Traceability of Base Metals Ores Using Mineralogical and Microtextural Parameters

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Abstract. The demand in mineral resources is increasing rapidly, but there is a lack of transparency in the trade of concentrates raw mineral materials because of speculation and involvement in the finance of armed conflicts. Because of the distance between primary extraction and the final production sites it is difficult to check the origin of these products. An identity card is required for mineral commodities, so that trading in the industry can be verified and the traceability of concentrates ensured. This problem may be considered as an inversion process: studying the products sold to identify the original ore. The discriminant parameters are mineralogical composition, identification of textural microfacies of the target minerals (pyrite, sphalerite and chalcopyrite), "pseudo-paragenetic sequence", and the contents and distributions of minor elements of target minerals. Statistical tests are used to compare the chemical composition of three target minerals. The application to Volcanic Massive Sulphide ore deposits shows that it is possible to distinguish target minerals between ore deposits in the Iberian Pyrite Belt province and from the Urals province using the selected characteristics. Ore deposits from different provinces may be discriminated using the identity cards, as well as different deposits in the same province.

Keywords. Traceability, identity card, target minerals, Volcanic Massive Sulphide

1 Introduction

Metal mining and marketing have an impact on the economy, society (negative or positive) and the environment. The metal market is a major factor in economic development. This is a major concern in developed countries, which are anxious to secure supplies in view of the strong demand for mobile phones, digital tablets, solar panels, batteries, … It is also growing concern for the "citizen-consumer", who needs to be sure that these items have not been produced contrary to his or her ethical or moral values. To avoid parallel markets of certain mineral resources, solutions have been proposed to locate the extraction sites of these resources for diamond via Kimberley Process (www.kimberleyprocess .com), for emeralds (Giuliani et al. 1998a, b), sapphire (Giuliani et al. 2005), ruby (Giuliani et al. 2005) and "coltan" (Gäbler et al. 2011, 2013; Melcher et al. 2008a, b, 2013; Savu-Krohn et al. 2011). A chain of control and certification has been set up by the diamond producer countries under the supervision of international experts. All diamonds must be accompanied by a certificate of origin (Kimberley process). The development of the $^{18}O/^{16}O$ isotopic identity card for emeralds helps to distinguish the source of a large number of high quality emeralds (Giuliani et al. 1998b). Fingerprints of coltan can be determined to find the place of origin of the mineral (Gäbler et al. 2011, 2013; Melcher et al. 2008a, b, 2013; Savu-Krohn et al. 2011). A similar need sometimes arises during mineral processing when multiple sources are used. The Luossavaara Kiirunavaara AB-plant (LKAB) in Sweden produces iron ore from Kiruna and Malmberget mines. These minerals are mixed. Iron oxides of Malmberget are different from those from Kiruna (coarser-grained, different types of joints of grains,…) (Oghazi et al. 2009) and behave differently during treatment. To clarify the importance of the source of the ore on the difficulties observed during treatment, a traceability study was attempted (Kvarnström and Oghazi 2008; Machault et al. 2013). However, there are very few studies on the tracea-bility of base metals. These metals are mainly used in industrial sectors and the evolution of their price depends to a large extent of the growth of the global economy.

The aim of this work is to establish parameters to be included in an identity card for each deposit, which will allow it to be discriminated from other deposits. This requires a method of traceability with low analytical cost, using easily accessible techniques mineralogical and microtextural characterization allow an unique signature to be established for each ore and each deposit studied (Machault et al. 2014). The ultimate objective of this study, which is part of a global programme to create an ore identity card, is the establishment of a database incorporating the characteristics of each deposit and each mineral processing plant (Machault et al. 2013). Periodic reviews of the database will ensure monitoring of traceability parameters over time.

2 An approach for the traceability of base metals in Volcanogenic Massive Sulphide

Traceability refers to the ability to track a product at different stages of its production, its transformation and its commercialization from the source of the product up to the end of its life, including possible recycling. It must allow the origin of the source concentrate to be determinated at each of these stages. Procedures to achieve a good traceability are governed by standards and/or national or international control organizations. In the case of mineral resources, traceability consists of associating a commodity to the mine from which it has been extracted. For base metals, the bulk ores bear mineralogical differences, which may provide characteristics to track the bulk ore. These characteristics may "survive" during mineral processing, so that we can find "footprints" of bulk ore in the concentrate. Hence metal ore traceability implies that, in the ideal case, for each province and also for each deposit, valuable mineral have an unique signature. The characteristics that can be observed in concentrated at grain-scale (mineralogical composition, chemical composition of the phases, microtexture) will depend on (1) the process of formation of the mineralization and its post-deposit history (type of ore deposit) and (2) the local geological setting including the host rocks (regional setting which is sometimes poorly understood). The concentrate is derived not only from natural processes, but also from industrial processes, which must be taken into account. In addition to the processing difficulties like mixing of bulk ores (Kvarnström and Oghazi 2008) we cannot exclude variations over time in the operation of a given mineralurgical plant. Finally, within a given mine, the nature of the bulk ore may vary over time as the exploitation of the site progresses. Hence, the signature of the concentrate depends on the characteristics of useful minerals, the type of deposit, the metallogenic province and the treatment the ore is subjected to. This signature is rigorously established only at a given moment of observation. In the case of base metals, traceability is the ability to find, for a given concentrate, the trace of all manufacturing stages (mineral processing) and the provenance (deposit) of all its components. The traceability of a metal concentrate would be possible to determine: (1) the province, the district, the deposit and bulk ore from which it was extracted; (2) the mining company; (3) the different places where it has been stored; (4) the manipulations and the equipment used in its manufacturing; (5) its transportation to its final destination; (6) its end-use; (7) its recycling; (8) its possible reutilization.

3 Methodology of traceability in the case of base metals in Volcanogenic Massive Sulphide

Figure 1 is a flowchart illustrating the methodological procedure followed in this study. We have selected the samples we considered as the most representative ones according to their texture and mineralogical compositions. Variability within a deposit can be significant. Comparisons are only valid at the time of sampling. That raises the problem of feasibility. The bulk ore characterization was conducted using a metallurgical microscope, a scanning electron microscope (SEM) and an electron microprobe. These techniques are used to study the textures, mineralogical composition, and chemistry of the minerals. Statistical analyses are then performed on the individual mineral phases to finally obtain an identity card of each studied ore (Fig. 1). During observations, a particular attention has been paid to: the identification of characteristics microfacies, the presence of trace minerals and finally the minor elements contained in the "target minerals". The "target minerals" are: (1) Pyrite for its ubiquity in the studied bulk ore deposits which allows to compare bulk ores from different mines; (2) Sphalerite, which can incorporate into its structure a large number of potentially valuable elements (Ge, Ag, In, Ga) or non-valuable elements (Fe, Cd, Hg, Mn, Sb); (3) Chalcopyrite that is repeatedly found associated with pyrite and sphalerite.

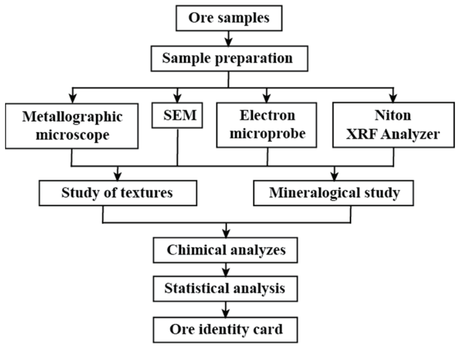

Figure 1. Organization chart of the method used for establishing identity cards

4 Presentation of the metallogenic context of the two studied provinces

We limit this study to a single type of deposit: Volcanogenic Massive Sulphide (VMS) deposits in order to consider a single metallogenic process. We chose to study bulk ores of nine deposits from two different provinces: the South-Iberian province and the Urals province.

5 Results

Bulk ores of deposits from the South-Iberian and Urals provinces have been characterized. It should be noted again that the observations and the measured parameters and therefore the ore comparisons, have been inferred only from the samples collected so that the conclusions are therefore only valid for the set of studied samples. In consequence such a traceability study requires to be updated periodically. Results will be expressed in qualitative or semi-quantitative form. The different parameters of the identity card (Fig. 2) from bulk ore of each ore deposit allow us to differentiate deposits from a single province and also to distinguish different provinces. We can evaluate the effect of regional heritage on the mineralogical composition and the chemistry of the bulk ore minerals.

The parameters of the identity card are: the mineralogical composition in the form of relative abundance, the microtextures of target minerals (the following provides a description as well as a tentative evolution in time of these microtextures, Fig. 3), the pseudo-paragenetic succession, the chemical composition and the distribution of target minerals and when possible, the "memory loss" parameter which is a characteristic of mineral processing (Machault et al. 2013).

6 Discussion

6.1. Appropriateness of the methodological approach used

We have established an original traceability method for base metals. This traceability method can be used to obtain a comprehensive identity card of the deposits. Mineral chemistry is considered to be the most promising tool for provenance analyses. The comparative results obtained from the statistical tests (Kolmogorov Smirnov and Colin White) are roughly similar, regardless of the elements or considered target minerals. Therefore the Colin White test appears to be the most effective test to compare the minor elements content in ore, since (1) it necessitates fewer individual data; (2) it is not influenced by the value of individual data and (3) it is not sensitive to element distribution heterogeneity.

6.2. Utilisation of discriminative parameters for ore traceability

This study contributes to the establishment of various parameters that differ from a deposit or a province to another. Some of these parameters are discriminative but a single characteristic is generally not enough to obtain a successful discrimination of all the studied deposits. It is therefore necessary to combine parameters, as provided in the ore identity card to get a satisfactory result. In our case, there is not any unique parameter that could provide a satisfactory differentiation between the nine deposits. A flow chart using logical criteria to discriminate ore deposits can also be established (Melcher et al. 2008a, b), but it requires a hierarchy of the considered parameters or criteria. At this stage of method development, the establishment of a hierarchy between the retained characteristics, valid for all VMS deposits, seems premature. However we are able to produce flow charts for each parameter showing their discriminative or satisfactory features (Fig. 4).

Deposit		Neves Corvo
Mineralogical composition	AA	Pyrite
	A	Cassiterite, Sphalerite, Chalcopyrite, Tetrahedrite, Galena
	F	Arsenopyrite, Stannite, Kesterite, Mawsonite
	R	Pyrrhotite, Bi minerals, Meneghinite, Bournonite, Co minerals, Cubanite, Enargite, Nekrasovite, Gudmundite, Stromeyerite, Electrum, Coloradoite, Roquesite, Clausthalite, Naumannite
Microtextures	Pyrite	euhedrale, colloform, agglomerate, framboidal
	Sphalerite	euhedral without inclusions, euhedral with growth bands, in cracks
	Chalcopyrite	massive, isolated grains or in cracks
Pseudo-paragenetic sequence		1) Framboidal pyrites, chalcopyrite and sphalérite cristallization 2) Colloform pyrites cristallization 3) Agglomerates of pyrites cristallization 4) Euhedral pyrites cristallization 5) Fracturing 6) Chalcopyrite and sphalerite cristallization
Minor elements	Pyrite	Pb, Cu, As, Co, Zn
	Sphalerite	In, Se, Fe, Cd, Cu, Hg
	Chalcopyrite	Pb, Ag, As, Sn
Elements distribution	Pyrite	irregular distribution : As very irregular distribution : Pb, Cu, Co extremely irregular distribution : Zn
	Sphalerite	irregular distribution : Fe, Cu very irregular distribution : In, Se ectremely irregular distribution : Cd, Hg
	Chalcopyrite	extremely irregular distribution : Pb, Ag, As, Sn
Experimental memory loss	PMexp(Fe) =	36 min
	PMexp(Zn) =	3408 min
	PMexp(Cu) =	14146 min

Figure 2. Identity card of Neves Corvo. Experimental memory loss refers to a characteristic of the mineral processing (Machault et al. 2013).

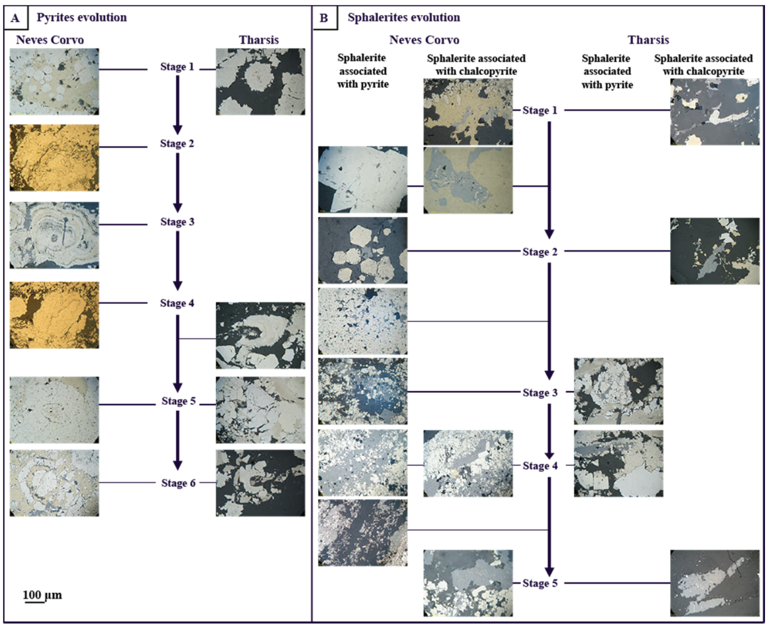

Figure 3. A. Framboidal pyrites evolution from Neves Corvo and Tharsis deposits (pictures taken through a metallographic microscope) stage 1-framboidal pyrite, stage 2-crusting–fibro-radial structure, stage 3-crusting with chalcopyrite– coprecipitation pyrite-chalcopyrite, stage 4-disappearance of spherulites in the inner part, stage 5-cristallization continues– growth of large crystals, stage 6-brecciation–deposition of other sulphides; **B.** Sphalerites associated with pyrite and chalcopyrite from Neves Corvo and Tharsis bulk ore (pictures taken through a metallographic microscope) stage 1- sphalerite, chalcopyrite, pyrite (micro-crusting), stage 2-the pyrire growth, stage 3-microfracturing–filling by sphalerite, stage 4-filling continues, stage 5-chalcopyrite inclusions in sphalerite. The scale shown is valid throughout the figure.

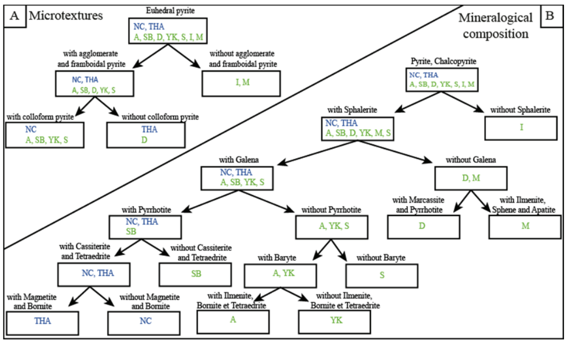

Figure 4. Tree parameters: **A.** microtextures to differentiate deposits; **B.** mineralogical composition. Deposits are: NC: Neves Corvo, THA: Tharsis, A: Alexandrinka, SB: Sibay, D: Dergamish, YK: Yaman Kasy, S: Safyanovka, I: Ivanovka, M: Mauk.

7. Conclusions

This study has contributed to: (1) establish nine ore identity cards for two metallogenic provinces: Neves Corvo and Tharsis in South Iberian province; Alexandrinka, Dergamish, Yaman Kasy, Safyanovka, Ivanovka, Mauk and Sibay in the Urals province; (2) discriminate the bulk ores from deposits in a given province and the bulk ores between distinct provinces; (3) reveal pyrite as a characteristic microtexture parameter for performing bulk ore traceability. This parameter is not influenced by the age of the deposit, the tectonics zone where the deposit is located and the nature of the rocks hosting the deposit.

This method forms the basis of a necessary protocol to establish base metals ore traceability. For this, to achieve the monitoring of ore parameters, it is necessary throughout the life of a mine, including costs for analyses and competent operators. Such studies will also contribute to increase the amount of data usuable for understanding the genesis of an ore deposit and the metallogenic processes involved. The deposits are unpredictable by nature. It is difficult to take into account the internal variability of the deposit. This leads to the necessity to ensure a continuous watch, which also provides a better understanding of deposits in particular on valuable low grade elements. The industrial and academic communities will also benefit from traceability monitoring, which will provide regular quantitative data throughout mineral processing potentially improving its efficiency. Finally, the establishment of traceability methods based on minor element contents will have an effect on mineral resource management especially for strategic (critical and valuable) elements which are sensitive to market fluctuations.

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