Chemistry of major sulfides from Ni-Cu (PGE) mineralization at the Ransko ore district (Bohemian Massif): A result from LA-ICPMS study

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Abstract. The concentrations of platinum-group (PGE) and chalcophile elements in base metal sulfides (BMS) represented by pyrrhotite (Po), pentlandite (Pn), chalcopyrite (Cp) and cubanite (Cub) from the Ransko Ni-Cu (Co-PGE) deposit (Bohemian Massif) were determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS). In high-grade ore, the pyrrhotite shows a strong enrichment in Ag, Ir and Rh whereas the pentlandite is enriched in Cu, Pd and Ir. Cubanite is compared to chalcopyrite significantly enriched in Ag, Sb, Re, Os and Au whereas chalcopyrite shows slightly higher median Pd and Cd values. Rhenium, Os, Ir, Ru, and Rh occur mostly in solid solution in pyrrhotite and pentlandite from high-grade ore, which has been interpreted to represent monosulfide solid solution (mss) cumulates. The distribution of TABS (Te + As + Bi + Sb + Sn) in BMS indicates crustal contamination.

1 Geology and Mineralization

The Ransko massif is the ultra(mafic) body located in a transition zone between the Moldanubian, the Kutná Hora crystalline unit and the Hlinsko Zone in the Bohemian Massif, Czech Republic (Figure 1).

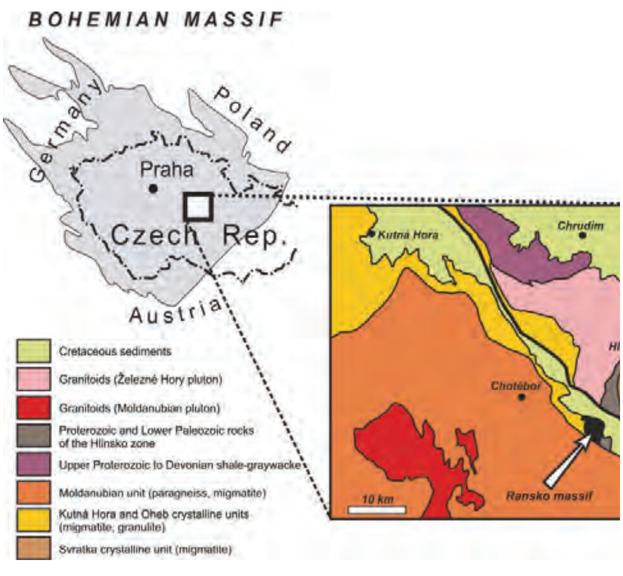

Figure 1. Geoloical position of the Ransko gabbro-peridotite massif (from Mísař 1974 modified by Ackerman et al. 2013).

It represents a strongly differentiated intrusive complex formed by peridotites and gabbroic rocks (gabbro, troctolite) with a magmatic segregation of low-grade Ni–Cu ores, a unique ore type in the Bohemian Massif. The exact geotectonic position of the Ransko massif and its relationship to adjacent units has been subject to several discussions (e.g. Synek and Oliveriová 1993, Štědrá and Nahodilová 2009, Pertoldová et al. 2010). While the Moldanubian and Kutná Hora units experienced polyphase Variscan high-grade metamorphism (~340 Ma), the adjacent part of the Hlinsko Zone was suggested to be Upper Proterozoic (Pitra and Guiraud 1994).

The Ransko massif has been subject of mining activity for a long time. For example, iron mining (oxidized, Fe-enriched caps) and smelting has been documented from the 14th until the end of the 19th century. Exploration for Ni-Cu-Co ores started in 1950s and resulted in finding of nine smaller ore bodies (e.g., Jezírka). Low grade Ni–Cu magmatic mineralization in troctolites is confined to a 3 km long and 1 km wide ore zone cutting the massif in a NE-SW direction (Mísař 1974). The ore zone is characterized by strong serpentinization and uralitization of the host rocks. Individual ore bodies are developed close to the contact of olivine-rich rocks (peridotite, troctolite) with gabbro, and particularly in the zones exhibiting varied alternation of troctolites with (olivine)gabbro. The Ni–Cu sulfide mineralization is not bound to a particular rock type but occur in various rock types as irregular lenses and horizons in a relatively strongly mineralized zone containing pyrrhotite and pyrite. Isolated and irregular occurrences of disseminated Cu-Ni ores were also discovered in troctolites and plagioclase-bearing peridotites. Within the Ni–Cu ores, Pašava et al. (2003) detected anomalous PGE concentrations with Pt+Pd contents up to ~0.7 ppm and revealed the presence of platinum-group minerals (PGM).

Based on paleomagnetic data, the Ransko massif was firstly assumed to be of Lower Cambrian age (Marek 1970). However, Re–Os data of barren and mineralized rocks from the Jezírka Ni–Cu body yield a regression of 341.5 ± 7.9 Ma assuming its Variscan age (Ackerman et al. 2013). This is exactly the same age of the mafic stock hosting Ni-Cu (PGE) mineralization at Aguablanca (Spain) (Romeo et al. 2006). Strongly mineralized Ransko peridotite with mantle like $^{187}Os/^{188}Os$ values suggest that PGE are predominantly of mantle origin. On the other hand, radiogenic $^{187}Os/^{188}Os$ values detected in barren and low mineralized samples indicate crustal contamination of parental magmas during their emplacement.

2 Results and Discussion

2.1 Samples and Methods

The polished sections of low (RAN7- olivine gabbro with 0.11 wt% Cu and 0.09 wt% Ni and RAN17- troctolite with 0.46 wt.% Ni and 0.19 wt.% Cu) and high Cu-Ni (R1- troctolite with 2.3 wt% Cu and 1.6 wt% Ni) mineralization from the Jezírka deposit from Ransko were first studied using a reflected light microscopy and afterwards by a FE–SEM scanning microscopy using Tescan Mira3 GMU housed at the Czech Geological Survey (CGS).

Trace elements in sulfides were analyzed at the LA-ICPMS laboratory at the CGS using Agilent 7900 ICP-MS coupled with an Analyte Excite Excimer 193 nm LA system equipped with a two-volume HelEx ablation cell. Up to 30 isotopes were detected depending on the mineral (^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{71}Ga, ^{74}Ge, ^{75}As, ^{77}Se, ^{101}Ru, ^{103}Rh, ^{107}Ag, ^{108}Pd, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{185}Re, ^{188}Os, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{201}Hg, ^{205}Tl, ^{208}Pb, and ^{209}Bi). We do not report Ru data for Pn and Rh data for Cp and Cub because of polyatomic interferences (Trubač et al. 2018).The laser was fired with spot size of 35-40 µm and fluence of 3.9-4.7 J/cm^2 with a laser pulse rate of 10 Hz. The GLITTER 3.0 software was used as a data reduction program. Internal standardization was based on Fe concentration determined by the SEM analysis and/or on the stoichiometric Fe values. Two reference materials were used for external calibration: the USGS MASS-1 (Wilson et al., 2002) and UQAC-FeS-1 (Savard et al. 2018, Duran et al. 2019) sulfide pellets. The UQAC-FeS-5 (Savard et al. 2018) and GSE-2g, a syntetic basalt material supplied by USGS (Mayers et al. 1976) were used for quality control.

2.2 Mineralogy

The ore minerals includes pyrrhotite, pentlandite, chalcopyrite and cubanite with minor pyrite, (Cr)magnetite, picotite, mackinawite, valleriite, ilmenite, galena, sphalerite, cobaltite–gersdorffite, native bismuth, gold, PGM represented by michenerite, froodite and sperrylite and tellurides represented by tsumoite, hessite and unnamed Bi-Ni telluride (Vavřín and Frýda 1998, Pašava et al. 2003 and references therein).

In this study, we newly identified an unnamed Pd-Bi-Sb phase in close association with michenerite and froodite, melonite (NiTe) in form of inclusions in pyrrhotite, and clausthalite (PbSe). Our high-grade ore sample (R1) is mainly composed of pyrrhotite, pentlandite and cubanite (Figure 2A) whereas low-grade ore (samples RAN-07 and RAN-17) is characterized by dominating pyrrhotite, pentlandite and chalcopyrite (Figure 2B).

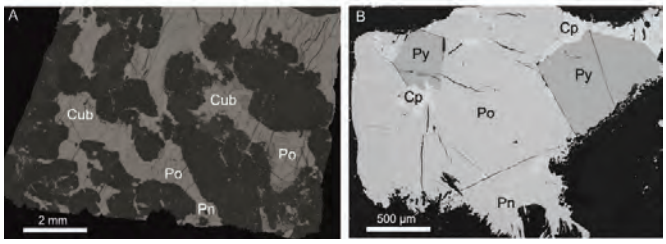

Figure 2. Photomicrographs of typical ore from Ransko. **A** – high-grade ore with pyrrhotite (Po), pentlandite (Pn) and cubanite (Cub). **B** – low-grade ore with pyrrhotite, pentlandite and chalcopyrite. Abbreviations: Cub – cubanite, Cp – chalcopyrite, Pn – pentlandite, Po – pyrrhotite and Py – pyrite.

2.3 Trace element concentrations in Base Metal Sulfides (BMS)

The ranges of concentrations of PGE in major base metal sulfides are shown on Figure 3.

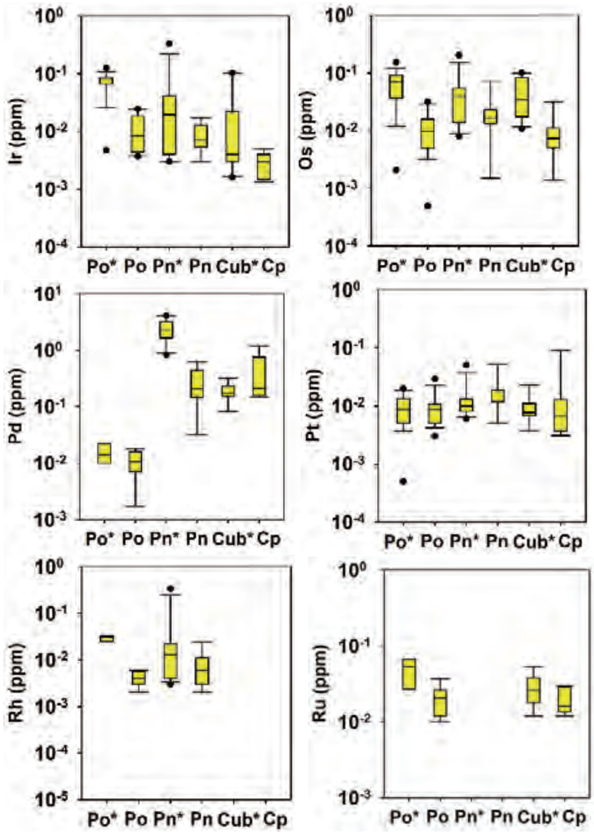

Figure 3. Box and whiskers plots for PGE in sulfides from Ransko. Po – pyrrhotite, Pn – pentlandite, Cub – cubanite, Cp – chalcopyrite, * sulfide from high-grade ore. The boxes are framed by 25th and 75th percentile, line within the box indicates median value. Whiskers displays 10th and 90th percentile and outliers are shown as one symbol representing 5th and 95th percentile.

The median concentrations of other selected trace elements (including TABS) in major BMS are shown in Table 1.

Iridium and Rh show the highest median values in Po from high-grade ore while Pt and Pd are dominating in high-grade ore Pn. Both the sulfides have the highest median Os values. Such distribution reflects very likely concentration of these metals in monosulfide solid solution similarly as reported from other Ni-Cu deposits (e.g. Aguablanca, NW Spain - Piña et al. 2012). Chalcopyrite is characteristic of the highest median values of Te, Cd, In and Zn while Cub bear peak median values of Ag, Re, Bi and Sb.

To investigate the role of crustal assimilation on the metal contents, we used As and Sb concentrations (Samalens et al. 2017; Mansur et al. 2021) in Pn (Figure 4). Both elements are incompatible with MSS and ISS and therefore, their concentrations in the sulfide liquid tend to increase with progressive fractionation.

Table 1. The median concentrations of selected trace elements in major BMS from Ransko (values in ppm).

	Po	Pn	Cub	Po	Pn	Cp
	high-grade ore			***low-grade ore***		
Co	13	15883	0.28	62.11	33543	0.34
Cu	0.84	482.2	235770	1.025	28.92	329996
Zn	0.55	1.01	205.7	0.58	1.03	474.31
As	0.43	0.89	0.39	0.40	0.89	0.30
Se	84	72.4	73.9	55.9	62.0	47.5
Ag	1.2	6.2	14.6	0.13	2.5	1.32
Cd	0.08	0.18	11.0	0.05	0.18	19.30
In	0.003	0.006	0.10	0.005	0.004	0.15
Sn	0.14	0.15	0.19	0.15	0.17	0.12
Sb	0.19	0.15	12.87	0.17	0.21	0.16
Re	0.056	0.086	0.161	0.085	0.021	0.003
Au	0.005	0.016	0.017	0.005	0.022	0.005
Tl	0.01	0.05		0.003	0.03	
Pb	1.23	2.58	5.62	0.87	4.73	4.16
Bi	0.75	0.51	0.90	0.28	0.89	0.45
Te	0.22	0.28	2.22	0.52	0.6	2.54

The values of Sb/Se and As/Se ratios in Pn from both types of ore at Ransko are well comparable with other magmatic Ni-Cu deposits which show external input of As and Sb in the sulfide liquid through crustal assimilation (see Mansur et al. 2021). High Sb values and a negative correlation between Sb/Se and As/Se in low grade ore likely reflect different crustal sources (lithologies).

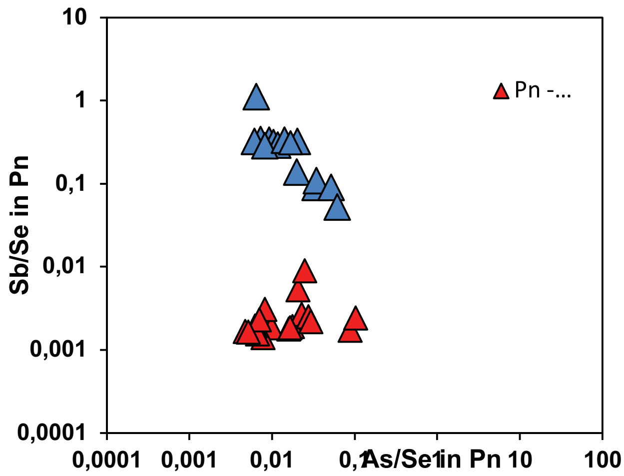

Figure 4. Binary plot of Sb/Se and As/Se in pentlandite (Pn) from the Staré Ransko Ni-Cu deposit.

In magmatic sulfide deposits, a fraction of the PGE is hosted by BMS, whereas the remaining PGE with TABS form PGM (e.g., Junge et al. 2015). Within Ni-Cu deposits, the effect of fractional crystallization on the composition of BMS is dominantly relative to the effect of PGM exsolution. Mansur et al. (2021) concluded that although there is no clear negative correlation between PGE and TABS concentrations in Pn, there is an increase in concentrations of both PGE and TABS from Cu-poor to Cu-rich ores (e.g., Pn from Noril'sk-Talnakh) which is consistent with the situation at Ransko (Figure 5).

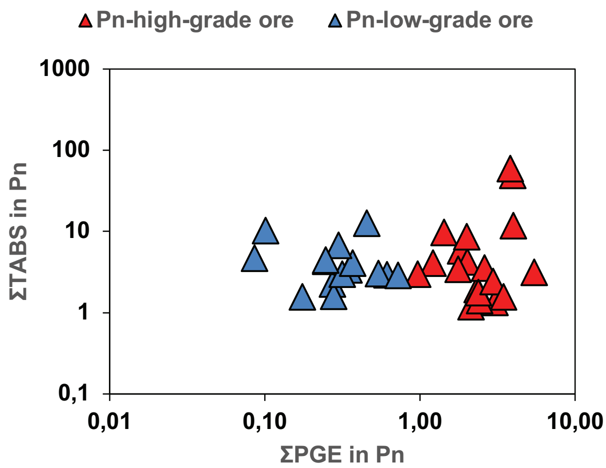

Figure 5. Binary plot of ΣTABS versus ΣPGE in Pn from Ransko Ni-Cu deposit. ΣTABS: Te + As + Bi + Sb + Sn. ΣPGE: Pt + Pd + Rh + Ir + Os.

To evaluate the influence of the R-factor on the BMS composition we used mantle normalized plots for strongly to highly (Figure 6 a,b), and slightly to moderately chalcophile elements (Figure 7 a,b). The elements are disposed from left to right in order of increasing partition coefficient into a sulfide liquid relative to silicate liquid ($D^{sulf/sil}$). The Po and Pn show similar shapes (Figure 6 a,b) suggesting similar R-factors during their formation.

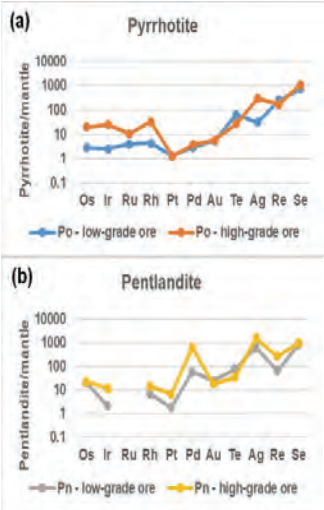

Figure 6. Strongly and highly chalcophile element primitive mantle normalized diagrams for median compositions of **(a)** Po and **(b)** Pn from Ransko. Primitive mantle values from Lyubetskaya and Korenaga (2007).

The median values of IPGE (Ir, Os, Ru) are higher in Po from high-grade ore in relation to Po from low-grade ore. The Pn from high-grade ore is typical of a strongly positive Pd and Ag anomalies while the Pn from low-grade ore shows more negative Ir, Pt and Re anomalies.

The mantle-normalized patterns for median Po composition are relatively flat and have slightly negative Cd, Co and In anomallies, a strong negative Zn anomaly and a strong positive Sb anomaly (Figure 7a). The patterns for median Pn compositions are similar to those for Po, but in contrast, Pn shows strongly positive Co anomaly not observed in Po patterns (Figure 7b).

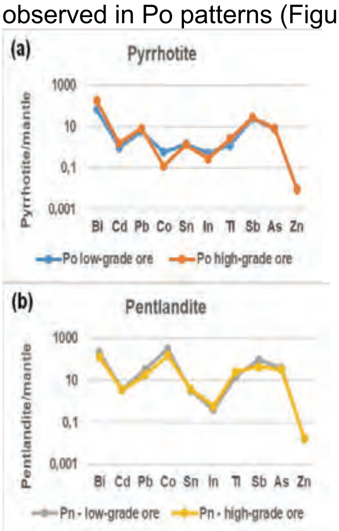

Figure 7. Slightly and moderately chalcophile element primitive mantle normalized TABS diagrams for median compositions of **(a)** Po and **(b)** Pn from Ransko.

Conclusions

The results of LA-ICPMS study of BMS at Ransko can be summarized as follows:

(1) In high-grade ore, the pyrrhotite shows a strong enrichment in Ag, Ir and Rh whereas the pentlandite is enriched in Cu, Pd and Ir. Cubanite is highly enriched in Ag, Sb, Re, Os and Au whereas chalcopyrite shows slightly higher median Pd and Cd values.

(2) Rhenium, Os, Ir, Ru, and Rh occur mostly in solid solution in pyrrhotite and pentlandite from high-grade ore representing monosulfide solid solution cumulates.

(3) The values of Sb/Se and As/Se ratios in pentlandite from both types of ore at Ransko most likely reflect external input of As and Sb in the sulfide liquid by crustal assimilation. This is also supported by the distribution of slightly to moderately chalcophile elements.

(4) There is an increase in concentrations of both PGE and TABS from Cu-poor to Cu-rich ores.

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