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ON THE ORIGIN OF THE PGE MINERALIZATION IN THE ELATSITE PORPHYRY Cu–Au DEPOSIT, BULGARIA: COMPARISON WITH THE BAULA–NUASAHI COMPLEX, INDIA, AND OTHER ALKALINE PGE-RICH PORPHYRIES

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Abstract

The Elatsite porphyry-copper deposit contains platinum-group minerals associated with base-metal sulfides, *i.e.*, merenskyite, moncheite, palladoarsenide and an undetermined Pd–Ag–Te–Bi mineral, all in a magnetite – bornite – chalcopyrite assemblage. Other minerals such as linnaeite, carrollite, siegenite, rammelsbergite, which are uncommon in typical porphyry-copper deposits, indicate a mantle derivation for the specific PGE–Co–Ni episode of mineralization. The Pt–Pd-rich facies is characterized by extremely low Os, Ir and Ru contents (respectively <3.0, <0.6 and <1.0 ppb), with up to 349 ppb Pt and 3440 ppb Pd. Mineralization results either from (1) multi-stage events involving a preconcentration of the PGE in magmatic disseminated (Ni–Cu–Co) sulfides related to a mantle-derived magmatic event, with subsequent selective hydrothermal remobilization, or (more probably) from (2) particular conditions in the partial melting of the mantle and magmatic evolution that rendered the precious metals available in the magma, along with a specific evolution that prevented the early formation of the sulfides whilst the PGE (mainly Pd) were concentrated in the hydrothermal fluids. This PGE–Co–Ni episode is a very specific event in the main mineralizing process giving rise to the massive deposition of the Cu-porphyry system. The characteristics of the PGE mineralization deviate from those of a purely hydrothermal PGE mineralization in a mafic environment, as exemplified by the Baula–Nuasahi mineralization (India), in that they tend to converge toward (and present striking similarities with) the PGE mineralization in alkaline porphyry deposits, such as are found in British Columbia.

Keywords: platinum-group minerals, platinum-group elements, porphyry copper, hydrothermal remobilization, Elatsite, Bulgaria.

Sommaire

Le porphyre cuprifère d'Elatsite, en Bulgarie, renferme une minéralisation en éléments du groupe du platine (EGP) associée à une paragenèse à magnétite – bornite – chalcopyrite. Les EPG sont sous la forme de merenskyite, monchéite, palladoarsenide et d'un minéral indéterminé de Pd–Ag–Te–Bi. D'autres espèces, telles linnéite, carrollite, siegenite, rammelsbergite, inhabituelles dans les porphyres cuprifères, indiquent une source mantellique pour cet épisode spécifique à EGP–Co–Ni. La minéralisation se caractérise par des teneurs très basses en Os, Ir et Ru (respectivement <3.0, <0.6 et <1.0 ppb) dans les faciès riches en Pt et Pd, avec jusqu'à 349 ppb Pt et 3440 ppb Pd. Elle résulte soit (1) d'un événement polyphasé impliquant une préconcentration des EGP dans des sulfures de Ni–Cu–Co disséminés, liés à un épisode magmatique d'origine mantellique, suivi d'une remobilisation hydrothermale sélective, ou, plus probablement, (2) de conditions particulières de fusion partielle du manteau et dans l'évolution magmatique, qui font que les métaux précieux restent disponibles dans le magma, et qui empêchent la cristallisation précoce des sulfures, alors que les EGP (principalement Pd) vont se concentrer dans les fluides hydrothermaux. Cet épisode à EGP–Co–Ni correspond à un événement très spécifique dans le processus de minéralisation qui mène au dépôt massif du Cu du système porphyrique. Cette minéralisation en EGP diffère sensiblement des minéralisations hydrothermales en EGP en contexte mafique, comme l'illustre l'exemple de la minéralisation de Baula–Nuasahi, en Inde, alors qu'elle présente des similarités frappantes avec les minéralisations en EGP dans les porphyres alcalins, tels ceux de Colombie-Britannique.

Mots-clés: minéraux du groupe du platine, éléments du groupe du platine, porphyre cuprifère, remobilisation hydrothermale, Elatsite, Bulgarie.

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INTRODUCTION

Mineralization involving the platinum-group elements (PGE) of the Elatsite porphyry copper deposit, in Bulgaria, has been the subject of several papers demonstrating that the PGE take the form of platinum-group minerals (PGM) (Petrunov *et al.* 1992, Petrunov & Dragov 1993, Tokmakchieva & Pazderov 1995, Dragov & Petrunov 1996, Tarkian & Stribrny 1999, Bogdanov *et al.* 2000, Fanger 2001, Tarkian *et al.* 2003). We thus have considerable information concerning the location of the PGM, with results of precise chemical analyses for some of them. These data justify consideration of the Elatsite deposit as a "PGE porphyry copper deposit" (*e.g.*, Von Quadt *et al.* 2001) or a "PGE–Au–Mo porphyry copper deposit" (Kamenov *et al.* 2002). However, detailed studies of the Elatsite deposit show the PGE mineralization to be present only in restricted zones and to apparently be related to a very specific mineralizing process because it includes many features that cannot be associated with a typical porphyry copper system.

Here, our aim is to demonstrate how this episode of PGE-bearing mineralization can be related to a very specific evolution of the complex polyphase Cu–Au deposit. In this respect, it should be noted that Tarkian *et al.* (2003), in describing the mode of occurrence and distribution of the PGE in the Elatsite samples, mention the presence of merenskyite and of a merenskyite–moncheite solid solution, and describe the PGM as being in part exsolved from chalcopyrite and bornite. Moreover, they did not identify the other PGM, such as palladoarsenide, michenerite, palladian rammelsbergite, $(Ni,Pd)As_2$, and undetermined phases like Pd_2Te_3, Pd_3Te_4, and unidentified Pd,Cu,Ni,Ag tellurides that are mentioned by Petrunov *et al.* (1992), Petrunov & Dragov (1993) and Dragov & Petrunov (1996). Here, one should note that the analytical results provided by Petrunov *et al.* (1992), obtained with an energy-dispersion spectrometer (EDS) attached to an electron microprobe, were recalculated to 100 wt.%, and the analytical conditions were not given. Their results need to be confirmed.

We first of all present new data on the PGE content of selected parts of the Elatsite deposit; then we describe the mineralogy of the PGE-rich samples, and we present results of new electron-microprobe analyses, not only of the PGM, but also of the Ni–Co thiospinels, Pb and Ag–(Bi) selenides, and Ag tellurides. Finally, we integrate all the information concerning the mineralogy of the deposit so as to better constrain the origin of the PGE enrichment. The Cu–Ni–Co–Te–Se signature characterizing the PGE-bearing episode of mineralization has also led us to compare the Elatsite deposit, hosted by granodiorite–monzodiorite porphyry stocks, with that of the Baula–Nuasahi Complex in India (Augé *et al.* 2002). There, the Cu–Ni–Co–(Au–PGE) mineralization, which has been studied in detail, is contained within a well-constrained gabbro environment. We then extend our comparison to other porphyry-copper deposits in various environments.

GEOLOGICAL SETTING AND MINERALIZATION

Most of the metallic deposits of eastern Europe are related to the Late Cretaceous igneous belt known as the "Tethyan Eurasian Metallogenic Belt". It extends from southwestern Romania (Apuseni Mountains) through Serbia (Timok Magmatic Complex) and Bulgaria (Panagyurishte district) to the Caucasus (Jankovic 1977). In Bulgaria, the Panagyurishte district lies in the central part of the Srednogorie zone and hosts major porphyry – epithermal Cu–Au deposits; these, from north to south, are Elatsite, Vozdol, Chelopech, Karlievo, Medet, Assarel, Krassen, Petelovo, Radka, Tsar Assen, Elshitsa, and Vlaikov Vruh (Fig. 1a).

The Elatsite porphyry copper deposit lies about 6 km northwest of the main volcanic center and the nearby Chelopech Au–Cu deposit (Fig. 1a). It is associated with Late Cretaceous subvolcanic dykes of granodiorite to quartz diorite, or monzodiorite, that dip to the south, in the direction of an inferred magma-chamber of a volcano-intrusive structure, which cuts Precambrian to Early Paleozoic phyllite of the Berkovitsa Group, and Late Paleozoic granodiorite of the Vezhen pluton. A U–Pb age of 92.1 ± 0.3 Ma (obtained on a single grain of zircon) is inferred for the monzodiorite porphyry (Von Quadt *et al.* 2002a, b, Peytcheva *et al.* 2003). A similar Ar/Ar age (91.2 ± 0.6 Ma) was obtained on magmatic hornblende from a monzodiorite, although hydrothermal white micas in the same rocks gave an Ar/Ar age of 79.9 ± 0.7 Ma (Lips *et al.* 2004).

The Elatsite deposit includes intrusive bodies cut by NW–SE and NE–SW faults. Its mineralized zone forms a large, NE–SW-trending and south-dipping ellipsoidal stockwork of 800 × 350 m (Popov *et al.* 2003) (Fig. 1b) in which the mineralization is both veinlet-disseminated in the granodiorite porphyry dyke and disseminated in the host metamorphic facies of the Berkovitsa Group.

Dragov & Petrunov (1996) recognized four main mineral assemblages (Table 1): 1) An early quartz – magnetite – bornite – chalcopyrite ± molybdenite assemblage (Stage 1) is developed irregularly as small veinlets and "nests" throughout the deposit (Fig. 1b, Petrunov *et al.* 1992). The assemblage is completed by a large variety of PGM and Co, Ni, Te, Se, Bi, Pb, Au and Ag minerals, and is associated with a potassic alteration indicated by hydrothermal biotite, amphibole and K-feldspar. Locally within the orebody, the magnetite forms well-developed lenses partly altered to hematite. 2) A quartz – pyrite – chalcopyrite assemblage (Stage 2) is associated with a strong phyllic (white mica) stage of alteration. This material constitutes the economic ore (Fig. 1b) and occurs throughout the deposit as veinlets, nests and disseminations. Rare Pd-bearing minerals (palladian rammelsbergite, palladoarsenide) and Co–Ni–As phases have been described as reaction products in this assemblage (Petrunov & Dragov 1993, Dragov & Petrunov 1998). 3) A quartz – pyrite –chalcopyrite – calcite assemblage (Stage 3) that is found at the margins of the main orebody, and which preceded 4) a late quartz – calcite – zeolite (stilbite, heulandite) stage of alteration (Stage 4).

TABLE 1. MINERAL ASSEMBLAGES DESCRIBED FROM THE ELATSITE, SKOURIES (GREECE) AND SANTO TOMAS II (PHILIPPINES) Cu-Au-(PGE) PORPHYRY DEPOSITS

Mineral		Elatsite, Bulgaria (1)				Skouries (2)	Santo Tomas II (3)
		Stage 1	Stage 2	Stage 3	Stage 4		
Sulfides, mostly							
Chalcopyrite	$CuFeS_2$	×	×	×		×	×
Bornite	Cu_5FeS_4	×				×	×
Magnetite	$Fe^{2+}Fe^{3+}{}_2O_4$	×				×	×
Pyrite	FeS_2		×	×	×	×	×
Molybdenite	MoS_2	×	×	×			×
Hematite	Fe_2O_3	×				×	
Pyrrhotite	$Fe_{1-x}S$	×				×	
Marcasite	FeS_2	×					
Galena	PbS				×		×
Sphalerite	ZnS	×					×
Tetrahedrite-tennantite	$(Cu,Fe)_{12}(As,Sb)_4S_{13}$		×				×
Native gold	Au	×				×	×
Au-Ag alloy	Au-Ag	×	×			×	×
Stromeyerite	AgCuS					×	
Tellurides							
Sylvanite	$(Au,Ag)_2Te_4$					×	
Hessite	Ag_2Te					×	×
Weissite	$Cu_{2-x}Te$	×					
Bi telluride	Unspecified					×	
Au telluride	Unspecified					×	
Native Te	Te	×					
Petzite	Ag_3AuTe_2						×
Thiospinels							
Carrollite	$Cu(Co,Ni)_2S_4$	×					
Ni-rich linnaeite	$(Co^{2+},Ni)Co^{3+}{}_2S_4$	×					
Siegenite	$CoNi_2S_4$	×					
Rammelsbergite	$NiAs_2$	×					
Co-rich gersdorffite	(Ni,Co)AsS	×					
Selenides, mostly							
Clausthalite	PbSe	×					
Naumannite	Ag_2Se	×					
Bodhanowiczite	$AgBiSe_2$	×					
Kawazulite	$Bi_2Te_2(Se,S)$	×					
Eucairite	AgCuSe	×					
Native Bi	Bi	×					
PGM							
Merenskyite	$PdTe_2$	×				×	×
Moncheite	$(Pt,Pd)(Te,Bi)_2$	×					×
Kotulskite	Pd(Te,Bi)						×
Palladoarsenide	Pd_2As		×				
Michenerite	(Pd,Pt)BiTe	×					
Pd-rich rammelsbergite	$(Ni,Pd)As_2$		×				
Unnamed 1	$(Pd,Cu)_2Te_3$	×					
Unnamed 2	$(Pd,Ag)_3Te_4$	×					
Unnamed 3	$PdNiTe_3$	×					
Alteration-induced minerals							
Biotite		×				×	×
K-feldspar		×				×	
White mica			×				
Zeolite					×		
Calcite				×	×		

(1) This study and Petrunov *et al.* (1992), (2) after Tarkian *et al.* (1991), (3) after Tarkian & Koopmann (1995).

SAMPLING AND ANALYTICAL TECHNIQUES

Eighteen samples from the Elatsite mine were analyzed for their precious-metal and minor- and trace-element contents. Ten composite-chip samples (EL–1 to EL–10), each representing a 20–40 m sampling length in the mineralized zone between Levels 1120 and 1240 East and between Levels 1120 and 1195 West (Fig. 1b), were analyzed for their metal content and to determine the characteristics of the different mineralized levels in the mine. Three samples were taken from the flotation unit, one each from the feed ore (EL–11), flotation concentrate (EL–12) and flotation tailings (EL–13). Finally, five hand specimens of massive ore from the supposed PGE-rich magnetite – chalcopyrite – bornite paragenesis at Levels 1150 East (EL–14), 1315 South (EL–15, –16, –17) and 1330 South (EL–18, Fig. 1b), were analyzed for the six PGE (Table 2).

The five PGE-rich hand specimens comprise submassive sulfides with fragments of altered host-rock, centimeter-size euhedral crystals of K-feldspar, and flexible flakes of mica. In addition, seven hand-specimens (256–A1, –A3, –A4, –B1, –1/2, 207–A and Ecn) that had been studied previously by one of us (RP) were also re-investigated for their levels of the PGM. The characteristics of these 12 hand specimens are summarized in Table 3.

Polished sections of the ore-bearing samples were studied under the ore microscope in reflected light in order to identify the mineral assemblages (Table 3) and detect the PGM. The PGM were then examined in more detail using a scanning electron microscope (SEM) equipped with a back-scattered electron (BSE) detector; this instrument was also used to detect smaller grains of the PGM.

The PGM and other ore minerals were then analyzed with a Cameca SX 50 electron microprobe at BRGM. The associated program used 16 elements with an acceleration voltage of 20 kV, beam current of 20 nA, and counting time of 10 s. For standards, we used pure metals, plus FeS_2 for Fe and S, PbS for Pb, AsGa for As and Sb_2S_3 for Sb. We used $K\alpha$ lines for Ni, Cu, Co, S, $K\beta$ lines for Fe, $L\alpha$ lines for Sb, Se, Te, Rh, Pt, Au, Ag, $L\beta$ lines for Pd, As, and $M\alpha$ lines for Pb and Bi. The interference between Ag$L\alpha$ and Pd$L\beta$ lines was corrected. The calculated detection-limit was ≤0.1 wt.% for most elements, around 0.2 wt.% for Pt, Pd, Pb, and around 0.3 wt.% for Fe and Au. These values are considered acceptable for the mineralogical discussion that follows. Because the tests showed Os, Ir and Ru to be below the detection limits, these elements were not included in the routine analytical program; moreover, the tables of analytical data do not show values below the detection limits.

Levels of concentration of the minor and trace elements in all 18 samples were determined by inductively coupled plasma – mass spectrometry (ICP–MS) after *aqua regia* digestion. The levels of Pt, Pd and Au in the composite-chip and flotation-concentrate samples were determined by ICP–MS after lead collection, and

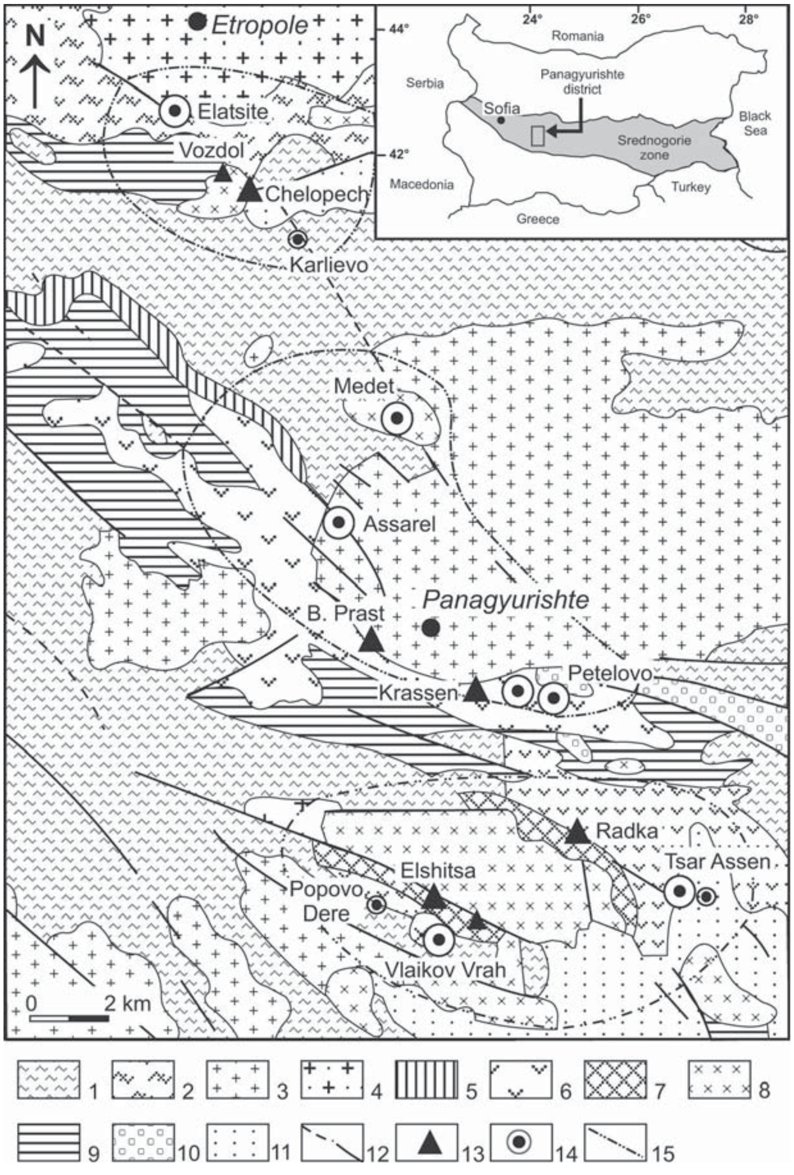

FIG. 1a. Simplified geological map of the southern part of the Panagyurishte district, showing the main porphyry and epithermal deposits (after Kouzmanov 2001). Map units: 1 Precambrian gneiss, 2 Paleozoic phyllite, 3 Paleozoic granite, 4 Paleozoic granodiorite, 5 Triassic sediment, 6 Cretaceous andesite, 7 Cretaceous dacite, 8 Cretaceous granite and granodiorite, 9 Maastrichtian flysch, 10 Tertiary conglomerate, 11 Quaternary sediment, 12 Fault, 13 Au–Cu epithermal deposit, 14 Cu porphyry deposit, 15 Limit of the mineralized zones (Elatsite – Chelopech, Assarel – Medet – Krassen – Petelovo and Elshitsa – Radka, respectively, from north to south).

that of the six PGE, plus Au and Re in the PGE-rich hand specimens were determined by ICP–MS after nickel sulfide fusion. All analyses were performed at the SGS Minerals Services Laboratories, Toronto, Canada.

PRECIOUS-METAL CONCENTRATIONS

The PGE content of the 10 composite-chip samples is fairly low, with Pt between 1.1 and 46 ppb, and Pd between 4 and 78 ppb; the gold content varies between 261 and 1350 ppb (Table 2). The Pt and Pd tend to correlate with one another (except in one sample, El–3), and the total Pt + Pd shows a general positive correlation with gold, the Au:(Pt + Pd) ratio being between 10 and 50 (Figs. 2a, b). The flotation concentrate exhibits a minor enrichment in Pt and Pd (76 and 347 ppb, respectively) compared to the feed ore, with 1.8 ppb Pt and 10 ppb Pd. The Au content of the concentrate reaches 8.85 ppm, as against 0.23 ppm for the feed ore.

The PGE content of the five mineralized hand-specimens is extremely varied, from a low of 4 ppb Pt and 2 ppb Pd (El–14) to highs of 349 ppb Pt (El–17) and 3440 ppb Pd (El–15); Pt and Pd show a slight correlation, and the Pd:Pt ratio ranges between 10.8 and 41.7. The gold content also varies, between a low of 1.8 ppm (El–14) and a high of 34.1 ppm (El–16; Table 2, Fig. 2a). The other PGE in the hand specimens are extremely low, with Os, Ru and Rh below detection limit (<3, <1 and <1 ppb, respectively) and Ir between 0.2 and 0.6 ppb (Table 2). The five PGE-rich samples are also characterized by a relatively low Ni (12–25 ppm, apart from one sample with 67 ppm), Cr generally below the detection limit (<1 ppm), Co between 30 and

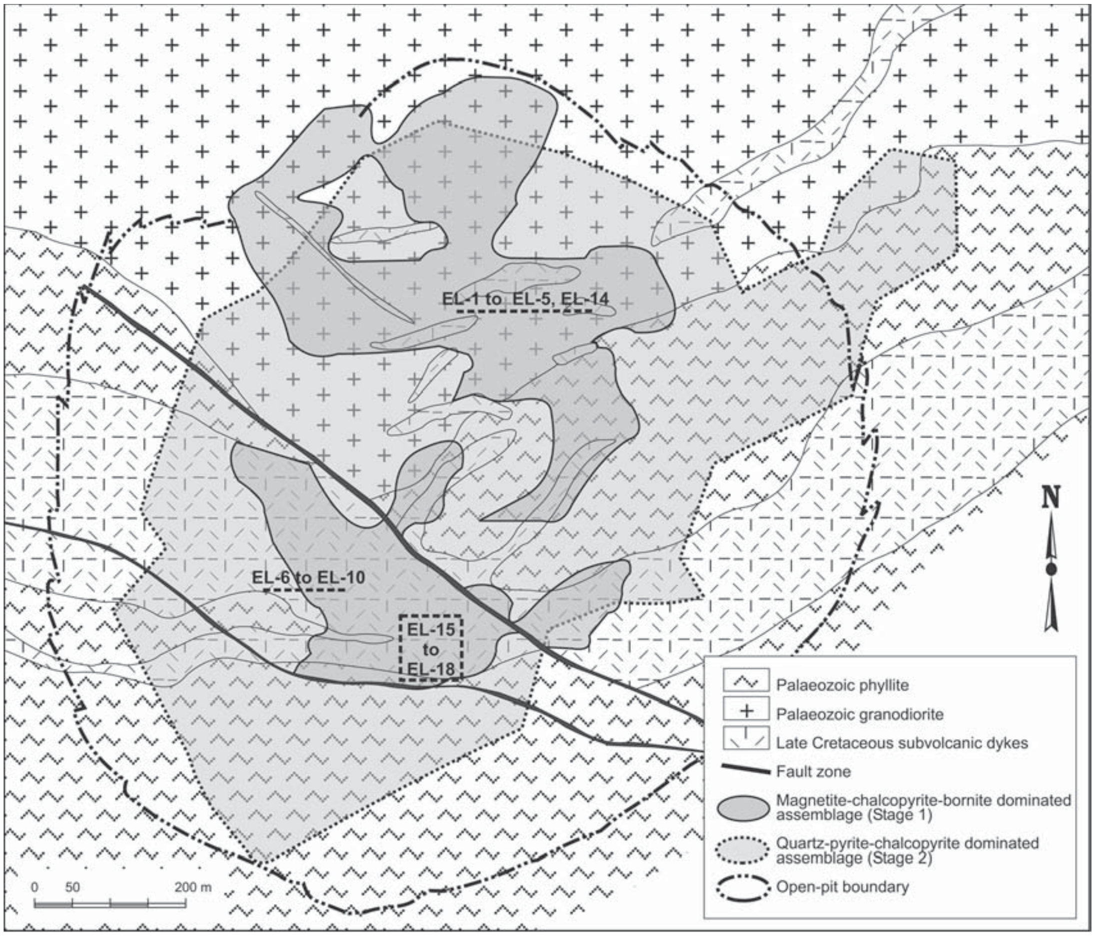

FIG. 1b. Simplified geological map of the Elatsite deposit (after Popov *et al*. 2000), showing the approximate location of the samples studied and the location of the two main mineral assemblages.

TABLE 2. MAJOR-, MINOR-, AND TRACE-ELEMENT CONCENTRATIONS, INCLUDING THE PGE, IN ORE SAMPLES FROM THE ELATSITE, BAULA-NUASAHI (INDIA) AND BRITISH COLUMBIA DEPOSITS

Sample no	Sample type	Au ppb	Pt ppb	Pd ppb	Rh ppb	Ru ppb	Os ppb	Ir ppb	Cu ppm	Ni ppm	Co ppm	Cr ppm	Mn ppm	Pb ppm	Ag ppm
Detection limit		1	0.5	1	1	1	3	0.1	0.5	1	1	1	2	2	0.2
ELATSITE (1)															
EL-1	ccs, level 1120 E	400	1.1	9					5330	19	9	242	337	11	1
EL-2	ccs, level 1150 E	560	3.3	11					4500	92	9	472	279	7	1.2
EL-3	ccs, level 1180 E	531	38.3	7					5230	124	7	502	272	8	1.3
EL-4	ccs, level 1210 E	579	7.4	9					5830	125	8	486	289	11	1.4
EL-5	ccs, level 1240 E	313	4	5					3990	110	13	426	366	8	1.1
EL-6	ccs, level 1120 W	261	1.1	4					5720	87	8	348	340	30	3.7
EL-7	ccs, level 1150 W	361	6.5	14					5480	101	8	367	652	17	1
EL-8	ccs, level 1165 W	1350	13.1	48					>10000	113	8	434	256	9	2.5
EL-9	ccs, level 1180 W	1110	20	71					>10000	140	7	541	471	24	3.6
EL-10	ccs, level 1195 W	1280	45.6	78					>10000	80	6	461	406	28	2.6
EL-11	flotation feed ore	232	1.8	10					4530	10	9	19	267	23	0.7
EL-12	flotation concentrate	8850	76	347					>10000	39	114	<1	40	795	>10
EL-13	flotation tailings	97	1.8	3					465	9	6	18	252	3	0.2
EL-14	mhs, level 1150 E	1820	4	2	<1	<1	<3	0.3	112000	67	35	16	328	67	17
EL-15	mhs, level 1315 S	1820	319	3440	<1	<1	<3	0.6	370000	12	43	<1	33	182	71
EL-16	mhs, level 1315 S	34100	64	2070	<1	<1	<3	0.4	370000	12	44	<1	27	157	88
EL-17	mhs, level 1315 S	7800	349	1980	<1	<1	<3	0.2	332000	25	30	<1	51	144	73
EL-18	mhs, level 1330 S	33000	7	292	<1	<1	<3	0.2	490000	22	43	<1	14	253	186
BAULA NUASAHI (2)															
FGH1 215	mhs	229	523	1790	22	37	4	6.9							
FGH1 228	mhs	130	425	1630	40	183	9	19.1							
FGH1 234	mhs	73	319	2270	43	205	9	19.3	5700	2220	240	52000			
FGH3 64	mhs	95	1410	2840	91	240	14	34							
FGH3 79	mhs	62	261	1530	16	99	5	10							
FGH4 59	mhs	70	516	2300	37	128	6	16.4	10000	2700	220	67000			
FGH5 52	mhs	127	421	4170	20	89	3	11.5		4100					
FGH5 75	mhs	224	1190	3690	49	192	13	24.5							
FGH5 94	mhs	151	1210	2440	91	341	28	42.5							
BLR42	mhs	630	1670	6090	89	161	22	27.1	44500	1800	120	96000			
BLR96	mhs	3250	1650	25800	1170	188	30	113	195000	7300	290	74000			
BRITISH COLUMBIA (3)															
GC92-1500, Galore Creek		5200	17	407	0.1	5	<0.1	0.1	76300						
GC92-1523, Galore Creek		68000	54	1039	0.5	9	<0.1	0.1	215400						
GC92-1541, Galore Creek		3600	15	103	0.1	<5	<0.1	0.1	180600						
GC92-1553, Galore Creek		60000	107	1581	0.5	5	<0.1	0.2	131600						
MBX, Mt. Milligan		6923	28	112	0.7	<5	0.7	0.2	7100						
66Z, Mt. Milligan		2705	17	51	0.3	8	0.3	0.1	100						
WBX, Mt. Milligan		5322	23	124	2.2	32	1.9	1.3	15900						
SST, Mt. Milligan		7339	62	588	0.9	33	0.6	0.3	5600						
MMSS-1, Mt. Milligan		18500	111	6312	2.1	7	0.7	0.6	67500						
88-148, Mt. Polley		23600	33	320	0.2	<5	<0.1	<0.1	206000						
89-143, Mt. Polley		6200	17	83	0.7	<5	<0.1	0.2	11500						
89-150, Mt. Polley		1600	7	23	0.3	<5	<0.1	0.1	19100						

(1) This study, (2) Augé *et al.* (2002), (3) Thompson *et al.* (2001). Abbreviations: ccs: composite chip sample, mhs: mineralized hand-specimen.

44 ppm, Ag between 17 and 186 ppm, and an extremely high Cu (the maximum value of 49.0 wt.% reflecting the very high proportion of chalcopyrite and bornite in these samples).

THE PLATINUM-GROUP MINERALS

The presence of PGM is characteristically related to the Stage-1 mineral assemblage, dominated by chalco-

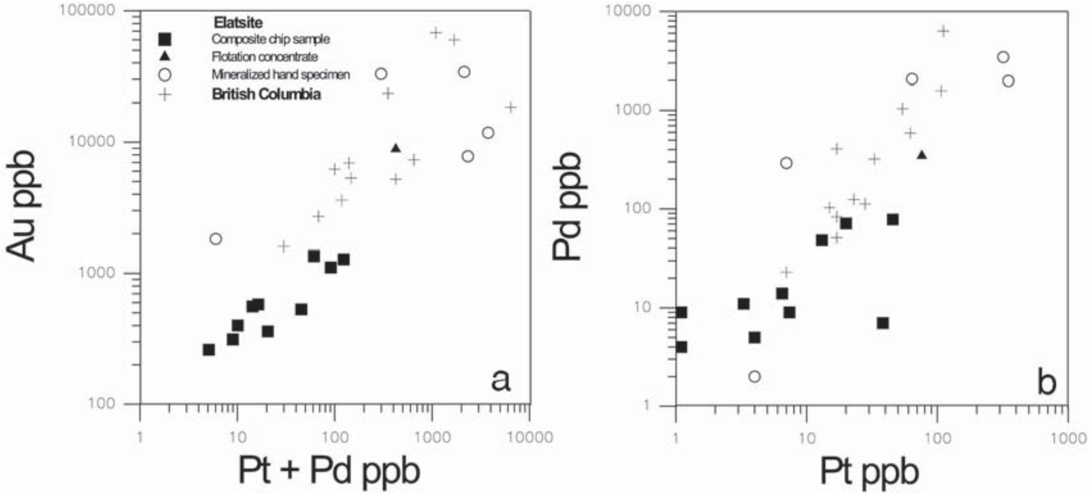

FIG. 2. (Pt + Pd) – Au (a) and Pt – Pd (b) correlation diagrams for various samples from the Elatsite (this study) and British Columbia deposits (after Thompson *et al.* 2001).

TABLE 3. MINERAL ASSEMBLAGES OBSERVED IN THE SAMPLES FROM ELATSITE, WITH RELATIVE ABUNDANCES OF THE DIFFERENT PHASES

	Stage 1											Stage 2
Sample	EL-14	EL-15	EL-16	EL-17	EL-18	256-B1	256-1/2	256-A1	256-A3	256-A4	Ecn	207-A
Chalcopyrite	A	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA
Bornite	A	A	A	A	A	C	A	AA	A	A	C	
Pyrite												VC
Covellite	C	T	T	T	T							
Magnetite	A	VC	VC	VC	VC	C	VC				R	
Hematite	C	C	C	C	C							
Au–Ag alloy		R		VC	C			T				
Molybdenite				R								
Tennantite								C	C	R		
Merenskyite		R	R	R	VC	R	C	R	R	T	C	R
Palladoarsenide			T			T	T					
Moncheite										T		
Hessite		VC	VC	VC	VC	R	C	R	R		C	R
Clausthalite		VC		R	C	T				T		
Bodhanowiczite				T		T						
Carrollite-siegenite		C	C	VC	VC	R		C	C	R		
Co-rich gersdorffite									T			

AA: very abundant, A: abundant, VC: very common, C: common, R: rare, T: trace.

pyrite – bornite – magnetite (Tables 1, 3). Microscopically, the bornite and chalcopyrite exhibit a myrmekitic intergrowth, and the magnetite, partly or totally replaced by hematite, shows evidence of replacement by sulfides (Fig. 3a); a similar observation was reported by Tarkian *et al.* (1991) for the Skouries deposit in Greece. The PGM and other minor phases are scattered throughout the samples as inclusions in chalcopyrite and bornite. Like the magnetite, the thiospinels and other Co–Ni–As phases are partly replaced by sulfides (Fig. 3b). The presence of PGM is not at all systematic in the Stage-1 magnetite – chalcopyrite – bornite assemblage, suggesting an apparently erratic character of the PGM distribution at the deposit scale.

Merenskyite

Merenskyite occurs as euhedral acicular grains of 4 to 80 μm, included in chalcopyrite and bornite or at the interface between these two phases (Figs. 3c, d, e, f). About 50 analyses of merenskyite were made on 21 grains from 10 samples of Stage 1 and one sample of Stage 2 (Tables 3, 4). Most of the compositions are rather homogeneous, close to the ideal composition $PdTe_2$. Some, however, contain small amounts of Pt (0–6.6 wt.%, ave. 2.2), Ni (0–7.3 wt.%, ave. 2.6), Cu (0.4–2.9 wt.%, ave. 1.1) and Ag (0–3.1 wt.%, ave. 0.4). The Ni–Pd–Pt triangular diagram (Fig. 4) confirms a solid solution between $PdTe_2$ and $NiTe_2$ (melonite), with up to $Pd_{0.56}Ni_{0.44}Te_{2.00}$, although Ni-rich merenskyite seems to be restricted to one sample (EL–16).

Unlike merenskyite from other contexts, the Elatsite merenskyite has very low amounts of Bi (0– 2.16 wt.%, ave. 0.56) and Se (Table 4). Although Cabri *et al.* (1979) reported Bi-poor grains in samples from the Stillwater Complex, these occur together with Bi-rich grains. Bismuth-rich merenskyite (12.3–36.4 wt.% Bi) occurs at Sudbury (Cabri & Laflamme 1976), and Gervilla & Kojonen (2002) reported high amounts of Bi in merenskyite from the Keivitsansarvi deposit, in Finland, where it occurs with other Bi-rich PGM such as michenerite (PdTeBi). Johan (1989) mentioned Bi-free Se-bearing merenskyite from a uranium vein-type deposit in the Bohemian Massif. Merenskyite has also been described in alkaline porphyry deposits from British Columbia (Nixon & Laflamme 2002, Nixon *et al.* 2004).

Palladoarsenide

According to Strashimirov *et al.* (2002), palladoarsenide is associated with the Stage-2 pyrite–chalcopyrite paragenesis. We found several anhedral grains of palladoarsenide (Tables 3, 5, Fig. 3g, h, i), however,

TABLE 4. SELECTED ELECTRON-MICROPROBE DATA ON MERENSKYITE FROM THE ELATSITE DEPOSIT

Sample	256-1/2	256-1/2	256-1/2	256-1/2	256-B1	256-B1	Ecn	256-A3	207-A	EL-16	EL-16	EL-18	EL-18	EL-18	EL-18	EL-18	EL-18	EL-18	EL-18
Anal. no.	32	36	39	43	61	63	64	69	77	9	11	30	37	41	42	46	86	87	90
Pt wt%	0.12	0.51	0.65	0.93	-	0.55	0.80	5.31	1.50	1.77	0.85	2.46	6.14	6.63	5.50	3.86	1.40	0.13	1.82
S	-	-	0.59	-	-	-	-	-	-	-	-	-	-	0.17	0.59	-	-	-	-
Fe	-	0.59	0.72	0.61	0.87	0.60	0.13	-	0.54	1.02	0.57	0.11	0.65	1.55	1.67	0.73	0.15	1.35	0.00
Pd	26.74	24.61	23.41	24.34	22.33	26.16	27.55	17.75	27.07	15.75	18.08	23.75	21.33	21.02	20.68	23.74	24.94	27.16	24.72
Ni	1.01	2.43	2.71	2.24	3.60	1.43	0.86	4.42	-	6.67	6.08	1.93	1.66	1.55	1.58	2.07	2.14	1.23	1.87
Pb	-	-	0.05	-	-	-	-	0.13	-	-	-	-	-	0.00	-	-	-	0.08	-
Cu	0.37	0.93	1.35	0.98	1.48	0.73	1.02	0.73	0.89	1.09	0.66	0.58	0.89	1.03	1.56	1.05	1.53	0.43	0.84
Sb	0.31	0.27	0.37	0.23	0.30	0.22	0.25	0.30	0.38	0.21	0.31	0.28	-	0.26	0.20	0.28	0.24	0.28	0.25
Co	-	-	-	-	-	-	-	-	-	-	0.11	-	-	-	-	0.11	-	-	-
Au	-	-	-	-	-	-	-	-	-	-	-	-	0.18	0.53	-	-	-	-	-
Te	69.53	71.06	70.93	70.59	72.65	71.05	71.73	71.18	68.55	71.50	72.61	70.12	68.99	68.54	68.17	69.73	71.03	71.20	70.73
Bi	0.46	1.04	0.30	0.15	-	0.21	0.14	0.51	0.63	1.97	0.43	1.07	0.30	0.41	-	0.70	0.50	0.37	0.60
Ag	2.31	-	-	0.91	-	-	-	-	1.63	0.40	0.43	0.46	0.41	0.42	0.41	0.45	-	-	-
Total	100.84	101.45	101.07	100.96	101.24	100.95	102.49	100.33	101.18	100.48	100.17	100.74	100.79	102.11	100.47	102.85	101.93	102.22	100.83
Pt *apfu*	0.075	0.304	0.386	0.564	0.000	0.335	0.477	3.227	0.939	1.055	0.506	1.513	3.858	4.139	3.401	2.335	0.828	0.079	1.102
S	-	-	2.127	-	-	-	-	-	-	-	-	-		0.627	2.207	-		-	-
Pd	30.483	27.084	25.299	27.138	24.220	29.123	30.136	19.777	31.038	17.229	19.718	26.742	24.553	24.075	23.469	26.346	27.161	30.184	27.458
Ni	2.082	4.848	5.308	4.535	7.104	2.885	1.705	8.915	-	13.214	12.023	3.930	3.468	3.209	3.250	4.165	4.215	2.467	3.769
Cu	0.706	1.721	2.445	1.826	2.692	1.367	1.868	1.368	1.713	2.000	1.203	1.092	1.718	1.983	2.965	1.951	2.794	0.806	1.570
Sb	0.304	0.261	0.349	0.219	0.285	0.214	0.235	0.293	0.383	0.202	0.294	0.276		0.259	0.193	0.274	0.226	0.270	0.240
Te	66.083	65.199	63.924	65.636	65.699	65.958	65.498	66.132	65.558	65.205	66.019	65.837	66.228	65.468	64.515	64.532	64.498	65.983	65.522
Bi	0.266	0.584	0.162	0.082	-	0.118	0.080	0.288	0.369	1.095	0.237	0.611	0.175	0.239	-	0.395	0.277	0.211	0.339

-: below detection limit.

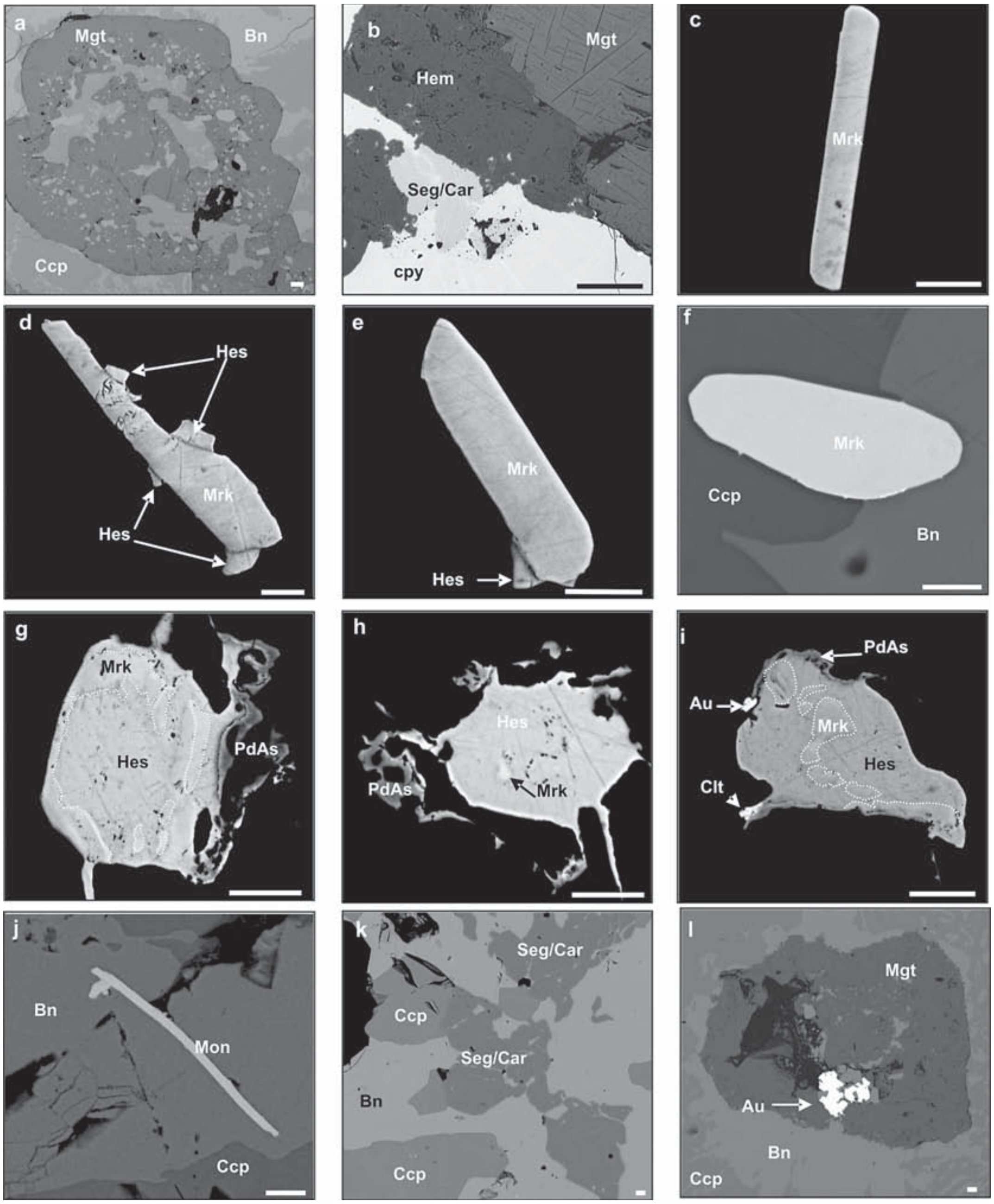

FIG. 3. SEM microphotographs of the ore minerals at Elatsite. (a) Magnetite partly replaced by a chalcopyrite–bornite assemblage (sample EL–17). (b) Magnetite partly replaced by hematite; the light grey crystal corresponds to carrollite–siegenite (sample EL–18). (c) to (f) Merenskyite crystals in the chalcopyrite–bornite assemblage (sample EL–18); in (d) and (e), the merenskyite is associated with hessite; in (f) an unidentified Bi-rich phase (in white) rims the lower part of the merenskyite grain. (g) to (i) Hessite with merenskyite "relics"; (g) and (h) sample 256–1/2, (i) sample EL–16; the hessite–merenskyite assemblage is rimmed by palladoarsenide; in (i), tiny grains of Au–Ag alloy and clausthalite are observed. (j) An acicular crystal of moncheite in bornite (sample 256–A4). (k) A chalcopyrite – bornite – carrollite–siegenite assemblage (sample EL–15). (l) Grain of Au–Ag alloy included in magnetite (sample EL–17). Symbols: Mrk: merenskyite, Hes: hessite, Ccp: chalcopyrite, Bn: bornite, Mon: moncheite, PdAs: palladoarsenide, Au: Au–Ag alloy, Mgt: magnetite, Hem: hematite, Seg/Car: siegenite–carrollite solid-solution series, Clt: clausthalite. Scale bar: 10 μm.

in samples characteristic of the Stage-1 PGE-rich magnetite – chalcopyrite – bornite paragenesis, but none in the Stage-2 paragenesis. The composition varies between $Pd_{2.03}(As_{0.92}Sb_{0.04}Te_{0.01})$ in sample 256–B1 and $Pd_{2.00}(As_{0.99}Sb_{0.01})$ in sample EL–16. The mineral forms anhedral wire rimming large grains of hessite (up to 20 µm) intimately associated with merenskyite. The presence of a significant Ag content in the palladoarsenide (Petrunov *et al.* 1992) was not confirmed in this study.

The only other As-bearing phase observed at Elatsite is tennantite, which appears in late veinlets not clearly located in the paragenetic succession. These veinlets cut the Stage-1 and Stage-2 mineralogical assemblages, and locally form tennantite – pyrite – chalcopyrite assemblages.

Palladoarsenide is typical in magmatic PGE deposits, such as the disseminated Cu–Ni sulfide ore at Noril'sk, where it was first described (Begizov *et al.* 1974, Cabri 2002), and the JM Reef of the Stillwater Complex (Todd *et al.* 1982). It has also been described in hydrothermal deposits such as the Lac des Iles Complex (Cabri 2002). Its composition, as reported in the literature, is close to the ideal, Pd_2As (Cabri 2002). Begizov *et al.* (1974) reported minor Ag and Au (3.2 and 1.4 wt.%, respectively), and Vuorelainen *et al.* (1982) reported 3.9 wt.% Sb and 1.1 wt.% Cu for palladoarsenide "in association with pyrite" from the Konttijärvi intrusion (intensely metamorphosed gabbro in Finland). With 1.2 wt.% Cu and 1.5 wt.% Sb, the composition obtained here is similar to that given by Vuorelainen *et al.* (1982).

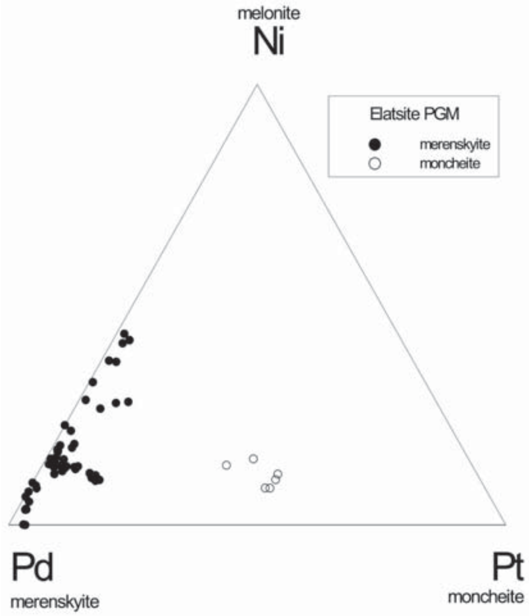

FIG. 4. Ni–Pd–Pt diagram (atom proportions) for merenskyite and moncheite from the Elatsite deposit.

Moncheite

The composition obtained on one grain in sample 256–A4 (Tables 3, 5, Fig. 3j) is intermediate between that of moncheite ($PtTe_2$) and that of merenskyite ($PdTe_2$), with a very small amount of Ni (Fig. 4). Note, however, that the compositions obtained all are slightly contaminated by the host chalcopyrite; the average corrected composition, obtained from results of seven analyses, is $(Pt_{0.47}Pd_{0.42}Ni_{0.09})_{\Sigma 0.98}(Te_{2.00}Sb_{0.01}Bi_{0.01})_{\Sigma 2.02}$. Tarkian *et al.* (2003) obtained a true end-member composition of merenskyite from the Elatsite suite, as well as a continuous merenskyite – moncheite solid-solution, with a maximum Pt content corresponding to $(Pd_{0.69}Pt_{0.39})Te_{1.92}$, *i.e.*, a rather platinian merenskyite.

Moncheite is a common PGM in magmatic Cu–Ni sulfide deposits worldwide, commonly found in chalcopyrite. It has also been described in the metagabbro-hosted hydrothermal copper ore of the New Rambler mine, Wyoming, USA (McCallum *et al.* 1976). Contrary to the compositions obtained here, most of the published data on moncheite compositions feature the presence of high amounts of Bi (6.1–28.3 wt.%, in Cabri 2002). Only two compositions given by Cabri (2002) show a low (<1.5 wt.%) Bi content; both are from the Stillwater Complex (Cabri *et al.* 1979). Augé *et al.* (2002) also gave compositions with a low Bi content (around 2 wt.%) for moncheite with a low Pd content (<1 wt.%), *i.e.*, close to the $PtTe_2$ end member, in the Baula–Nuasahi Complex, in India.

Undetermined Pd–Ag–Te–Bi phase

This phase occurs in the composite grain "c1" of sample 256–B1, associated with merenskyite, palladoarsenide and hessite. It is the only composition of the assemblage to show Bi (Table 5). The average composition obtained, expressed in atom proportions, is $Pd_{0.25}Ag_{0.13}Te_{0.43}Bi_{0.18}$, which could correspond to the stoichiometry $(Pd,Ag)(Te,Bi)_2$. Note that a minor amount of Ag was detected in the merenskyite.

THIOSPINEL AND Ni–Co–(As) PHASES

Thiospinel and other Co–Ni-bearing phases were investigated by Dragov & Petrunov (1998), who described linnaeite $[Co^{2+}Co^{3+}{}_2S_4]$, carrollite $[Cu(Co,Ni)_2S_4]$, siegenite $[CoNi_2S_4]$ and rammelsbergite $[NiAs_2]$. In the samples studied here, these phases appear as large grains (200 µm) included in Stage-1 chalcopyrite and bornite (Tables 1, 3 and 6, Figs. 3b, k), and show evidence of replacement of sulfide. In spite of the fact that thiospinel and the PGM occur in the same samples, nowhere were relationships seen between the two minerals that would establish a relative chronology in their crystallization.

SELENIDE AND TELLURIDE MINERALOGY

Pb and Ag–(Bi) selenides

Widespread micrometric clausthalite (PbSe) grains are included in chalcopyrite and bornite (Tables 1, 3). An Ag–Bi–Se phase with a formula close to that of bohdanowiczite ($AgBiSe_2$) also was identified in one sample (256–B1), in contact with a grain of merenskyite (Table 6).

Ag tellurides

Like the Pb selenides, grains of hessite with a composition close to the ideal Ag_2Te (Table 6) appear mainly as micrometric inclusions in chalcopyrite and bornite. The only exception concerns larger grains (up to 20 μm) associated with the palladoarsenide–merenskyite assemblage (Figs. 3 g, h, i). Tarkian *et al*. (2003) noted that hessite in the Elatsite deposit is commonly associated with merenskyite, surrounding or replacing it. They also described lamellar inclusions of hessite in merenskyite (interpreted as due to exsolution). This local close association between the two minerals is confirmed in the present study (Figs. 3d, e), but without any evidence of replacement textures.

OTHER UNCOMMON MINERALS

Au–Ag alloy

Grains of a Au–Ag alloy occur as large (up to 200 μm) inclusions, commonly in contact with magnetite crystals and as wires in bornite (Fig. 3l). The compositions show variable amounts of Ag (9.1–20.7 wt.%) and Cu (0.1–1.7 wt.%, see Table 5).

Molybdenite

Flakes of molybdenite (up to 160 μm) were observed in sample El–17.

TABLE 5. SELECTED ELECTRON-MICROPROBE DATA ON Pd MINERALS AND GOLD FROM THE ELATSITE DEPOSIT

	Un1	moncheite				palladoarsenide			Au–Ag alloy				
Sample	256-B1	256-A4	256-A4	256-A4		256-B1	EL-16		EL-16	EL-18	EL-18	EL-18	EL-18
Anal. no.	56	48	51	53		55	20		7	33	34	93	94
Pt wt%	0.54	20.20	20.49	21.79		0.08	0.06		-	-	-	-	-
S	-	2.75	2.73	1.06		-	-		0.67	-	-	-	-
Fe	0.14	1.25	1.19	1.20		0.39	3.15		0.18	0.64	0.28	-	-
Pd	19.76	10.26	9.26	10.63		70.95	71.10		0.97	-	0.19	-	-
As	-	-	-	-		22.51	24.80		0.24	-	-	-	-
Ni	-	1.07	1.47	1.13		0.87	-		-	-	-	-	-
Pb	0.16	0.28	0.04	0.12		-	-		-	-	-	-	-
Cu	0.35	8.89	8.57	5.11		1.19	0.32		1.05	0.69	0.11	0.10	0.27
Sb	0.10	0.30	0.35	0.31		1.48	0.15		-	-	-	-	-
Se	0.23	-	-	-		-	-		-	-	-	-	-
Co	-	-	-	-		-	-		-	-	-	-	-
Au	-	-	-	-		-	-		75.04	88.82	89.54	89.98	89.82
Te	41.79	55.30	57.39	60.01		0.31	-		-	-	0.12	-	-
Bi	28.27	0.57	0.46	0.48		-	-		-	0.12	-	-	-
Rh	-	-	-	0.17		-	-		0.13	-	-	-	-
Ag	10.48	-	-	-		0.43	1.62		20.36	9.30	9.11	9.12	9.35
Total	101.82	100.86	101.95	102.01		98.20	101.19		98.65	99.56	99.36	99.19	99.44
Pt *apfu*	0.367	15.761	15.635	15.820	As	30.595	33.083	Cu	2.806	1.984	0.332	0.275	0.780
Pd	24.610	14.683	12.949	14.144	Pd	67.921	66.793	Au	64.995	82.287	84.052	84.150	83.370
Ni	-	2.785	3.724	2.729	Sb	1.236	0.124	Ag	32.199	15.729	15.616	15.574	15.851
Cu	0.734	-	-	-	Te	0.247	-						
Sb	0.111	0.380	0.424	0.364									
Te	43.386	65.979	66.939	66.619									
Bi	17.924	0.412	0.328	0.323									
Ag	12.868	-	-	-									

-: below detection limit.

TABLE 6. SELECTED ELECTRON-MICROPROBE DATA ON RARE SULFIDES, TELLURIDES AND SELENIDES FROM THE ELATSITE DEPOSIT

	Co-rich Gdf	Sie	carrollite			hessite						clausthalite		Boh
Sample	256-A3	256-A1	El-18	El-18		256-1/2	256-1/2	256-B1	Ecn	El-16		256-B1		256-B1
Anal. no.	71	80	83	97		27	33	57	66	17		59		
S wt%	20.01	42.28	41.57	41.08		0.03	0.12	0.25	-	-		-		0.28
Fe	0.31	0.26	-	-		0.17	0.11	1.03	0.35	0.39		-		1.33
As	45.12	-	-	-		-	-	-	0.13	-		-		-
Ni	21.39	30.75	2.85	3.66		-	-	-	-	-		-		-
Pb	-	-	-	-		-	-	-	-	-		67.96		0.17
Cu	4.75	2.67	17.51	16.99		0.21	0.66	1.10	0.94	0.16		-		1.86
Sb	-	-	-	-		0.17	0.10	0.21	0.13	0.36		-		-
Se	0.52	0.52	-	-		0.16	0.12	0.31	0.42	-		30.24		33.01
Co	11.03	23.92	37.44	37.04		-	-	-	-	-		-		-
Te	-	-	-	-		37.73	37.38	37.92	41.98	40.01		0.36		3.45
Bi	-	-	-	-		-	-	-	0.10	-		1.78		40.28
Ag	-	-	-	-		63.39	61.16	60.62	58.74	59.73		-		20.47
Total	103.13	100.4	99.37	98.77		101.83	99.53	101.17	102.79	100.65		100.34		100.85
S *apfu*	33.450	57.200	57.440	57.090	S	0.095	0.415	0.879	0.149	0.125	Pb	45.510	Se	52.221
Fe	0.300	0.200	-	-	As	-	-	0.124	0.190	-	Se	53.020	Bi	24.078
As	32.280	-	-	-	Sb	0.160	0.093	0.194	0.122	0.338	Te	0.390	Ag	23.701
Ni	19.530	22.730	2.150	2.780	Te	33.387	33.890	34.176	37.490	35.986	Bi	1.179		
Cu	4.010	1.820	12.210	11.920	Ag	66.358	65.602	64.627	62.050	63.550				
Se	0.350	0.280	-	-										
Co	10.030	17.610	28.140	28.010										

-: below detection limit. Symbols used: Gdf: gersdorffite, Sie: siegenite, Boh: bohdanowiczite.

DISCUSSION

All the PGM described here from the Elatsite suite, along with other minerals of the Stage-1 magnetite – chalcopyrite – bornite assemblage, such as carrollite, siegenite, rammelsbergite and Co-rich gersdorffite, show many similarities with hydrothermal PGE–Cu–Ni sulfide mineralization in a mafic–ultramafic environment. These similarities bring into question the possibility that Elatsite is a typical "PGE-bearing porphyry copper deposit" (Tarkian *et al*. 2003). Moreover, although Pt and Pd are distributed irregularly through the deposit, they are preferentially associated with the magnetite – chalcopyrite – bornite assemblage, an assemblage that is far from being systematically PGE-rich.

In order to trace the origin of the local PGE enrichment in the specific mineral assemblage of the Elatsite deposit, we compared it against the well-constrained environment of PGE mineralization at the Baula–Nuasahi Complex in India, studied in detail (Augé *et al*. 2002, Augé & Lerouge 2004). Like the Elatsite mineralization, the Baula–Nuasahi Cu–Ni–Co–PGE mineralization is hydrothermal, but in a gabbro environment. The two environments have many similarities in terms of minor sulfides, relative concentration of Pd, and the association of Pd with Cu.

Mineralization at Baula–Nuasahi

The Baula–Nuasahi Complex, on the southern flank of the Singhbhum Archean nucleus, northeastern India, exposes a series of Meso-archean igneous suites comprising: (1) a petrographically homogeneous gabbro–anorthosite unit, (2) a peridotite unit 150–180 m thick, with three layers of chromitite; (3) a pyroxenite unit 80 m thick, and (4) the Bangur gabbro (~3.1 Ga), which defines an oblong intrusion cross-cutting the older igneous suites in the southern part of the complex. The Bangur gabbro has a curvilinear northwest-trending apophysis, 2 km long and up to 40 m wide, consisting entirely of a magmatic breccia with ultramafic and chromitite wallrock clasts in a gabbro matrix.

The mineralization at Baula–Nuasahi occurred at a relatively high temperature from mafic-magma-derived fluids in the breccia apophysis. The breccia matrix, which contains the mineralization, underwent intense hydrothermal alteration, the breccia blocks being much less affected. Oxygen, hydrogen and sulfur isotopes show that the hydrothermal fluids were derived from magmatic volatile phases with no contribution from an external source, and oxygen isotope geothermometry reveals that the progressive hydrothermal alteration occurred during cooling from a 700–1000°C level down to the interval 500–600°C. The pervasive hydrothermal alteration in the apophysis likely represents upward channeling of late-magmatic fluids along a narrow, near-vertical, subplanar conduit that led away from the main magma-chamber (Augé & Lerouge 2004).

The base-metal sulfide (BMS) content of the mineralized samples varies from disseminated to rare submassive. The PGM are systematically associated with the BMS, and the close association of these two assemblages with hydrous silicates not only confirms the hydrothermal origin of the Cu–Ni–Co–PGE mineralization, but indicates that the precious and base metals were derived from the same fluids.

Precious-metal concentration

The 11 samples from the BMS-enriched breccia-zone matrix at Baula–Nuasahi (Table 2) are all characterized by a systematic PGE enrichment, with a Pd:Pt ratio varying between 2.0 and 15.6. Contrary to the Elatsite mineralization, they show relatively high values in Os (3–30 ppb), Ir (7–42.5 ppb, with the exception of 113 ppb in BLR96), Ru (37–341 ppb) and Rh (16–91 ppb, with the exception of 1170 ppb in BLR96). Sample BLR96 has the highest PGE content, and also yields the highest Cu value; it has, moreover, been demonstrated that the PGE content correlates with the proportion of the (chalcopyrite-dominant) BMS (Augé *et al*. 2002).

The Ni and Co contents of the Baula–Nuasahi massive sulfides (1800 to 7300 ppm and 120 to 290 ppm, respectively) are much higher than at Elatsite, but Cu is lower, with a maximum of 19.5% (submassive chalcopyrite). High Cr values (up to 10%) have been recorded in the mineralized breccia samples, but only because chromite grains had been mechanically incorporated in the breccia matrix (and subsequently altered by the hydrothermal mineralizing fluids).

Mineralogy

The PGM in the PGE–BMS mineralization at Baula–Nuasahi are clearly dominated by Pd phases in antimonide, telluride and antimonotelluride form, followed by Pt arsenide, Ru sulfide and Ru sulfarsenide. Most of the PGM are included in (or adjacent to) BMS. In rare cases, they are found in the hydrous silicates or accompanying trails of BMS, and their origin is clearly connected to that of the BMS. The Pd minerals at Baula–Nuasahi cover a large compositional range that includes sudburyite (PdSb), mertieite II (Pd_8Sb_3), an unnamed Pd(Sb–Te,Bi) mineral, Bi-rich sudburyite, and merenskyite (with Sb-rich and Bi-rich varieties).

By comparison, the Elatsite PGM are restricted to tellurides (and rare arsenides). Moreover, these tellurides (moncheite and merenskyite) are characteristically impoverished in Bi and Sb, indicating a low concentration of these elements in the fluid from which the mineralization was derived. Arsenic occurs as Pd arsenide at Elatsite, and as Rh sulfarsenide at Baula–Nuasahi.

The PGE–BMS mineralization at Baula–Nuasahi, like that at Elatsite, is characterized by a Co–Ni–As–(Sb) signature, but with a different mineralogical expression. Chalcopyrite and pyrrhotite are the dominant species

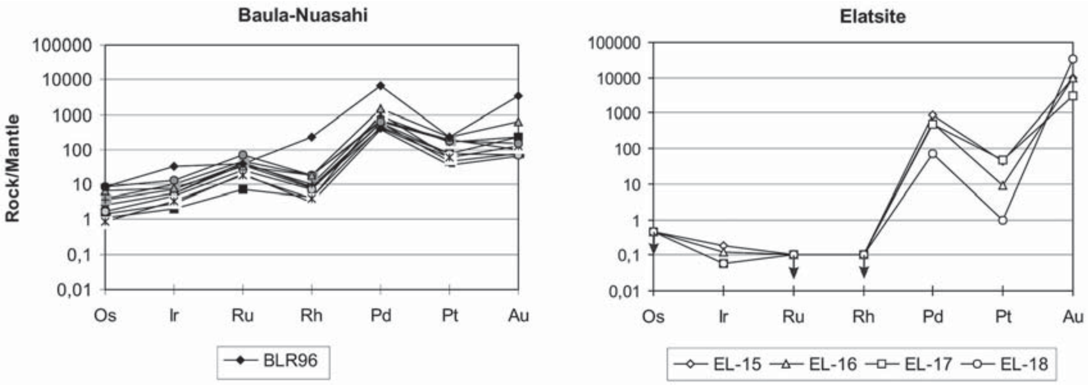

FIG. 5. Mantle-normalized platinum-group-element content for PGE-mineralized samples from the Baula–Nuasahi breccia zone (India) and the Elatsite deposit. Values for Os, Ru and Rh in the Elatsite samples have been taken at half the detection limit (respectively 1.5, 0.5 and 0.5 ppb, arrow). Normalization values are from Barnes & Maier (1999).

of BMS, associated with minor amounts of bornite and pyrite. Nickel, Co, As and Sb are expressed as pentlandite, millerite and violarite, and as minerals belonging to the cobaltite–gersdorffite solid-solution series. Traces of maucherite, nickeline, molybdenite, galena, heazlewoodite and orcelite also are observed. The pyrite crystals are characterized by significant Co (up to 5.4 wt.%), Ni (up to 2.32%) and As (up to 1.65%).

Distribution of the PGE

Differences between the Baula–Nuasahi and Elatsite environments are clearly revealed in the mantle-normalized PGE diagram (Fig. 5). Compared to the Baula–Nuasahi samples, the Elatsite samples show considerable impoverishment in Os to Rh, as well as a flat pattern (which is not significant, with the values being below the detection limit), and then relatively parallel patterns from Rh to Au. Note that Baula–Nuasahi sample BLR96, with very high PGE values, is discordant within the Baula–Nuasahi trend.

The patterns given by the two deposits are in good agreement with the mineralogical observations, *i.e.*, an abundance of Pd minerals, rare Pt minerals, and the presence of Au in both environments, with Os-, Ir-, Ru- and Rh-bearing minerals lacking in the Elatsite mineralization and rare in the Baula–Nuasahi mineralization. There is thus no reason to envisage the presence of PGE in solid solution in the base-metal minerals.

When comparing the two environments, it appears that the Pd in the Baula–Nuasahi Complex is dominantly in the form of the antimonide, whereas in the Elatsite mineralization it is dominantly a telluride, and that the Baula–Nuasahi Complex contains Os-, Ir-, Ru- and Rh-bearing minerals, which are totally lacking at Elatsite.

Comparison with other PGE porphyry copper deposits

The mineral assemblages of two other PGM-bearing porphyry systems described in the literature, Skouries in Greece (Tarkian *et al.* 1991, Eliopoulos & Economou-Eliopoulos 1991, Economou-Eliopoulos & Eliopoulos 2000) and Santo Tomas II in the Philippines (Tarkian & Koopmann 1995), are summarized along with the Elatsite data in Table 1. Data from the Buchim (Macedonia: Petrunov *et al.* 2001), Mamut (Malaysia: Tarkian & Stribrny 1999) and Majdanpek (Serbia: Tarkian & Stribrny 1999) deposits are too limited to really help in a comparison.

Comparing the three deposits mineralogically (Table 1), it seems that for all three, the precious-metals mineralogy is dominated by Pd species (and more especially by Pd tellurides, dominantly merenskyite), Ag (hessite) and Au (petzite). Selenides and thiospinels have not been reported from Skouries and Santo Tomas II.

The most striking aspect of the Elatsite mineralization, compared to other "classical" porphyry deposits, is not only the uncommon presence of PGM, but also that of selenides, tellurides and Co-, Ni-(As)-bearing phases. Moreover, the thiospinels, Te- and Se-bearing phases and Au, where present, occur together with the PGM, suggesting cogenesis.

It should also be noted that nearly all the porphyry deposits of the Bulgarian Panaguyrishte district are characterized by such anomalous elements: Co- and Ni-bearing pyrite at Medet (Strashimirov 1982) and Radka (Kouzmanov *et al.* 2002), cobaltite, linnaeite and millerite at Tsar Assen (Bogdanov & Bogdanova 1978), and siegenite and bravoite at Assarel (Bogdanov 1987).

Cases of Cu–Au–PGE mineralization have also been described from alkaline plutonic complexes, *i.e.*, composite formations of varied age, with associated igneous rocks ranging from granitic to mafic and ultramafic. High PGE contents seem to be restricted to the complexes with a granite – gabbro – ultramafic rock succession, and are considered to be related to an alkaline porphyry deposit model. For example, an extremely high abundance of Pd and high Pd/Pt values are reported in the bornite occurrence hosted by a biotite – K-feldspar pegmatite vein at Friday Creek, in British Columbia (Nixon & Laflamme 2002). Not only are Pd tellurides the predominant PGM, but Nixon & Laflamme (2002) showed images of merenskyite laths in bornite that are surprisingly similar to the laths at Elatsite (Figs. 3c, d, j); these authors also mentioned the presence of temagamite, Pd_3HgTe_3, and kotulskite, PdTe.

Thompson *et al.* (2001) reported PGE concentrations at five alkaline porphyry deposits from British Columbia. The samples they studied were mineralized composites from drill holes, crushed and prepared for making heavy-mineral concentrates. The concentrates contain a mixture of sulfides (bornite, chalcopyrite and pyrite) and oxides (magnetite and hematite). The results from three deposits are given in Table 2 and plotted on Figure 2. The Pt, Pd and gold contents and distribution appear similar to those of the Elatsite deposit. The values obtained for the other PGE are extremely low (generally below 1 ppb; Table 2). Further mineralogical studies by Nixon *et al.* (2004) revealed merenskyite, temagamite, mertieite II, kotulskite and Pt–Pd-bearing melonite in various samples from the same deposits, and underline the role of pyrite in the concentration of the PGE; up to 42 ppm Pd was detected in solid solution in pyrite. Here again, the nature, mode of occurrence and habitus of the PGM present striking similarities with those of the Elatsite deposit.

The presence of hessite, clausthalite and carrollite associated with a pyrite – chalcopyrite – bornite – molybdenite assemblage is also reported in Cu-porphyry-type deposits of the Guichon Creek batholith and Copper Mountain stock in British Columbia (Johan & Le Bel 1980).

The model proposed by Thompson *et al*. (2001) to account for the occurrence of PGE in alkaline porphyry deposits is based on the fact that alkaline magma originates from an enriched source-region in the mantle. The alkaline (oxidized) nature of the magma prevents early fractionation of the sulfides, whereupon the precious metals remain in the magma to be subsequently transported into the porphyry environment by magmatic-hydrothermal fluids. A preconcentration of the PGE in magmatic sulfides, with subsequent remobilization due to hydrothermal processes, is also suggested.

A preconcentration episode is also proposed by Watkinson *et al*. (2002) for the Cu–PGE mineralization in the alkaline Coldwell Complex, with the formation of PGE-bearing disseminated magmatic sulfides in gabbroic rocks. The late-stage exsolution of the magmatic fluids, indicated by alteration of the silicates, would remobilize the disseminated sulfides and reprecipitate the PGE–Cu mineralization with hydrous minerals at intermediate to low temperatures.

The Elatsite model

It is well established experimentally that Pd and Pt are much more soluble and remobilizable under hydrothermal and low-temperature conditions than are the other PGE, and that chloride is one of the favored forms of PGE transport in such solutions. The solubility sequence for the PGE at 25°C is Pd > Pt > Os > Ir (Mountain & Wood 1988); at higher temperatures (300–400°C), Pt and Pd only become highly soluble in very acidic and oxidizing Cl-rich aqueous fluids (Wood 1987, Gammons *et al*. 1992, Gammons 1996). The common factor in PGM derived from hydrothermal processes (whatever the temperature of formation and origin of the fluid) seems to be the association of Pd (and, to a lesser extent, Pt) with elements such as Te, Sb, Bi, As, Hg, Sn, *etc*. It is therefore reasonable to envisage that these elements are concentrated in hydrothermal solutions (Evstigneeva & Tarkian 1996) and that they precipitate as complex PGM.

At this stage of the discussion, the main questions that arise concern (1) the possible source of the PGE in the Elatsite system, and (2) the origin of the "mafic assemblage" (*i.e*., the PGM and the Co–Ni minerals). Does it result from a hydrothermal remobilization of pre-existing concentrations of metal (as magmatic sulfides) or does it represent a direct crystallization of minerals from a hydrothermal solution?

We can envisage a mantle contribution in the Elatsite magmatism on the basis of the isotope data that indicate (1) an upper mantle origin for the parent magma of the Srednogorie intrusive rocks in an arc–subduction environment (Zagorcev & Moorbath 1987, Zimmerman *et al*. 2003), and (2) an enriched source in the mantle, with crustal contamination, for the Elatsite porphyry rocks (Von Quadt *et al*. 2002a). Moreover, the presence of mafic (gabbroic) rocks is known both in the environment of mineralization and more generally within the Panagyurischte district. In addition, Von Quadt *et al*. (2001) recognized fined-grained "basaltoid" dykes as part of the Elatsite deposit.

Mungall (2002) discussed the conditions under which large Au and Cu deposits can be generated in suprasubduction zones. The first requirement is the availability of chalcophile elements [such as Cu, and possibly a mobilization of Ni and PGE (J.E. Mungall, written. commun.)] to the arc magma in the mantle source-region. This transfer involves oxidation of the mantle wedge to relatively high values, which according to Mungall (2002) is achieved by ferric iron carried in solution by the slab-derived partial melts. Thus, arc magmas with a high mineralizing potential will either have adakitic, sodic-alkaline or potassic-ultrapotassic affinities, corresponding to a specific tectonic setting such as the subduction of very young lithosphere, or result from very slow or oblique convergence, flat subduction, or the cessation of subduction.

We thus conclude that under specific conditions of suprasubduction zone settings, the PGE may well be mobilized from a mantle source-region. For the British Columbia porphyries, Thompson *et al*. (2001) suggested that the alkaline nature of the magma prevented the early fractionation of the sulfides, thus providing a possible explanation of the PGE enrichment in porphyry deposits.

The geodynamic evolution of the Panagyurishte district is still, as far as we know, not very well constrained. Lips (2002) has nevertheless shown that the associated calc-alkaline magmatism corresponds to the first magmatic expression of the subduction; interestingly, nearly all the deposits of the district are marked by this mantle signature (with the presence of minerals of Co, Ni and the PGE).

In their model of the Elatsite deposit, Tarkian *et al*. (2003) described three types of fluid-inclusion populations in the quartz veinlets associated with the PGM – magnetite – bornite – chalcopyrite assemblage of Stage 1, and the chalcopyrite – pyrite assemblage of Stage 2. All three types are found in the two assemblages, suggesting that the fluids involved were similar for both. Based on fluid-inclusion data, Tarkian *et al*. (2003) concluded that Pd and Pt were transported jointly as chloride complexes in highly saline magmatic-hydrothermal solutions at temperatures ranging from >700 to 340°C, and with Pd being more strongly mobilized than Pt.

The extremely low Os, Ir, Ru and Rh (generally <1 ppb) characterizing the Elatsite deposit is also characteristic of PGE–Cu deposits in alkaline-type complexes (Table 2, Thompson *et al*. 2001, see also Barrie *et al*. 2002). One explanation for this could be the one provided in the two-stage model suggested by Thompson *et al*. (2001) and supported by Watkinson *et al*. (2002), whereby hydrothermal remobilization of a pre-existing PGE concentration preferentially mobilizes Pd and, to a lesser extent, Pt; the other PGE, much less mobile under hydrothermal conditions, are only very slightly affected.

If such a mechanism occurred at Elatsite, it would explain the difference between the Elatsite and Baula–Nuasahi PGE mineralization. With its relative enrichment in Os, Ir and Ru, the Baula–Nuasahi Complex exhibits a clear magmatic affinity, and the PGE–BMS are the expression of late-magmatic fluids. At Elatsite, the Pd–Pt–Cu mineralization could represent a secondary hydrothermal mobilization of a similar late magmatic preconcentration, with a selective remobilization of Pd and, to a lesser extent, Pt, and virtually no remobilization of the other PGE. Because of a lack of field evidence, this model remains speculative.

CONCLUSIONS

As the characteristic bornite – chalcopyrite – magnetite – selenide – telluride – Co–Ni thiospinel – PGM assemblage has a clear mantle-derived signature, the Elatsite PGE–Au–Cu mineralization probably resulted from multiple events. The model proposed for the Elatsite deposit can be summarized as follows:

1) Generation of an Au–PGE–Cu-rich magma following sulfide-undersaturated melting of fertile asthenosphere induced by a flux of Fe_2O_3 *via* slab melts.

2) Emplacement of this mantle-derived adakitic (?) or potassic calc-alkaline magma, whose oxidized H_2O-rich nature prevented early fractionation of the sulfides.

3) Concentration of Cu and precious metals by magmatic-hydrothermal fluids in the porphyry environment. Expression of magmatically generated, high-salinity fluids, possibly mixed with meteoric water, were responsible for the transport of Au and Cu (Eastoe 1982, Tarkian *et al*. 2003).

4) Local deposition of PGM, thiospinel and Ni–Co–As minerals from PGE-rich fluids (Stage 1).

5) Massive deposition of ore minerals in the Cu-porphyry system from the fluids, and potassic alteration (Stage 2).

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