12th Biennial SGA Meeting
12–15 AUGUST 2013, UPPSALA, SWEDEN

Mineral deposit research for a high-tech world

Proceedings

VOLUME 2

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Volume 2

Edited by
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The 12th Biennial Meeting was organised by the Geological Survey of Sweden with assistance from Uppsala University, Stockholm University, the Geological surveys of Finland and Norway, Luleå University of Technology and the Swedish Museum of Natural History.

Suggested citation for entire volume:
Jonsson, E. et al. (ed.), 2013: Mineral deposit research for a high-tech world. Proceedings of the 12th Biennial SGA Meeting, 12–15 August 2013, Uppsala, Sweden. ISBN 978-91-7403-207-9. 1882 pp.

Suggested citation for an individual paper:
Sundberg, N. & Karlsson, E., 2013: Metallogeny of the Fennoscandian Shield. Mineral deposit research for a high-tech world. Proceedings of the 12th Biennial SGA Meeting, 12–15 August 2013, Uppsala, Sweden, ISBN 978-91-7403-207-9, 1450–1452.

A digital version of these volumes is available from the SGA website at www.e-sga.org

Cover photograph: View of the Aitik open pit copper mine in the very north of Sweden. Mining operations started in 1968 and the current mining depth is 430 m. The open pit is c. 3 km long and 1.1 km wide. The production in 2012 was 34,3 million tonnes of ore containing 67 100 tonnes of copper, 51 700 tonnes of silver and 1,9 tonnes of gold. Photo: Olof Martinsson, Luleå University of Technology.

ISBN 978-91-7403-207-9 set of 4 volumes

Layout: Jeanette Bergman Weihed, Kerstin Finn, Rebecca Litzell, SGU
Print: Elanders Sverige AB

Au-Pd bearing pyrites and chalcopyrites from the Buchim porphyry copper deposit, Eastern Macedonia

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Abstract. Interesting chemical compositions have been determined from the study of pyrite and chalcopyrite samples from the active Buchim open pit mine. Namely, beside the standard Fe, S, and Cu, increased concentrations of gold and palladium always followed by some amounts of arsenic were determined. In all the analysed pyrites, gold concentrations were within the range 0.027÷7.746% while the palladium concentrations were within the range 0.010–6.784%. Gold concentrations in all analysed chalcopyrites were within the range 0.009–9.095% while the palladium concentrations were within the range 0.020–8.110%. It is evident that concentrations of gold and palladium in the studied pyrite and chalcopyrite are almost always accompanied by increased concentrations of arsenic in the range of 0.002–0.761%. Increased gold and palladium concentrations have been determined in particular phases, especially in pyrite; in chalcopyrite they are due to metal substitution in the mineral lattice.

Keywords. gold-palladium phases, pyrite, chalcopyrite, Buchim mine

1 Introduction

The Buchim porphyry copper deposit is situated in the border area between the Serbo-Macedonian massif and the Vardar zone. In terms of its metallogeny it belongs to the Lece-Chalkidiki metallogenic zone (Serafimovski, 1993), where manifestations of porphyry copper and epithermal ore are developed. On a more local scale the Buchim copper mine is located in eastern central Macedonia, 10 km west of the town of Radovis. The mine started production in 1980 and produced four million tonnes of ore annually with 0.25% Cu, 0.27% Au, and 1 g/t Ag. Estimated reserves are approximately 100 million tonnes of low grade Cu-Au ores with some Ag and Mo and include primary (the most important Cu-Au resources) as well as secondary (related to the zone of oxidation-cementation enrichment) and mixed types of ores. The deposit is a porphyry copper type deposit (Serafimovski et al., 1996) and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites (Čifliganec, 1993).

Basic ore paragenesis was studied by Pavičević and Rakić (1983), Čifliganec (1993), Serafimovski et al. (2006), and others. Beside the basic ore paragenesis (pyrite, chalcopyrite, magnetite, bornite, enargite, etc.), Bi-Se mineral phases and especially Au-Pd mineral phases were also determined. Petrunov et al. (2001) published preliminary microscopic and microprobe data of the occurrence of the platinum group elements (PGEs) within the Buchim porphyry copper deposit for the first time. An increased content of Pd as well as Pd-mineralization (PGM) was established in the Cu-Au ores of the deposit in Buchim, Macedonia. Thus, this is the fourth case in the territory of the Balkan Peninsula after Bor-Majdanpek, Serbia (Janković, 1990), Skouries, Greece (Tarkian et al., 1991), and Elatsite, Bulgaria (Petrunov et al., 1992) where the Cu-porphyry style of hydrothermal PGM has been found.

As an alkaline porphyry deposit, the Buchim deposit represents, beside copper, a significant gold resource for Macedonia and fits quite well into the recently reported elevated levels of PGEs, particularly Pd and Pt, described in the Cordillera of British Columbia (Copper Mountain, Galore Creek), Allard Stock, La Plana Mountains, and Copper King Mine in the USA, Skouries porphyry deposit in Greece, Elatsite in Bulgaria, and so on (Economou-Eliopoulos, 2010). With the latest studies, results were obtained for Au-Pd-bearing pyrite and chalcopyrite, which are the subject of this particular paper.

2 General features of the Buchim porphyry copper deposit

The ore deposition is genetically connected with the intrusion of Tertiary, Oligocene-Miocene (27.5–24.5 m.y., Serafimovski, 1993, or 24.5–24.0 m.y., Barcikowski et al., 2012), subvolcanic latitic and latite-andesitic bodies within Precambrian metamorphic rocks-gneisses, micaschists, and amphibolites. Primary Cu-Au mineralization occurs around the subvolcanic bodies, being most abundant amid the hosting gneisses. Four ring-shaped ore bodies are located within and around the magmatic bodies (Figure 1). The main (Central) ore body is approximately 500 m in diameter and 250 m in vertical extent and has been worked in a large open pit. The ore consists of 0.25% Cu, 0.27g/t Au, 1g/t Ag, 13g/t Mo, and 1-4% pyrite. The igneous rocks have been altered to clays and micas. Important metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, haematite, and cubanite. According to the results of exploration, the copper mineralization covers an area of 1.5–2.0 km^2 and is traced to a depth of 300 m.

The Central, Bunardzik, Vrsnik, and Cukar ore bodies are contoured (Figure 1); the Central ore body has the largest copper reserves. Three ore bodies are morphologically related to stocks, and the fourth body is presumably a fragment of a previously existing sheetlike layer of manto-type oxidized and redeposited ore (Figure 1).

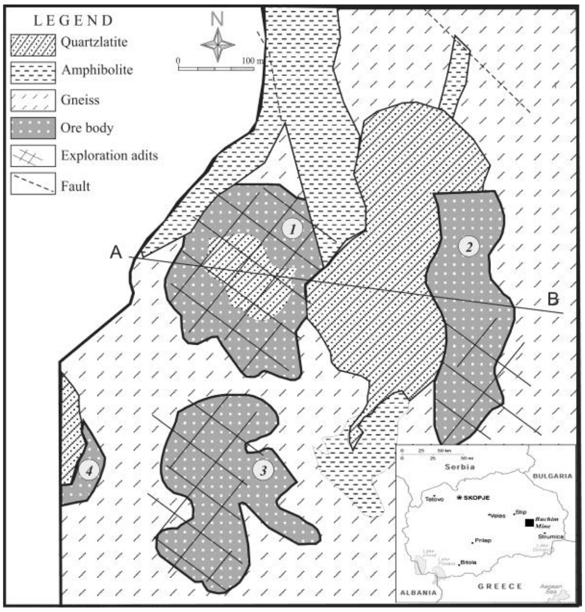

Figure 1. Simplified geological map of the Buchim porphyry copper deposit (Serafimovski, 1993).
1. Central ore body; 2. Vršnik ore body; 3. Čukar ore body; 4. Bunardžik ore body

The country rocks adjoining the porphyry stocks are silicified, chloritized, and sericitized, and underwent argillic alteration. Early potassic alteration developed as well.

Titanite, rutile, magnetite, haematite, chalcopyrite, pyrite, bornite, gold, molybdenite, petzite, calaverite, and argentite were identified as ore minerals. Enargite, tetrahydrite, galena, and sphalerite are less abundant. Chalcocite and covellite are predominant in the Cukar ore body, being accompanied by pyrite, tenorite, and occasional native copper, malachite, and azurite. The ore mineralization was formed in the following sequence: titanite, rutile, and magnetite crystallized first, followed by pyrrhotite, cubanite, vallerite, and the early generation of chalcopyrite. After deposition of these minerals, the hydrothermal ore-forming solution became enriched in sulfur, giving rise to pyrite crystallization. The late chalcopyrite and galena formed at the final stage of ore deposition (Serafimovski, 1993).

3 Methodology

The field sampling took place within the boundaries of an active Buchim open pit mine. Samples were taken from the Central ore body, between levels of 580 m and 540 m, for microscopic and microprobe study. In total 40 ore samples were studied under a Zeiss Axiolab Pol reflected light polarized microscope (at magnifications of 100 to 500) in the optical laboratory of the Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia. Quantitative elemental analyses of ten of the most interesting samples were performed under a JEOL JXA-8200 Electron Probe Micro-Analyser WD/ED Combined Microanalyser (equipped with a SE- and BSE-detector, five-WDS crystal spectrometer and an EDS analyser) in the analytical facilities at the Institute of Geochemistry and Petrology, ETH-Zurich, Switzerland. The selected electron beam conditions were a beam current of 20 nA at an acceleration voltage of 15 kV. Beside the analysis of elements, microphotographs were also taken.

4 Results and discussion

Our preliminary microscope and microprobe investigations determined two main mineral assemblages: magnetite-pyrite-chalcopyrite (Mt-Py-Cp) and pyrite-chalcopyrite (Py-Cp) as major hosts of Au and Pd.

Characteristic for the Mt-Py-Cp assemblage (earlier and high-temperature) is the geochemical association Fe-Cu-Ni, Co-As-O-S+Au, Ag, and Pd, with magnetite, chalcopyrite, pyrite, and cobaltite, Ni-Co-Fe-sulfides, and native Au (subordinate and rare). Pd is included in the structure of the main, subordinate, and rare minerals.

Later enrichment of the hydrothermal fluids with Cu, Bi, Se, Te, Pb, As, Au, and Ag led to the formation of a py-cp assemblages overprinting Mt-Py-Cp aggregates. New minerals were formed, partly as a result of the inclusion of elements "*in situ*": aikinite, bismuthinite, friedrichite, wittichenite, soucekite, emplectite, paderaite, merenskyite, michenerite (Serafimovski et al., 2006), other Pd-Bi-Te phases, tennantite (including. Pd-, Co-, and Ni-bearing), Ni-Co pyrite, Ni-Te phases, Bi-Pb-Ag-S phases, Cu-Fe-Bi-S phases, galena, clausthalite, sphalerite, native gold, and electrum, and (in the uppermost levels) enargite, luzonite, and pearceite (Petrunov et al., 2001).

Au-Pd association has been determined within the pyrite and chalcopyrite of the major ore-bearing phase in the Central ore body in the Buchim mine. It should be stressed that this Au-Pd association occupies certain levels (580–540 m) within the Buchim open pit. There, ore-bearing pyrite and chalcopyrite are in association with magnetite and are usually massive and coarse grained. The studied pyrites are of four different generations and increased concentrations of Au and Pd were determined in so-called block pyrites or massive pyrites with emphasized crystallinity and sizes up to 0.5 mm. Au-Pd phase occurs as a separate mineral phase, which is distinguished by a special colour (gull grey to pink grey; Figure 2). That mineral phase in the composition mostly corresponds to the pyrite (Table 1), but as can be seen from the table, increased gold (7.746% Au, Table 1, analysis 10) and palladium (6.784% Pd, Table 1, Analysis 11) concentrations are directly associated with decreased concentrations of iron and sulfur as major constituents of pyrite.

In practice this means that there is substitution of major pyrite constituents by gold and palladium. The fact that gold and palladium form such a mixture in the main mineral phase in pyrite and chalcopyrite equally (temperatures around 250 ºC) and their absence in later phases of the ore-bearing process could indicate stabilization of the crystal lattice of the pyrite in the later evolution of the process.

From the table it can be seen that, among the 12 analyses shown, gold is present in concentrations within the range of 0.027–7.746% and increased gold concentrations are usually accompanied by increased concentrations of palladium, except in analysis No. 3.

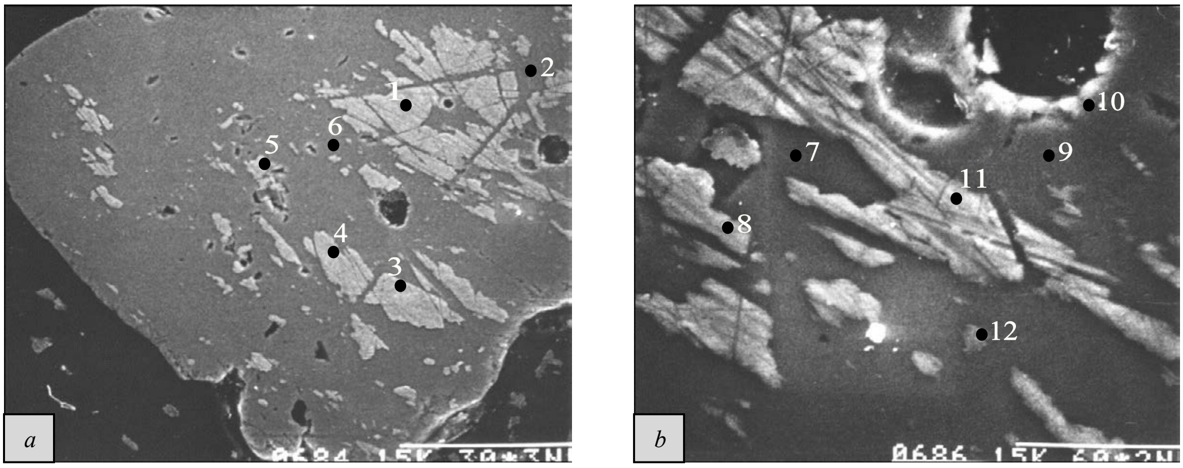

Figure 2. Electron microprobe photographs of pyrites (dark) and Au-Pd phases (light grey), from the Buchim porhyry copper deposit, with analysis points. *a) primary photograph, b) detail*

Palladium concentrations were within the range of 0.040–6.784%. Increased concentrations of gold and palladium caused reductions of Fe and S from their ideal values for pyrite, which should be around 45.55% Fe and 53.45% S. It should be mentioned that increased concentrations of arsenic were found in all analyses where gold and palladium showed increased values (0.019–0.761% As), too. The relation between concentrations of gold, palladium, and arsenic in pyrite and chalcopyrite from the Buchim deposit showed a high degree of geochemical correlation (Pockov, 1997). This probably points to the wide range of physicochemical conditions and the interplay between magmatic and hydrothermal processes during the formation of the deposit.

Figure 1. Electron probe microanalyses of pyrites

Analysis	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Au (%)	6,979	0,21	7,627	6,512	0,12	7,54	0,22	0,027	0,1	7,746	6,47	0,033
Fe (%)	39,228	43,636	40,575	39,976	45,458	43,556	43,854	45,438	45,123	39,177	38,932	45,531
S (%)	44,438	53,503	47,352	44,398	53,534	47,342	52,668	51,818	53,265	46,169	45,452	53,926
Cu (%)	0	0	0,01	0,022	0,062	0,012	0	0	0,02	0,034	0	0,024
As (%)	0,157	0	0,019	0,684	0,141	0,02	0,02	0,761	0	0,028	0,042	0,157
Ag (%)	0	0	0,21	0	0	0,73	0,04	0	0,02	0	0	0
Pd (%)	6,33	0,01	1,25	5,65	1,23	0,04	0	2,34	0	6,02	6,784	0,28
Ge (%)	0,31	0,35	-	-	-	0,21				0,25	0,38	
Zn (%)	0,22		-	-	-		0,37			0,26	0,35	
V (%)	0,33	0,25	0,27	0,21	-	0,22	0,41			0,21	0,32	
Ni (%)	0,24	0,47	-		-	0,21	0,54			0,15	0,28	
Se (%)	-	-	0,74	0,52	-	-						
Bi (%)	-	-	0,48	0,65	-	-						
Te (%)	-	-	0,35	0,39	-	-	0,21					
Σ sum	**98,232**	**98,429**	**98,883**	**99,012**	**100,545**	**99,88**	**98,332**	**100,384**	**98,528**	**100,044**	**99,01**	**99,951**

The studies of chalcopyrite from the Buchim deposit were performed on numerous ore samples, and different types of chalcopyrites were analysed. This was possible because the chalcopyrite is the major ore mineral within the Buchim deposit and the main bearer of copper. Its presence in the Buchim ore is around 1%. Our detailed studies confirmed the microscopy findings of some former authors, but some new phases were also found. Beside the already determined Bi-Se mineralization, the mineral paragenesis py-mgt-chp, which is the bearer of increased concentrations of Au and Pd, was confirmed. We would like to stress that the determined concentrations of Au and Pd were related to only one type of chalcopyrite (massive and coarse grained, Figure 3) of the so-called major ore-bearing phase of the Cu-mineralization within the Buchim mine or second generation chalcopyrite.

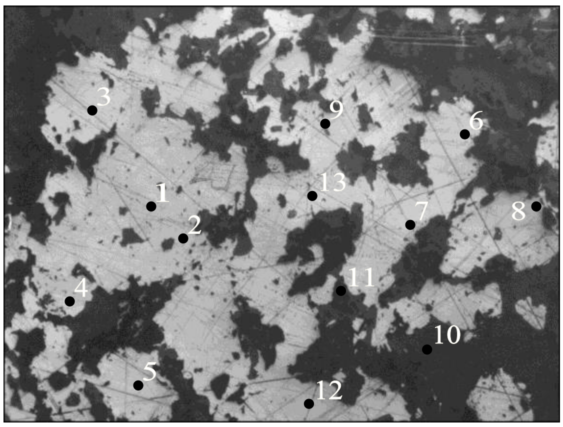

Figure 3. Microprobe photograph of chalcopyrite from the Buchim porhyry copper deposit, with analysis points.

This type of chalcopyrite mainly occurs in veins, veinlets and massive impregnations in association with magnetite and medium-to-high temperature pyrite.

The results of the microprobe analysis are shown in Table 2, where it can be seen that increased concentrations of Au and Pd were determined in 13 microprobe analyses. Gold concentrations were within the range 0.009–9.095%, while the palladium concentrations were 0.020–8.111%. By analogy with the studied pyrite, increased concentrations of As were determined here, too. However arsenic showed lower values here compared to those in pyrite. In chalcopyrite the Au-Pd concentrations are probably related to the mixed mineral phases that we were unable to fully determine, but with the noted presence of Au-Pd in chalcopyrite we have confirmed that there are numerous mineral phases such as Bi-Se minerals (laitakarite, friedrichite, cosalite, etc.), already determined previously by Serafimovski (1993) and Serafimovski et al., (2006).

Additional studies are needed to determine the stages of the Au-Pd pair. Within our latest studies particular phases that have resulted from the deformation of the chalcopyrite crystal lattice were determined, but their definite separation was not possible at the moment.

Figure 2. Electron probe microanalyses of chalcopyrites

Analysis	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**12**	**13**
Au (%)	6,335	0	6,457	0,286	9,095	7,29	6,923	0,14	0,116	0,23	7,159	0,009
Fe (%)	25,923	29,08	25,128	29,112	25,972	25,728	26,679	29,775	29,707	29,52	25,729	29,346
S (%)	28,737	34,324	29,736	33,595	26,964	28,643	27,884	34,371	35,299	35,577	28,66	34,882
Cu (%)	29,463	33,675	28,678	33,514	26,638	28,912	29,824	34,211	34,153	34,225	27,942	33,692
As (%)	0	0,022	0,048	0	0,045	0,005	0,108	0	0,055	0,074	0,002	0,005
Pd (%)	7,38	0,02	8,11	0,3	7,97	6,81	5,98	1,33	0,42	0,28	7,46	1,43
Ge (%)	0,22	-	-	0,38	0,42	0,35	-	-	-	-	0,29	-
Zn (%)	0,35	-	-	0,44	0,36	0,41	-	-	-	-	0,35	-
V (%)	0,38	0,37	-	0,42	0,44	0,45	0,22	-	-	-	0,42	-
Ni (%)	0,33	-	-	0,35	0,41	0,48	-	-	-	-	0,35	-
Se (%)	-	0,33	0,22	-	-	-	0,49	-	-	-	-	-
Bi (%)	-	0,42	0,31	-	-	-	0,52	-	-	-	-	-
Te (%)	-	0,35	0,25	-	0,22	-	0,42	-	-	-	-	-
Σ sum	**99,118**	**98,591**	**98,937**	**98,397**	**98,534**	**99,078**	**99,048**	**99,827**	**99,75**	**99,906**	**98,362**	**99,364**

We would also like to point out that significant concentrations of the standard geochemical association of elements for the Buchim chalcopyrite, such as Ni, Co, Pb, Zn, Ag, and so on, were not determined in these studies.

5 Conclusion

The studied mineral association in the Buchim porphyry copper deposit confirmed that the most common mineral is pyrite with a presence of 3%, while chalcopyrite is the major bearer of copper mineralization with a presence of 1%. Microscope and microprobe investigations have determined two main mineral assemblages: magnetite-pyrite-chalcopyrite (mt-py-cp) and pyrite-chalcopyrite (py-cp), as major hosts of Au and Pd. The gold content in the studied pyrite is within the range of 0.027–7.746% while the palladium content is within the range 0.040–6.784%, and they are related with the special mixture mineral phases characterized by gull gray colour.

Increased concentrations of Au-Pd in chalcopyrite are related to the massive medium-to-high temperature chalcopyrite, which constitutes the major ore phase within the Buchim deposit and occupies a certain level within the deposit (580–540 m). For more detailed definition of the PGM, additional studies are needed

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