and carbonates (« calcaire troué de l'Asghill »). A bimodal volcanism has been mapped nearby, so a sedex-volcex type origin is favoured in a rifted basin model (Bois J.P., 1973; Pouit G., 1979).

In the Devonian period of the Pyrenees mountains, various strata-bound Pb-Zn-Ba mineralisations (Nerbiou, Arrens, Carboire…) are also recorded in very similar sedimentological context as the previous Ordovician period. However, basin depth variations seems to be more important and the occurrences are smaller but their lateral extensions (base metals anomalies over 10 Km) remains important.

A raw estimate of the *in situ* low grade base metal resources in the Pyrenees is about 10 Mt averaging 6-7% Pb+Zn.

During the continental rift sediments deposition in younger carboniferous basin, only U mineralisation (St. Hyppolite) is associated with lacustrine bituminous shales in the Vosges mountain (Moreau *et al.*, 1980) and some epigenetic gold mineralisation in the Visean basin of Viges (Bonnemaison et Braux, 1987).

Like in the Kupferschiefer, the permo-triassic unconformity is a very important metallogenic event in the surrounding areas of the hercynian folded shield. Bitumen deposits in small endoreic basins are known in the NE area of Massif central (Epinac) and U mineralisation in the Lodève shallow autunian grey marls borderland basin (17Kt U metal, Chateauneuf J.J., 1987; Béziat *et al.*, 1995).

Various Pb-Zn-Ag mineralisation and F, Ba stratabound mineralisation (Morvan area, Chaillac deposit) are connected either with red bed type unconformity sandstone deposits (Largentière deposit) or base metals associated marl mineralisation in shallow triassic evaporitic basin invading a pre-karstified cambrian dolomite horst (Les Malines deposit, Verraes J., 1980) attributed to MVT type deposit (Disnar J., 1996).

The black, organic rich sediments of the Middle-Upper Jurassic boundary are host to REE mineralisation in the Dauphiné basin and similar low grade P, REE and U mineralisation has been described in the upper part of the lower Cretaceous calcareous epicontinental sea of the same area (Laval *et al.*, 1990).

It is also worth to mention that in the late Eocene of the Paris basin, small U, Cu, S enrichment have been described in connection with local organic rich layers in fluviatile conglomerates (Meunier J.D. *et al.*, 1992).

2.4. BLACK SHALE HOSTED MINERALISATIONS IN AFRICA AND SAUDI-ARABIA (TABLE 2)

Beside the famous Copper belt in Shaba-Zambia, various stratabound mineralisations have been discovered in Northern,Western and Eastern Africa.

In the Archean era, the primitive crust was very thin and a lot of mafic primitive basalt erupted in rifted areas surrounded by very large epicontinental seas. Weathering of these balsaltic Komatiites (greenstone belt) supplied Fe, Co, Ni, Cr to the sediments. Upwelling favoured the development of high oxidized waters in the upper oceanic layers and the subsequent precipitation of the banded ironstone (BIF) sequences. However, in marginal basin, anoxic conditions prevailed and black muddy pyritic layers were deposited. This is the case in the Moto area of RDC, where a very important gold mineralisation is associated with disseminated pyrite, arsenopyrite mineralisation (Lavreau J., 1980) in a BIF-black shale lithology.

In the Neoproterozoic era, various Ni-Mo-Fe mineralisations (Jebel Mardah, Wadi Qatan gossan) and polymetallic base and precious metals (Ar Rjum, Shaib Lamisah) are known in black shales deposited in rifted basins of the Hulayafah group of Saudi Arabia (Salpeteur I, 1985; Nehlig P., 1999), with very commonly associated metavolcanics.

Similarly, but in deeper basal slope tubiditic sediments, stratabound tungsten, tin and P, REE (grey monazite) mineralisations are well known in the Kibaran metasediments of the East African mobile belt including Uganda, Rwanda, Burundi. Disseminated scheelite and wolframite in black graphitic shales have been described early in 1960 by de Magnée *et al.* and their stratabound regional extension was further confirmed by the UNDP geochemical surveys conducted in the seventies (Salpeteur, 1981). In the same lithologies (turbidite sanstone and black pyritic shales), grey monazite enriched in europium has been later discovered (Laval *et al.*, 1993).

At the Upper Proterozoic-lower Cambrian boundary, various stratabound Cu (U) mineralisations are known (red bed type), for example in the “série pourprée“ of Central Sahara (Caby R., 1971).

In the Cambrian period, numerous stratabound mineralisations are known, related to black shale sediments with dolomitic Mn carbonates indicating a shallow continental margin context. Disseminated Cu, or Cu-Mn mineralisations have been described in Jordan (Wadi Araba) for example (Bigot M., 1981) and in Morocco in the Tizirit and Takhamt areas (Agard J. *et al.*, 1952).

In the same country, a carboniferous skarn type deposit of graphite: Sidi Bou Othmane, is clearly related to the contact between a younger granite and black shales associated with carbonates.

In the Rhamani occurrence, SW of Béchar in Western Algeria (Fuchs *et al.*, 1996), Cu (up to 2%) and silver (up to 30 ppm) is enriched with Pb, Zn, V, Cr, Ni, V, Co in paleochannel of Cambrian sandstones deposited on Pan-African volcanites and intrusives.

Going up in the time stratigraphic scale, various Cu, Zn and Cu, U mineralisations are related to the ***Permo-Triassic*** unconformity:

- in Saudi Arabia: the Cu-Zn mineralisation in sandstone, organic rich shales of the Khuff formation at As Sfarat;
- in Maroc: the Cu, U disseminated mineralisation in black marls and coal seams at Bigoudine, Boulbaz in the Haut Atlas mountain.

In the Western Central Sahara (Algeria), a stratabound Cu mineralisation is hosted in paleochannels near a lagoonal shoreline basin at the boundary between Upper Jurassic and lower Cretaceous (Aïn Sefra prospect, Kolli O., 1998).

The lower Cretaceous of Northern Algeria is also a very important period of Pb-Zn deposition in relationship with euxinic black shales and dolomites (e.g. the Boudkhema Pb-Zn deposit with bituminous and pyritic shales and dolomites (Thouari B., 1991), and the Kupferschiefer type Cu, Pb, Zn deposit of Kef Semmah (with more than 100,000 t metal resources).

In the ***late Cretaceous*** of Marocco, a bitumen deposit is known in black carbonates at Mogador.

3. Conclusion: where to invest for future mineral resources discoveries?

This very short review of the major black shales hosted mineralisations in the world shows clearly where to focus the future exploration work to enhance the base metal production, a urgent need for the new developing countries like India and China.

Copper (Ag, Pb, Zn) Kupferschiefer type and red bed are probably one of the major resources woldwide, particularly in central Africa, Asia and Central Europa.

Pb-Zn mineralisations of sedex type are very promising in Canada, Australia, Kazaktskan, Iran and Alaska.

Sedex type polymetallic Cu, Pb, Zn, Ag ore are widespread: Canada (Abitibi), Australia and Europe: the Iberian Pyrite belt.

The very strong increase of recent base metal and precious metal due to market demand open new horizons for mineral exploration:

- reassessment of the *in situ* reserves according to these new figures;
- in ancient district, like in Europe, the development of new sustainable technologies for extracting and beneficiate the low grade ores is a key factor to make easier the political acceptance of new mine development. For that objective, bioleaching processes are very interesting because they are low energy process, low CO_2 emitting;
- in new area open to exploration, particularly in Africa, and Australia the development of new geophysical and geochemical tools for the delineation of sedex deposits associated with black graphitic shales will be a key point, notably in deeply weathered areas with thick regolith cover. Hydrogeochemical and biogeochemical methods will be recommended in these areas.

Sampling and chemical analysis of past dump mines for precious (Au, PGE) and rare elements (Ge, Tl, Te, Cd,...) may also open new economic resources, from surface material ,easy to process. Very often, indeed, these elements (gold and PGE) were not analysed or analysed by unreliable methods.

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