

# Platinum-Group Element Abundances in Pyrite from the Main Sulfide Zone, Great Dyke, Zimbabwe

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**Abstract.** The Main Sulfide Zone (MSZ) of the Great Dyke of Zimbabwe hosts the world's second largest reserve of platinum-group elements (PGE). It comprises a sulfide assemblage made up of pyrrhotite, pentlandite, chalcopyrite and minor pyrite. Several studies have highlighted that pyrite can be an important carrier of PGE and therefore, we have measured PGE and other trace element abundances in pyrite of the MSZ from the Hartley, Ngezi, Unki and Mimosa mines by LA-ICP-MS. Pyrite occurs as individual euhedral or subhedral grains or clusters of crystals mostly within chalcopyrite and pentlandite (occasionally in form of symplectitic intergrowths) and is generally absent within pyrrhotite. At Hartley and Ngezi, pyrite contains higher Os, Ir, Ru, Rh and Pt contents than co-existing pyrrhotite, pentlandite and chalcopyrite from the same sulfide aggregate. In contrast, at Mimosa and Unki, PGE values in pyrite are low and similar to co-existing sulfides. Pentlandite is always the main sulfide carrying Pd. Although the origin of pyrite in this type of mineralization is commonly attributed to the activity of hydrothermal fluids, we suggest that pyrite may have formed by late, low temperature (< 300°C) decomposition of residual Ni-rich mss.

**Keywords.** Pyrite, sulfides, platinum-group elements, LA-ICP-MS, Great Dyke, Zimbabwe

## 1 Introduction

Pyrite is a relatively common minor sulfide in Ni-Cu-PGE magmatic sulfide deposits, however its origin is poorly understood. Experimental studies show that pyrite may form by decomposition of S-rich monosulfide solid solution (mss) at temperatures below 700°C (Naldrett et al. 1967; Craig 1973). However, this process does not seem to be common because most natural sulfide melts do not contain the required amount of sulfur. Alternatively, it has been proposed that pyrite forms as result of partial to total replacement of pre-existing sulfides (mainly, pyrrhotite) due to the activity of late magmatic, hydrothermal and/or metamorphic fluids (e.g., Djon and Barnes 2012; Piña et al. 2013; Smith et

al. 2014; Holwell et al. 2014; Vukmanovic et al. 2014).

Recently, several studies indicate that pyrite from Ni-Cu-(PGE) magmatic sulfide deposits can host significant amounts of PGE (e.g., Oberthür et al. 1997; Dare et al. 2011; Djon and Barnes 2012; Piña et al. 2013; Smith et al. 2014). These studies show that pyrite contains similar amounts of Os, Ir, Ru and Rh to coexisting pyrrhotite and pentlandite, and is the only base metal sulfide hosting significant amounts of Pt. Detection of trace amounts of Pt in pyrite is especially relevant because Pt is typically not present in the other base metal sulfides but occurs as discrete platinum-group minerals (PGM, e.g., sperrylite PtAs<sub>2</sub>).

In this contribution, we report new PGE, Au, Ag, Co, Se, As, Te, Bi and Sb abundances in pyrite from the Main Sulfide Zone in four mines of the Great Dyke of Zimbabwe. In addition to assessing the role of pyrite as carrier of PGE in this mineralization, we use trace element contents and textures of pyrite to discuss the possible mechanisms involving in its formation.

## 2 Pyrite from the Great Dyke of Zimbabwe

The Great Dyke of Zimbabwe (2575.4 ± 0.7 Ma, Oberthür et al. 2002) represents the world's second largest reserve of PGE after Bushveld Complex in South Africa (Oberthür 2011). It is a 550 km long and 4 to 11 km wide, linear, mafic and ultramafic layered intrusion emplaced into Archean granites and greenstone belts of the Zimbabwe craton. The Great Dyke shows a well-defined igneous stratigraphy divided into a lower Ultramafic Sequence (dunite, harzburgite and pyroxenite) and an upper Mafic Sequence (gabbro and norite) (Wilson and Prendergast 1989). The economic PGE mineralization is restricted to disseminations of intercumulus sulfides (from 0.1 to 10 vol. %) in the several meters-thick Main Sulfide Zone (MSZ) situated in pyroxenites some meters below the transition from the Ultramafic to the Mafic Sequence. Based on the degree of sulfide mineralization and PGE ratios, the MSZ is

divided in a basal PGE-rich subzone that slightly overlaps with an overlying base metal sulfide (BMS)-rich subzone.

Pyrite mainly occurs in the upper part of the PGE-rich subzone and in the BMS-rich subzone of the MSZ. Sulfides occur as disseminations of polymineralic aggregates interstitial to silicates. These aggregates are made up of pyrrhotite, equal amounts of pentlandite and chalcopyrite and minor pyrite. Pentlandite mostly forms coarse grains and minor flame-shaped exsolution lamellae in pyrrhotite, and chalcopyrite typically occurs along the peripheries of sulfide aggregates or as isolated monomineralic grains. According to Oberthür (2011), the presence of pyrite indicates increasing  $fS_2$  up sequence in the MSZ.

## 2.1 Pyrite textures

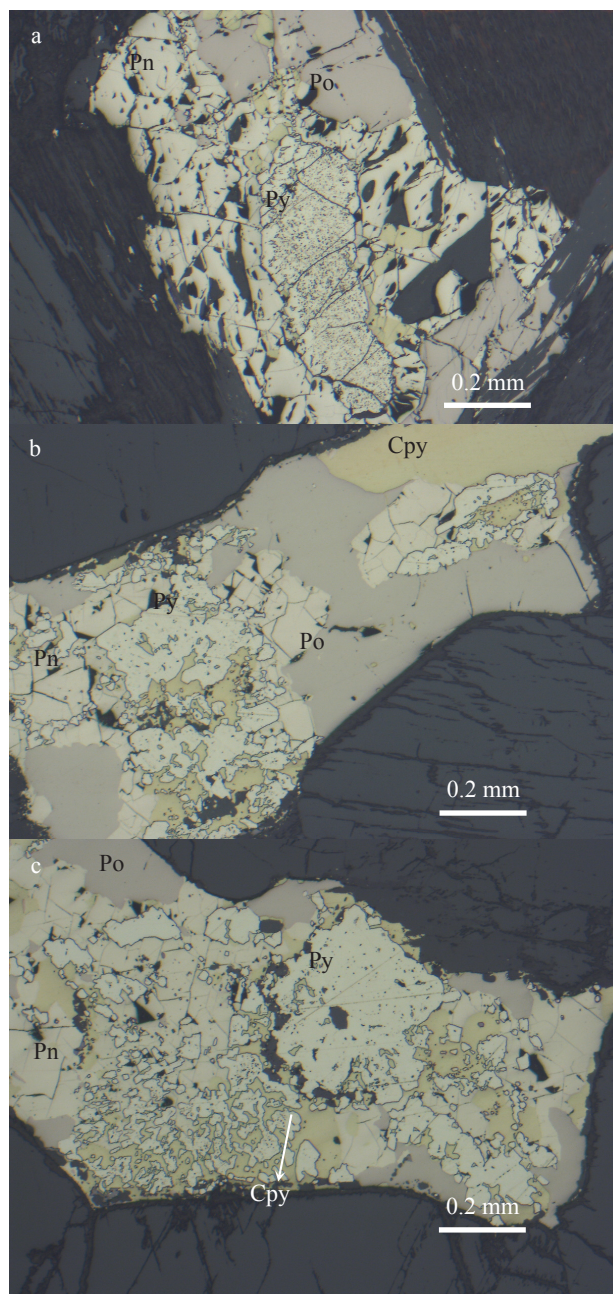
The studied samples come from the Hartley, Ngezi, Unki and Mimosa mines (located from north to south along the Great Dyke). Samples are located just above the Pt-peak of the MSZ. At Unki and Mimosa, pyrite forms clusters of small individual euhedral to subhedral crystals within chalcopyrite, pentlandite and, to a lesser extent, pyrrhotite (Fig. 1a). At Hartley and Ngezi, pyrite forms small individual grains within pentlandite and chalcopyrite (Fig. 1b). Locally, these grains appear to have coalesced during growth, resulting in poikiloblastic aggregates that enclose chalcopyrite and pentlandite grains. Some pyrite grains seem to form symplectitic intergrowths with chalcopyrite and pentlandite (Fig. 1c).

## 2.2 PGE and other trace element abundances

Trace elements (PGE, Au, Ag, Re, Co, Se, As, Te, Bi and Sb) were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at LabMaTer, Université du Québec à Chicoutimi (UQAC), Canada, using a Resonetics Resolution 193 nm Excimer laser with a M-50 ablation cell and an Agilent 7,700x quadrupole mass spectrometer, and following the analytical protocol of Piña et al. (2013).

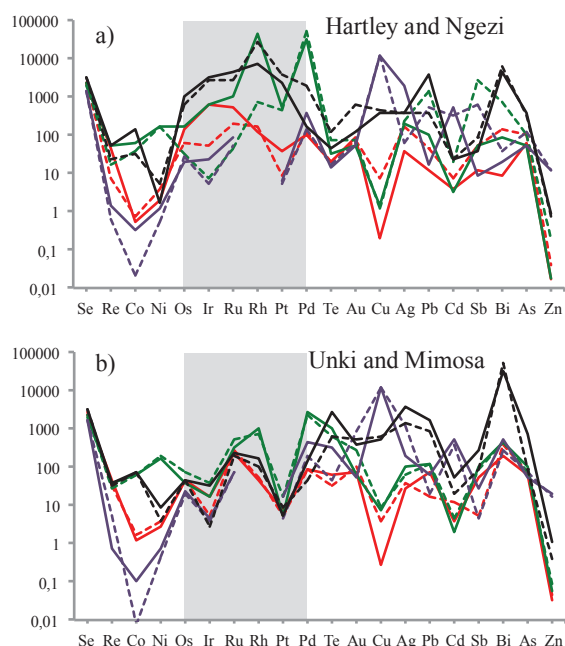
There are notable differences between trace element abundances of pyrite from Hartley and Ngezi mines (located in the North Chamber of the Great Dyke) and pyrite from Mimosa and Unki mines (located in the South Chamber) (Fig. 2). At Hartley and Ngezi, pyrite is relatively rich in PGE with contents ranging from 0.3 to 99 ppm Pt, 0.7 to 61.1 ppm Rh (both Pt and Rh contents are typically > 10 ppm), 1.2 to 47.1 ppm Ru, 0.1 to 7.8 ppm Os and 1.0 to 20.2 ppm Ir. These values are higher than those in co-existing pyrrhotite, pentlandite and chalcopyrite (Fig. 2a). PGE abundances in pyrite from Hartley and Ngezi mines are in agreement with previous contents reported by Oberthür et al. (1997) from the Hartley mine using micro-pixe (40 ppm Ru, 10 ppm Rh, 9 ppm Pd and 233 ppm Pt on average). At Mimosa and Unki mines, PGE concentrations in pyrite are low (< 0.11 ppm Pt, < 0.34 ppm Rh, < 2.5 ppm Ru, < 0.37 ppm Ir and < 0.40 ppm Os) and similar to those in pyrrhotite and pentlandite (Fig. 2b). Palladium in pyrite is commonly below 2 ppm in all studied mines except in one sample from Ngezi which contained up to 60.4 ppm

Pd. Osmium, Ir, Ru, Rh and Pt are positively correlated each other, whereas Pd poorly correlates with all other PGE. In contrast to the PGE, Au, Te, Ag, Sb and Bi contents are higher in pyrite from Mimosa and Unki than in pyrite from Hartley and Ngezi (Fig. 2). Gold is positively correlated with Te and Bi. In the pyrite samples from Hartley and Ngezi, Pt correlates with Au.



**Figure 1.** Representative photomicrographs in reflected-light, showing pyrite from the Mimosa (a), Ngezi (b) and Hartley (c) mines. Pyrite (Py) occurs mostly within pentlandite (Pn) and chalcopyrite (Cpy) and not within pyrrhotite (Po).

Trace element distribution between co-existing pyrrhotite, pentlandite, chalcopyrite and pyrite in a single polymineralic aggregate from Ngezi mine is shown in Figure 3. Platinum, Os, Ir, Ru, Rh, Co, Se and Bi are preferentially concentrated in pyrite (as also indicated by the primitive mantle-normalized profiles of Figure 2), whereas Pd prefers pentlandite.



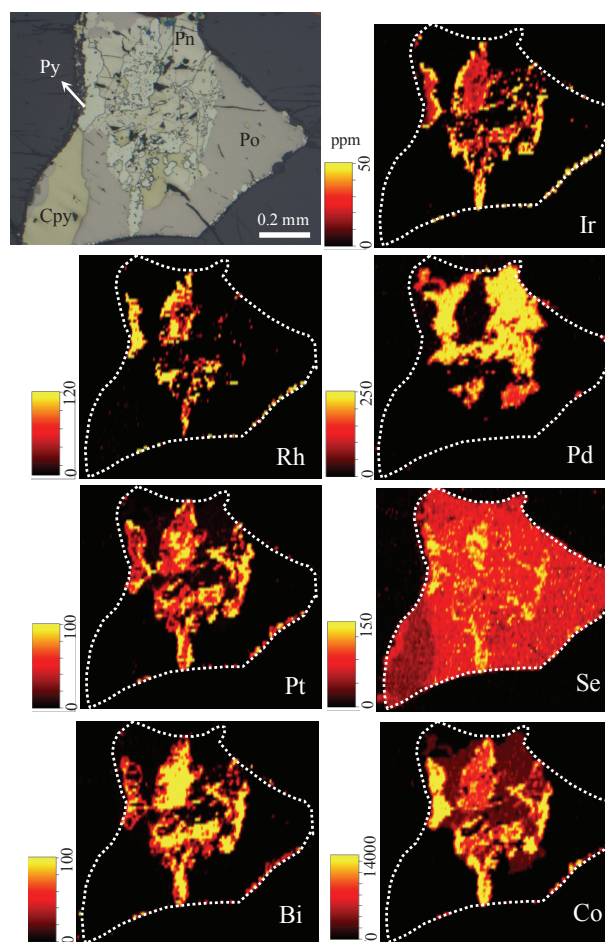
**Figure 2.** Primitive mantle-normalized trace element average patterns as determined by LA-ICP-MS for pyrite (black), pyrrhotite (red), pentlandite (green) and chalcopyrite (violet) from: a) Hartley (solid lines) and Ngezi (dashed lines), and b) Unki (solid lines) and Mimosa (dashed lines). Elements are ordered from left to right according to decreasing mss compatibility.

### 3 Discussion

#### 3.1 Mechanisms of pyrite formation

The formation of pyrite in Ni-Cu-(PGE) magmatic sulfide deposits is commonly attributed to the activity of late magmatic or hydrothermal fluids that trigger the replacement of pyrrhotite by pyrite due to addition of S (i.e., increasing  $fS_2$ ) or removal of Fe (Oberthür 2011; Djon and Barnes 2012; Piña et al. 2013; Smith et al. 2014; Holwell et al. 2014; Duran et al. 2014). Although previous studies described that pyrite in the MSZ of the Great Dyke predominantly occurs within pyrrhotite (Oberthür et al. 2003) as observed in other magmatic sulfide ore deposits (e.g., McCreedy in Sudbury, Canada, Dare et al. 2011; Aguablanca, Spain, Piña et al. 2013), in our study, pyrite is typically closely associated with pentlandite and chalcopyrite and generally absent in pyrrhotite. This feature is relevant for the origin of pyrite. If hydrothermal fluids had played some role in the formation of pyrite, the alteration mechanism should successfully explain the selective replacement of pentlandite and chalcopyrite (not pyrrhotite) by pyrite, since secondary pyrite typically forms at the expense of pyrrhotite. In addition, some studies have suggested that secondary pyrite inherits PGE contents from the replaced sulfides (Dare et al. 2011; Piña et al. 2013; Smith et al. 2014). Pyrite within chalcopyrite has relatively high Os, Ir, Ru and Rh contents (Fig. 4). However, host chalcopyrite does not contain Os, Ir or Ru (typically below the detection limit) and thus these elements could not be inherited directly from chalcopyrite. Therefore, we suggest that some other mechanism different to

hydrothermal alteration must be considered to explain the pyrite formation.

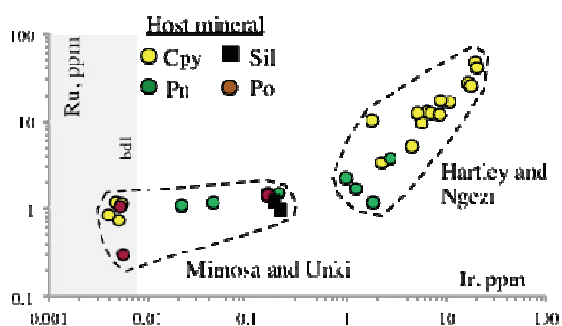


**Figure 3.** Trace element maps of coexisting pyrrhotite, pentlandite, chalcopyrite and pyrite from Ngezi mine. Mapping was carried out by line scans ablating the whole aggregate. The maps show semi-quantitative values. All elements shown are preferentially concentrated into pyrite with the exception of Pd that concentrates in pentlandite. Osmium and Ru (not shown) follow the same distribution as Ir and Rh.

The pyrite textures observed in the samples from Hartley and Ngezi mines are quite similar to those described for pyrites from the Keivitsansarvi Ni-Cu-PGE sulfide deposit in northern Finland (Gervilla and Kojonen 2002), from orogenic peridotites of the French Pyrenees (Lorand and Alard 2011) and from the UG-2 reef in the Bushveld Complex, South Africa (Naldrett et al. 2009). In all these cases, pyrite mainly occurs associated with pentlandite and/or chalcopyrite forming locally fine symplectitic intergrowths. Experimental studies in the system Fe-Ni-S (Craig 1973; Misra and Fleet 1973) demonstrate pyrite only coexists with Ni-rich pentlandite at temperatures below 300-250°C. In the UG-2 reef, Naldrett et al. (2009) indicate that loss of Fe to the chromite from sulfides on cooling, accompanied by significant rise in  $fS_2$ , caused the formation of pyrite-pentlandite assemblages by decomposition of Ni-rich mss at temperatures below 250°C. At Keivitsansarvi, the reaction of Fe-rich vaesite ( $NiS_2$ ) with the coexisting mss on cooling gave rise to a mss richer in Ni from which pyrite and pentlandite ultimately formed. In contrast,

Lorand and Alard (2011) suggest that the formation of pyrite intergrowth with pentlandite and chalcopyrite was due to subsolidus sulfurization processes that increased the  $fS_2$  of the system. They suggest that pentlandite may be first sulfurized into mss at temperatures above 300°C and then the mss broke down into pentlandite + pyrite symplectites upon cooling below 300°C.

It is suggested here that in the MSZ, pyrite may form during low-temperature equilibration of Ni-rich mss coexisting with intermediate solid solution (iss). Pentlandite composition is closely related to sulfides with which the pentlandite is associated. The tentative <135°C Fe-Ni-S phase diagram indicates that pentlandite coexisting with pyrite is relatively rich in Ni (Naldrett et al. 2009). Pentlandite in the pentlandite-pyrite assemblages from the Great Dyke has Fe:(Fe+Ni) wt. % ratios ranging from 0.46 to 0.49. These composition ranges are similar to those observed in pentlandite equilibrated with pyrite and pyrrhotite in the Marbridge deposit, Quebec (Graterol and Naldrett 1971).



**Figure 4.** Ruthenium versus Ir contents for pyrite from the Great Dyke, Zimbabwe.

### 3.2 Pyrite as sulfide hosting PGE

Previous studies have indicated that most Pd and Rh are hosted in pentlandite, whereas Pt is dominantly present in form of PGM in the MSZ (Oberthür et al. 2003). Our results indicate that among all base metal sulfides, pyrite is individually the sulfide phase hosting the highest contents of PGE (with the exception of Pd that is preferentially concentrated in pentlandite). Mass balance calculation to determine the percentage of each PGE present in each sulfide has not been carried out to date and, thus, the importance of pyrite as carrier of PGE in the mineralization is not quantified. Nevertheless, since most of PGE appear show higher preference for pyrite when present (Fig. 3), we envisage that pyrite may account for significant amounts of PGE (particularly, Rh and Pt) in those zones with the highest modal abundances of pyrite.

### Acknowledgements

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### References

- Craig JR (1973) Pentlandite-pyrrhotite and other low-temperature relations in the Fe-Ni-S systems. *Amer J Sci* 273:496-510
- Dare SAS, Barnes S-J, Prichard HM, Fisher PC (2011) Chalcophile and platinum-group element (PGE) concentrations in the sulfide minerals from the McCreeby East deposit, Sudbury, Canada, and the origin of PGE in pyrite. *Miner Deposita* 46:381-407
- Djon MLN, Barnes S-J (2012) Changes in sulfides and platinum-group minerals with the degree of alteration in the Roby, Twilight, and High Grade Zones of the Lac des Iles Complex, Ontario, Canada. *Miner Deposita* 47:875-896
- Duran CJ, Barnes S-J, Corkery JT (2014) Sulfide-rich pods from the Lac des Iles Pd-deposits, western Ontario, Canada. 12th International Platinum Symposium, Abstract Vol. pp 245-246
- Gervilla F, Kojonen K (2002) The platinum-group minerals in the upper section of the Keivitsansarvi Ni-Cu-PGE deposit, northern Finland. *Can Miner* 40:377-394
- Graterol M, Naldrett AJ (1971) Mineralogy of the Marbridge No. 3 & No. 4 Nickel-Iron Sulfide Deposits. *Econ Geol* 66:886-900
- Holwell DA, Keays RR, Firth EA, Findlay J (2014) Geochemistry and mineralogy of platinum-group element mineralization in the River Valley intrusion, Ontario, Canada: a model for early stage S saturation and multi-stage emplacement and the implications for 'contact-type' Ni-Cu-PGE mineralization. *Econ Geol* 109:689-712
- Lorand J-P, Alard O (2011) Pyrite tracks assimilation of crustal sulfur in Pyrenean peridotites. *Miner Petrol* 101:115-128
- Misra KC, Fleet ME (1973) The chemical composition of synthetic and natural pentlandite assemblages. *Econ Geol* 68:518-539
- Naldrett AJ, Craig JR, Kullerud G (1967) The central portion of the Fe-Ni-S system and its bearing on pentlandite exsolution in iron-nickel sulfide ores. *Econ Geol* 62:826-847
- Naldrett AJ, Kinnair J, Wilson A, Yudovskaya M, McQuade S, Chunnett G, Stanley C (2009) Chromite composition and PGE content of Bushveld chromitites: Part 1 - the Lower and Middle Groups. *Applied Earth Science: Transactions of the Institution of Mining and Metallurgy, Section B* 118:131-161
- Oberthür T (2011) Platinum-group element mineralization of the Main Sulfide Zone, Great Dyke, Zimbabwe. *Reviews in Econ Geol* 17:329-349
- Oberthür T, Cabri LJ, Weiser TW, McMahon G, Müller P (1997) Pt, Pd and other trace elements in sulfides of the main sulfide zone, Great Dyke, Zimbabwe: a reconnaissance study. *Can Miner* 35:597-609
- Oberthür T, Davis DW, Blenkinsop TG, Höhndorf A (2002) Precise U-Pb mineral ages, Rb-Sr and Sm-Nd systematics for the Great Dyke, Zimbabwe – constraints on late Archean events in the Zimbabwe craton and Limpopo belt. *Precambrian Res* 113:293-305
- Oberthür T, Weiser TW, Gast L, Kojonen K (2003) Geochemistry and mineralogy of platinum-group elements at Hartley Platinum Mine, Zimbabwe. *Miner Deposita* 38:327-343
- Piña R, Gervilla F, Barnes S-J, Ortega L, Lunar R (2013) Platinum-group elements-bearing pyrite from the Aguablanca Ni-Cu sulfide deposit (SW Spain): a LA-ICP-MS study. *Eur J Mineral* 25:241-252
- Smith JW, Holwell DA, McDonald I (2014) Precious and base metal geochemistry and mineralogy of the Grasvally Norite-Pyroxenite-Anorthosite (GNPA) member, northern Bushveld Complex, South Africa: implications for a multistage emplacement. *Miner Deposita* 49:667-692
- Vukmanovic Z, Reddy SM, Godel B, Barnes SJ, Fiorentini ML, Barnes S-J, Kilburn MR (2014) Relationship between microstructures and grain-scale trace element distribution in komatiite-hosted magmatic sulphide ores. *Lithos* 184-187:42-61
- Wilson AH, Prendergast MD (1989) The Great Dyke of Zimbabwe - I. Tectonic setting, stratigraphy, petrology, structure, emplacement and crystallization. In: Prendergast MD, Jones MJ (eds) *Magmatic sulfides - the Zimbabwe Volume*. Institution of Mining and Metallurgy, London, pp 1-2