Mineralia Slovaca, 42 (2010), 57 – 68
ISSN 0369-2086

Importance of alluvial gold geochemistry for exploration: Examples from placers in the Western Carpathians

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Abstract

LA-MCP-MS low detection method was applied for the first time on samples of gold from the Western Carpathians. Total 377 gold samples from 19 localities in main tectonic units have been assayed for the set of 60 elements. The methodology proved to be very useful for identifying genetic types of mineralizations from which the gold has been sourced. The presence of microinclusions in gold was inevitable to identify the trace element patterns. This allowed us to interpret the nature of primary source in the localities where it has not been identified yet. The very low detection limits enabled us to plot REE normalized patterns for gold and to identify trace element patterns for gold from different localities. As a result, gold from Hybica proved to be of exotic origin, significant volume of gold from placers in Rožňava proved to have the origin in apatite-U-REE mineralization. The supergene gold (Uderiná, Podrečany) was defined to have increased content of Ba, Mn and Fe. Low content of PGE was identified in gold samples from the Western Carpathians generally.

Key words: placer gold, trace elements, LA-ICP-MS, metallogeny, Western Carpathians

Introduction

The chemical composition of gold has started to be systematically studied with expansion of electron microprobe analysis in the 1980s and the spectroscopic analysis of gold samples and archeological gold artefacts in the late 1970s. The contents of Au, Ag, Hg, rarely also Cu, Sb, Fe, Te, Ni have been reported with 0.X % accuracy in number of studies. Extensive searching for unknown primary source of gold e.g. in Zlatno, Zlatníky, Malinová, Rimavská Baňa, Podrečany, etc. did not have desirable effect despite of time and financials devoted. This paper summarizes results of chemical analysis using Laser Ablation ICP-MS of gold samples from the selected localities in the Western Carpathians. The samples have been sourced from the personal collections of the authors and were analytically and statistically evaluated in PhD. thesis of Schmiderer (2009). This method was applied for the first time on gold from the Western Carpathians. Chapman et al. (2000) and Chapman and Mortensen (2006) applied LA-ICP-MS to study gold samples from UK, Ireland, Scotland and Alaska, USA to determine the nature of the source mineralization. LA-ICP-MS was applied in the thesis of Schmiderer (2009) on fingerprinting of gold to determine the origin of gold in prehistorical gold artefacts from Austria and Germany. LA-ICP-MS allows in-situ determination of ultra-trace elements. Main advantage of LA-ICP-MS is the low detection limit combined with a wide linear dynamic range and low sample consumption. Modern calibration methods allow fully quantitative measurements for a wide range of trace elements and detection limits in the high ppb-area (Schmiderer, 2009). Therefore new insights into ore-forming processes are possible using this method. The results were used to determine the source of gold from an archeological artefact, named "The Skydisc of Nebra". This work comprises 2073 assays of the gold samples from Austria, Czech Republic, France, Germany, Italy, Poland, Romania, Slovakia and Switzerland. This paper summarizes results of 377 assays from the following 19 localities in the Western Carpathians:

A. Tatric tectonic unit – Pezinok, "Slnečné údolie" (7 gold flakes); Magurka, Ľupčianka creek (16 assays); Vyšná and Nižná Boca – Bocianka creek + primary gold (10 assays); Sopotnička valley (9 assays); Kriváň – High Tatra Mts., primary gold from old mining workings (8 assays); Hybe, Hybica creek (8 assays); Malinová and Chvojnica, Chvojnica creek and tributaries + Malinová paleoplacers (36 assays); Zlatno, Stráňka creek (16 assays); Zlatníky, Livina creek (Malé Hoste, Šišov, Zlatníky) + Zlatníky paleoplacers, (72 assays);

B. Veporic tectonic unit – Kokava nad Rimavicou, Bohaté (6 assays); Rimavská Baňa, Repno (10 assays); Hnúšťa, Uhrinovský creek (8 assays); Uderiná, primary gold from exploration shaft (10 assays); Podrečany, Sedem chotárov (8 assays);

C. Gemeric tectonic unit – Rožňava, Rožňavská valley (10 assays); Poproč, Petrova valley (10 assays);

D. Central Slovakian Neogene Volcanic field – Kremnica, Kremnický creek + primary gold (19 assays); Pukanec, Obecný creek (22 assays);

Methodology

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a quite new analytical method for the simultaneous measurement of major, minor and trace elements in solid materials. During the measurements a short-pulsed laser ablates a small amount of material (ca 50 μm^3 per pulse) in helium atmosphere. Diameters of the beam used for the assays were in range 15 – 30 μm. The gas with the ablated particles goes into the plasma of a standard quadrupole mass spectrometer. The samples were assayed at Curt-Engehorn Centre for Archaeometry in Manheim on Nebulizer-MCN 6000 (analysed by A. Schmiderer).

The samples were assayed for the set of the following 60 elements: S, Ti, V, Mn, Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U.

Detection limits for individual elements are shown in Tab. 1.

Results

Chemical assays of gold using LA-ICP-MS from the studied localities do not reflect true chemical composition by means of the average trace element contents. The results of individual assays are distorted by the presence of microinclusions (Fig. 1) of associated minerals (primary and secondary inclusions in the gold samples). Despite of this fact the presence of microinclusions is very important for better understanding of metallogeny of the gold-deposits. Microinclusions of >1 μm size are usually visible in BSE, while smaller inclusions are hard to observe with this method due to scratches and voids on the polished sections. Concerning the localities where the primary source is unknown, the microinclusions of associated minerals are even inevitable for determination of their origin. The tables (Tabs. 2 – 4, 6) summarize the average content of the selected trace elements in the localities within individual tectonic units. The relationship between contents of Au and Ag is displayed in Fig. 2. The overall statistics comprises only such major elements which vary between the localities or within individual geotectonic units. The assays are not corrected to the inclusions of the associated minerals.

Tab. 1
Review of the detection limits for LA-ICP-MS method in ppm

47Ti	6.090	72Ge	1.084	103Rh	0.003	137Ba	0.196	165Ho	0.001	193Ir	0.001
51V	2.210	75As	0.770	105Pd	0.179	139La	0.007	166Er	0.001	195Pt	0.008
52Cr	0.955	80Se	29.848	107Ag	18.600	140Ce	0.002	169Tm	0.000	197Au	27.543
55Mn	1.201	85Rb	0.739	111Cd	0.112	141Pr	0.001	172Yb	0.005	201Hg	160.015
56Fe	2.524	88Sr	0.029	115In	0.015	146Nd	0.001	175Lu	0.001	205Tl	0.528
59Co	0.107	89Y	0.015	118Sn	1.627	147Sm	0.001	178Hf	0.001	208Pb	0.622
60Ni	11.799	90Zr	0.010	121Sb	1.006	153Eu	0.001	181Ta	0.001	209Bi	0.023
63Cu	2.095	93Nb	0.010	125Te	0.168	157Gd	0.001	182W	0.565	232Th	0.001
66Zn	0.475	95Mo	0.120	127I	26.767	159Tb	0.001	185Re	0.003	238U	0.001
71Ga	0.180	101Ru	0.052	133Cs	0.032	163Dy	0.001	189Os	0.001		

* assays of 33S are only semiquantitative

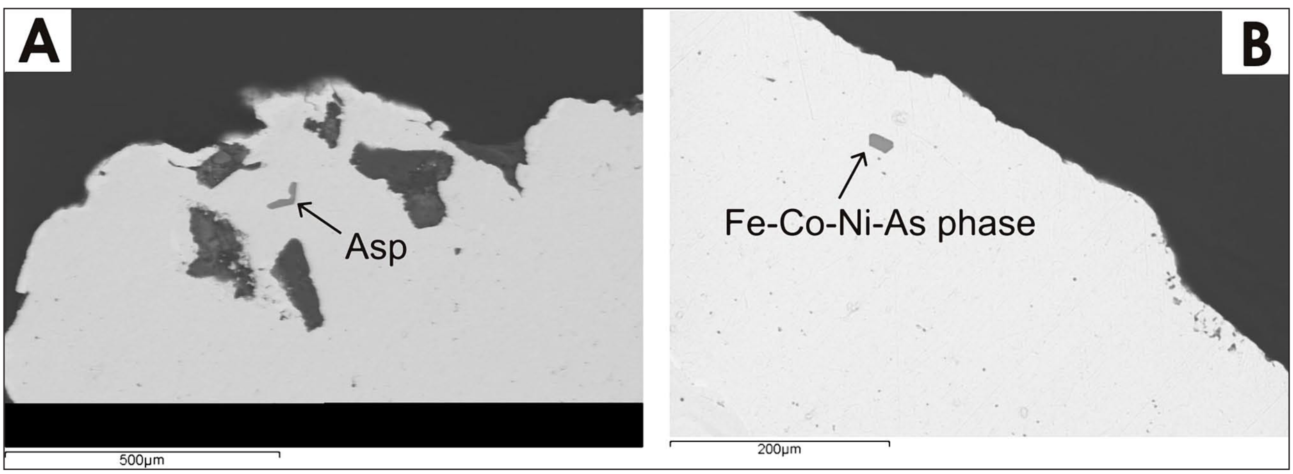

Fig. 1. A – Relatively large microinclusion (cca 50 μm) of arsenopyrite in alluvial gold from Pezinok. B – Relatively big microinclusion (cca 10 μm) of unspecified Fe-Co-Ni-As mineral in alluvial gold from Chvojnica.

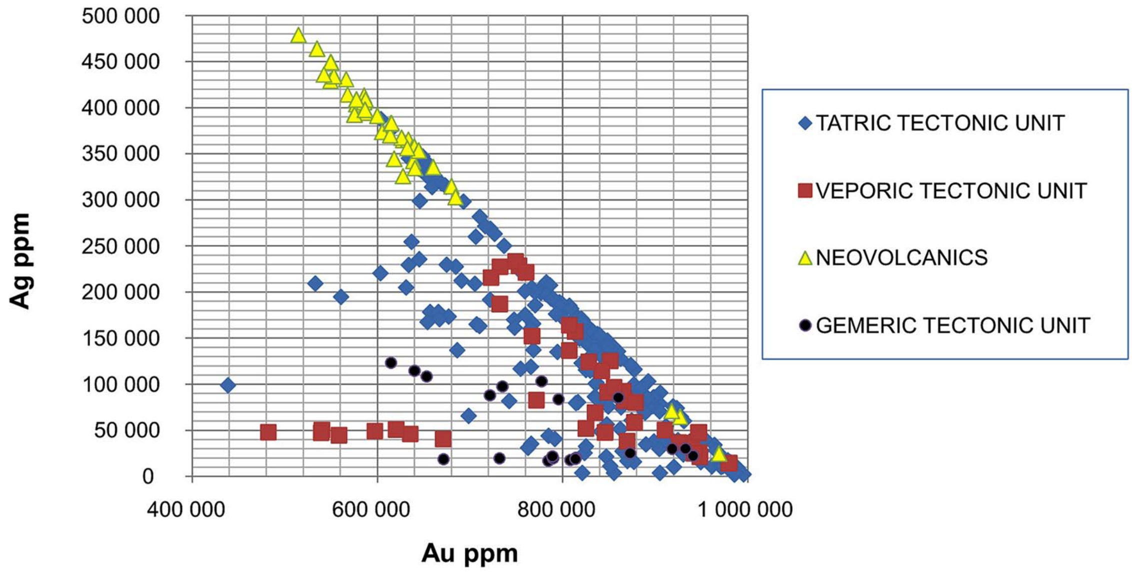

Fig. 2. Relationship between Au and Ag in studied gold samples.

Tab. 2
Comparison of average content (ppm) of selected elements in gold samples in localities in the Tatric tectonic unit

Locality	As	Ba	Mn	Fe	Cu	Sb	Pb	Zn	Te	Bi	Sn	REE
Magurka	205.3	7	8.4	14 668	146.2	2 381.5	257.9	415.47	2.4	1.7	2**	15.71
Boca	84.8	15.4	50.1	2 868.9	496.1	22 175	177.2	7.71	9.1	6.5	9.6	7.14
Kriváň	3 087	15.3	179	7 358	123.9	1 079.8	2 595.1	9.11	5.6	2.8	2.3**	5.81
Pezinok	254.4	11.4	15.8	2 146.2	65.7	89.6	12.5	41.56	12.1	2.6	25.1	56.34
Sopotnička	118.2	8.4	36.1	5 159.6	337.9	9.3	3.1	12.2	4.7	0.3	12.8	4.44
Malá Magura	3.9	17.5	6.1	1 822.8	104.6	55.4	23.6	29.29	4	3.9	9.4	15.26
Zlatníky	26.4	19.6	72.4	6 362.8	83.1	10**	174.7	11.52	2.9**	1.7	6.6**	13.47
Zlatno	0.5*	1.4	1.5**	97.7	465.6	5.8	1.5**	5.95	2.9	0.1**	1.1*	16.72
Hybica	1.2**	5.2	7.8	825.4	34.2	1.9*	1.8	6.12	6.3	0.4	76.8	2.78

* average below detection limit
** ≥50 % of assays below detection limit

Tatric tectonic unit

Gold from *Magurka* is typical with high, very variable contents of As, Sb, Pb (Tab. 2), indicating the presence of abundant microinclusions of sulphides, sulphoarsenides (or arsenopyrite?) and Fe, Sb and Pb sulphosalts. Cu content reaches a maximum of 468 ppm, which means that gold probably does not contain inclusions of Cu minerals. Elevated contents of Co (>7 ppm) positively correlate with As (r = 0.92) and Fe (r = 0.76). Sb/Pb ratio is high (9.35). Content of other elements is not significant in comparison to the other localities.

Geochemical characteristic of gold from *Boca* is slightly different from the typical Sb-As mineral associations in the Tatric unit. High and variable contents of Fe (6.8 to 13 553 ppm), Sb (7.1 – 202 018 ppm) and Cu (104.4 to 10 990 ppm) indicate the presence of inclusions of sulphides and/or sulphosalts. Average content of Cu (496 ppm) is the second highest average Cu content from all the assayed samples from the Western Carpathians (Tabs. 2 – 5). Relatively low contents of As (max. up to 426 ppm) and Pb (max. up to 637 ppm) are also remarkable. Low As and Pb contents (Tab. 2) indicate low chance of substantial part of gold associating with arsenopyrite, or Pb-Sb sulphides and sulphosalts.

Gold from *Kriváň* in the High Tatras Mts. is characterized by similar trace element pattern as gold from Magurka. The only substantial difference is low Sb/Pb ratio (0.42), which indicates association of gold with Pb-Sb sulphosalts rather than with stibnite and Sb-Pb sulphosalts. Zn content is max. 66 ppm (Tab. 2), which excludes the possibility of a significant amount of sphalerite associated with gold. Locally increased content of Mn (up to 656 ppm) is unusual for gold from the Western Carpathians.

Gold from *Pezinok* carries traces of the host intrusion as a locally increased Sn content (max. up to 132 ppm;

Tab. 3
Comparison of average content (ppm) of selected elements in gold samples on localities in the Veporic tectonic unit

Locality	As	Ba	Mn	Fe	Cu	Sb	Pb	Zn	Te	Bi	Sn	REE
Rimavská Baňa	0.2*	0.5**	1.4**	66.3	205.1	27.6	2.7**	3.22	47.6	56.3	11.1	0.47
Kokava n/Rimavicou	5.8	5.1	5.4	1 333.8	497.8	3.3	36.2	1.77	165.4	573.6	4.9	3.47
Hnúšťa	7	8.6	3.8	1 511.1	325.8	45.3	60.1	29.08	8.3	38.3	3.8	85.78
Uderiná	5.4	34.4	25.7	5 118.2	162.7	19.8	5	15.55	6.3	0.1	7.4	6.64
Podrečany	5.5	19.4	383	2 439.9	104.2	1.5**	6.1	218.99	5.2	0.4	2.4*	51.7

* average below detection limit
** ≥50 % of assays below detection limit

Tab. 2) and systematically increased Nd (avg. 51.9 ppm, max. up to 165 ppm). Nd contributes 92 % to the overall content of REE (avg. 56.3 ppm) in gold from this locality. The contents of other REE have background in 0.X ppm, which means that gold contains microinclusions of some unspecified Nd mineral. The content of V varies in the range of several ppm only (avg. 4.6 ppm), which excludes the possibility of the presence of Nd-vanadate. Gold from Pezinok has the highest average REE content from all the localities within Tatric unit – 56.3 ppm and very high LREE/HREE ratio (35). Variable high contents of As (max. 1 636.1 ppm) and Fe (max. 6 977.9 ppm) indicate gold in association with pyrite and arsenopyrite. Maximum content of Sb (364 ppm) and Pb (41 ppm) excludes the possibility of substantial part of gold in association with sulphides and/or sulphosalts of Sb and Pb.

Sopotnička valley gold samples have relatively high contents of Fe (up to 37 403 ppm, avg. 5 159.6 ppm). Increased content of As associates with Fe and S in only one sample. We assume, that primary gold associates mostly with pyrite, which is oxidized during weathering and transport in alluvial environment and association of gold with arsenopyrite in the primary ore is very rare. Systematically increased content of W (max. 18.6 ppm, avg. 4.5 ppm) is typical for gold from this locality. Cu content is systematically elevated and its content from this locality is in average the second highest in the Western Carpathians (338 ppm, max. 636 ppm). The content of other elements is very low (Tab. 2), which excludes association of Au with Pb, Zn, Sb, Bi sulphides and sulphosalts.

Placers at *Malinová* and *Chvojnica* (Malá Magura Mts.) sourced gold of relatively monotonous composition (Tab. 2). Positive geochemical anomaly was observed only at Sb (max. 532 ppm). Low values (max. 76 ppm) were observed at Cu. In two samples Cu content reached as much as 1 412 and 1 312 ppm and these values do not associate with elevated content of any other trace element.

Similarly to gold from Malá Magura Mts. the gold from *Zlatníky* locality has monotonous composition. Increased contents of Fe and Zn were observed (Tab. 2), which suggests the association of gold with pyrite and sphalerite. Contents of Pb and Bi correlate very well in the samples with min. 10 ppm Pb content (r = 0.99 from 16 samples). Au contents in the samples of gold from Zlatníky are very variable ranging from 63.42 % to 98.83 %. Relatively high Sb content (up to 128.2 ppm) was identified in one sample of gold of low fineness (669 228 ppm Au). Increased Cu content (>100 ppm) has been identified in 27 % of gold samples from Zlatníky with max. value 642 ppm Cu. Ti content was found to be relatively often but not systematically elevated. A part of the samples have systematically increased content of Sn (max. up to 99 ppm), which can indicate a character of the host rock. The gold from this locality has very low LREE/HREE ratio (3.6), the lowest from all localities in the Tatric unit.

Gold from *Zlatno* has significantly different geochemical features than gold from other localities in the Tatric tectonic unit. It is typical by very high Hg content, which is the most abundant trace element in gold samples. The samples from this locality have also provided the lowest content of Fe, As, Pb, Ni, Sn, Bi and Ba from all localities in the Tatric tectonic unit and also low content of Sb (Tab. 2) and the highest average content of Pd 4 ppm.

Geochemical characteristic of gold from *Hybe (Hybica creek)* locality is very specific and can be correlated only with gold from Zlatno. Gold samples have relatively high content of Au (avg. 889 189 ppm), but the contents of Pb, As, Sb are very low (Tab. 2). Sn contents from this locality are the highest in the Western Carpathians and reach 76.8 ppm in average. Contents of REE are very low (avg. 2.78 ppm) and LREE/REEE ratio is 7.43.

Veporic tectonic unit

Gold from eluvial-deluvial to alluvial placers at *Kokava* is typical by the highest content of Te (max. up to 499 ppm) and Bi (max. up to 3 417 ppm) in the Western Carpathians. Variable anomalous contents of Fe, Cu and Zn (Tab. 3) suggest probable presence of pyrite, chalcopyrite and sphalerite inclusions. Average Cu content (498 ppm) is the highest average content of Cu from all the samples of gold from the Western Carpathians. Very low Sb and As contents indicate low chance of primary gold associating with tetrahedrite, stibnite, Sb-sulphosalts and arsenopyrite.

Unknown primary Au mineralization at *Hnúšťa-Likier* is typical with elevated average contents of Fe (avg. 1 511.1 ppm), Cu (325.8 ppm) and Sb (45.3 ppm; Tab. 3). Average content of Cu is 326 ppm (max. up to 653 ppm). Sb contents are increased systematically, but reach only max. 114 ppm. One sample assay returned as much as 473 ppm Pb and 229 ppm Bi. The gold has also remarkable systematically

Tab. 4
Comparison of average content (ppm) of selected elements in gold samples in localities in the Gemeric tectonic unit

Locality	As	Ba	Mn	Fe	Cu	Sb	Pb	Zn	Te	Bi	Sn	REE
Poproč	8.5**	2.4	1.1*	112	135.5	3 026	58.1	51.07	3.9	0.5**	1.5*	31.98
Rožňava	62.1	16.2	22.8	2 208.2	233.4	46.9	235.8	54.2	1.8	6.7	1.3*	62.86

* average below detection limit
** ≥50 % of assays below detection limit

elevated content of Cd (avg. 13 ppm, max. up to 21 ppm) and Nd (avg. 57 ppm, max. up to 266 ppm).

The primary source of Au mineralization at *Rimavská Baňa-Repno* locality was probably very poor on Fe minerals. Max. content of Fe is 277 ppm, average 66.3 ppm, which represents the lowest Fe content in all studied localities in the Western Carpathians. Systematically increased content of Cu in 189 – 313 ppm range represents probably stable accessory in gold. Anomalous contents were observed in one sample for Te (445 ppm) and Bi (560 ppm). Gold samples from this locality are typical with increased contents of Pd (max. up to 31 ppm) and the lowest REE content from all localities in the Western Carpathians (Tab. 3).

The gold from *Uderiná* is typical with anomalous Fe values (5 118.2 ppm). Systematically increased values of Ti (avg. 266 ppm, max. 698 ppm), Cr (avg. 12 ppm, max. 33 ppm), Mn (max. 51 ppm) and Ba (max. 163 ppm) were identified (Tab. 3). Moderately increased contents (ca 10x more than analytical background) were identified for the following elements – Ce, La and Nd. Very low content of REE (average 3.93 ppm) and the lowest LREE/HREE ratio (1.45) in the Western Carpathians indicate that the gold probably does not associate with monazite. Very low contents of As, Sb, Pb, Bi, Zn (15.5 ppm) and Te (6.3 ppm; Tab. 3) suggest, that gold does not systematically associate with typical sulphidic or Bi, Te mineral association.

Unknown primary source of gold from *Podrečany* is characterized by anomalous values of Fe and Mn (Tab. 3), which corresponds to presence of inclusions of associated minerals. Low contents of S indicate association of gold with Fe oxides, less with Mn oxides. Systematically increased contents are very typical for Ba (Tab. 3) and all REE, particularly Ce (avg. 17 ppm, max. 56 ppm), La (avg. 12 ppm, max. 55 ppm), Y (avg. 4 ppm, max. 15 ppm) and Nd (avg. 11, max. 48 ppm). The contents of Y, Sr and Ba very well correlate with contents of REE (Ba/REE 0.9, Y/REE 0.998, Sr/REE 0.92).

Gemeric tectonic unit

Alluvial gold from *Rožňava* was probably derived from multiple sources. It has variable content of number of elements ranging from analytical background to extreme values proving the presence of inclusions of associating minerals. It has extreme content of Ti up to 33 193 ppm. Correlation pattern for Ti, Zr, Nb, Ta, Hf, REE, W and U shows very high mutual correlation of these elements

Tab. 5
Correlation pattern for selected elements in gold from Rožňava locality

	U	W	REE	Nb	Zr	Ti	Y
Y	0.995	0.951	0.950	0.985	0.994	0.997	
Ti	0.998	0.955	0.948	0.989	0.997		
Zr	0.990	0.973	0.945	0.996			
Nb	0.977	0.989	0.938				
REE	0.956	0.908					
W	0.935						

(Tab. 5). Max. content of Pb (2 215 ppm) associates with max. content of Zn (380 ppm) and do not associate with the above mentioned elements. As and Sb do not reach extreme values (Tab. 4), but in some gold flakes the elevated values of As and Sb were observed (As max. 197 ppm, Sb 193 ppm). As and Sb do not mutually correlate (r = 0.36) and also do not correlate with the above mentioned elements. Max. content of Se is only 5.6 ppm, but in comparison to analytical background (lower 0.X ppm) is its content elevated in every assay of gold from this locality.

Poproč is typical with systematically increased, in one third of the gold flakes even extreme, content of Sb (2 127 to 16 486 ppm). Contrary, the gold from this locality has very low content of Fe, As, Pb (Tab. 4) and Zn (4.0 ppm). The content of Pb in one sample reached 502 ppm, otherwise Pb values are close to the detection limit. Sn content reached max. 3.6 ppm. Two samples have moderately high content of REE (179.4 ppm, resp. 35.7 ppm).

Central Slovakian Neogene Volcanic Field

Gold from *Kremnica* has increased content of Ag max. up to 43 % and systematically increased contents of Sb, As and Te (Tab. 6). One third of the assayed gold samples have high content of Pb (max. 761 ppm) and Zn (average 41.3 ppm, max. 212 ppm). The values of Cu and Mn are very variable (Cu 7.5 – 438 ppm, Mn 0.3 – 726 ppm). Some gold flakes have rarely increased content of W up to 40 ppm. Eleven analyses from Kremnica locality are from primary gold and 8 analyses are from alluvial gold. In general the difference between primary and alluvial gold is reflected in significantly higher content of Mn and V in alluvial gold.

Gold from *Pukanec* is typical with the following association of elements: Mn, Se, Te, Bi, Pb, Zn and Cu (Tab. 6). Extreme and variable values of these elements suggest common inclusions of the associated minerals in

Tab. 6
Comparison of average content (ppm) of selected elements in gold samples in localities in the Central Slovakian Neogene Volcanic Field

Locality	As	Ba	Mn	Fe	Cu	Sb	Pb	Zn	Te	Bi	Sn	REE
Kremnica	44.9	15.9	47.8	2 911.2	90.3	278.5	122.3	624.4	41.7	1.5	7.4	8.3
Pukanec	6.7	14.6	572	2761.1	374.7	11.6	213.5	41.28	12 267	9 385.9	4.4	11.91

the gold samples. One assay returned as much as 410 655 ppm Bi, 469 038 ppm S and 269 344 ppm Te. The total of all elements in this analysis significantly exceeds 100 %, but the assumption based on the ratio of the contained elements allows us to estimate, that the inclusion has a chemical composition similar to joseite, baksanite, etc.

General conclusions

Summary of analytical data

The individual metallogenic types of Au mineralization in different geotectonic units can be distinguished by the results of applied methodology on the gold samples from the localities in the Western Carpathians. Significant differences in chemical composition of gold and microinclusions have been identified also within the same geotectonic unit between individual localities. Comparison of chemical composition of gold (Fig. 2) has confirmed the presence of several generations of gold (Bakos et al., 2002b). Given that the statistical data is significant, the presence of various generations would be confirmed probably in all tectonic units. The gold of highest fineness (950 – 999) is mostly present as gold rich rims on the samples of alluvial gold. The other group of high purity gold (900 – 950) samples occurs on the localities in crystalline basement rocks in the Western Carpathians with low content of the base metal sulphides. Third group of gold samples is characterized by sulphidic stage of mineralization with intermediate fineness of gold (700 to 900). The presence of this generation of gold has not been confirmed in Neogene volcanics yet. The last group of gold with lowest fineness (500 – 700) is represented by the gold from Neogene volcanics and rarely from the localities in Tatric tectonic unit (the youngest stage of mineralization rich in Ag). Gold of highest fineness occurs mostly in paleoplacers on Malinová locality (max. 99.5 % Au), Zlatníky and Zlatno in Tatric tectonic unit and in Rimavská Baňa and Kokava nad Rimavicou in the Veporic tectonic unit. We assume that the primary gold in these localities was of high fineness as well as in the other localities in the Tatric tectonic unit. Fineness of gold from Zlatníky is very variable which is complying with observations of Žitňan and Chovan (2007). Transport of gold in alluvial sediments causes further refining of gold (Bahna et al., 2002). Gold of highest fineness was identified in paleoplacers in the Tatric tectonic unit (up to 99.54 % Au). Gold samples from the Gemeric tectonic unit are typical with relatively low contents of Ag (up to 123 170 ppm Ag) and variable contents of Hg (17 930 to 267 321 ppm). Gold of lowest fineness (Fig. 2) occurs in Pukanec and Kremnica, located in the Central Slovakian Neovolcanic Field (51 – 55 % Au). This fact is also known from the previous works (Bahna and Chovan, 2002; Maťo et al., 1987).

The reliability of the used method for Hg assays is disputable. The laser ablation method cannot provide reliable quantitative assays of Hg due to contamination of the equipment during the assays and the values of Hg are generally higher than those from EMPA. E.g. percentage of Hg identified by laser ablation from the samples of primary gold from Kriváň varies in the range 4.1 – 8.6 %. Hg content assayed by EMPA provided several times lower values ranging 0.48 – 1.92 % (Bakos and Chovan, 2006). The solution of this problem exceeds the frame of this paper and therefore we do not emphasize this issue. The lowest

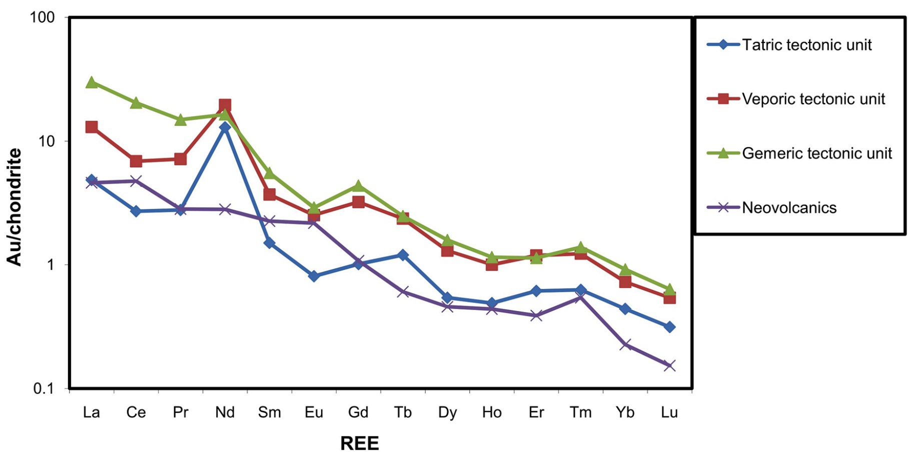

Fig. 3. Comparison of the average REE content normalized to chondrite within geotectonic units.

content of Hg from all studied samples has been identified in locality Pukanec (max. 0.48 %, avg. 0.12 %). Second lowest content of Hg has been identified at Kremnica (max. 3.3 %, avg. 0.8 %). The highest content of Hg was identified in the samples from Podrečany, where almost exclusively only Au amalgams with low Ag content were identified (max. up to 5 % Ag). The other locality with high Hg content is Uderiná (1.3 – 12.2 %), which corresponds very well with the occurrence of intermetallic Au, Ag, Hg alloys (Maťo and Maťová, 1993). Regardless of small statistical data file, the pattern of Hg content can be observed with the lowest Hg content in epithermal mineralizations in the neovolcanic unit and the highest in supergene mineralizations of the Veporic unit.

PGE

Contents of PGE in gold from all studied localities are in average very low or below the detection limits. Although some localities have slightly increased content of Pd and Ir in comparison with analytical background. Content of Pd does not correlate with Ir in any sample. Increased content of Pd is typical for Rimavská Baňa (avg. 5.53 ppm) and for a part of gold from Zlatno (avg. 3.97 ppm). Increased Ir content is typical for gold from Hybe locality (avg. 1.5 ppm) and also for Uderiná (avg. 1.09 ppm) and Podrečany (avg. 0.97 ppm). The origin of increased Pd and Ir contents is not clear. The lowest content of PGE was identified in localities in the Gemeric unit (avg. 0.4 ppm).

REE

Chondrite-normalized REE patterns of gold from the Western Carpathians indicate enrichment of gold in LREE and only moderate enrichment resp. depletion in HREE compared to chondrite (Fig. 3). Particularly remarkable is the anomalous content of Nd. Its positive anomaly is most evident in samples of gold from Tatric and Veporic tectonic units. Nd is also the most abundant REE in gold from the Western Carpathians (max. 165.7 ppm from Pezinok or 56.8 ppm from Hnúšťa). In the Tatric tectonic unit the highest Nd

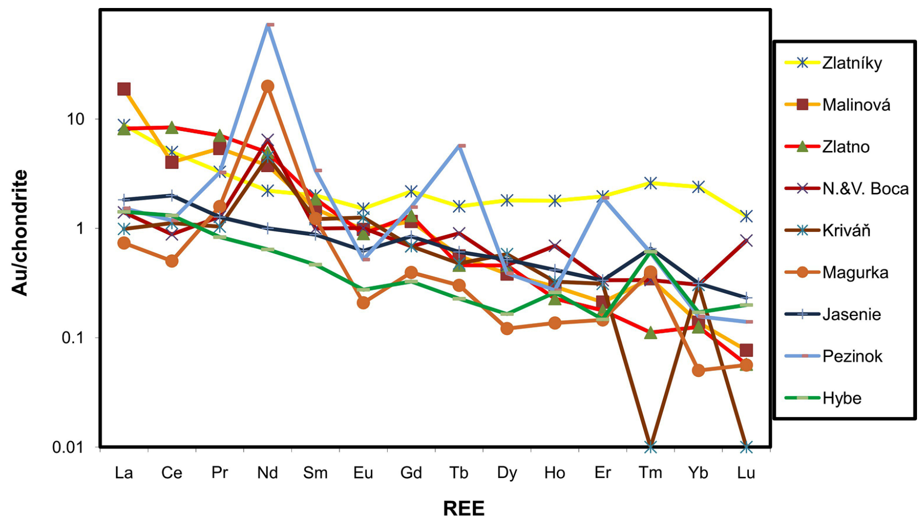

Fig. 4. Comparison of average REE values normalized to chondrite on the samples from the Tatric tectonic unit.

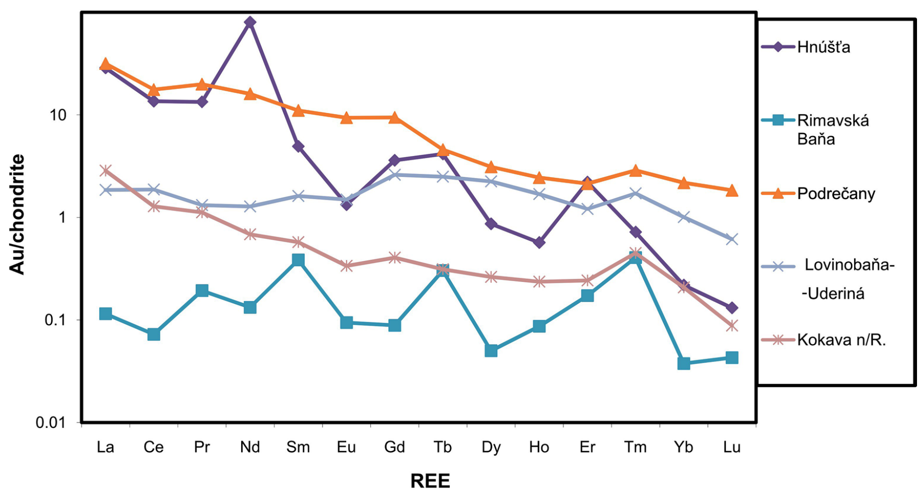

Fig. 5. Comparison of average REE values normalized to chondrite on the samples from the Veporic tectonic unit.

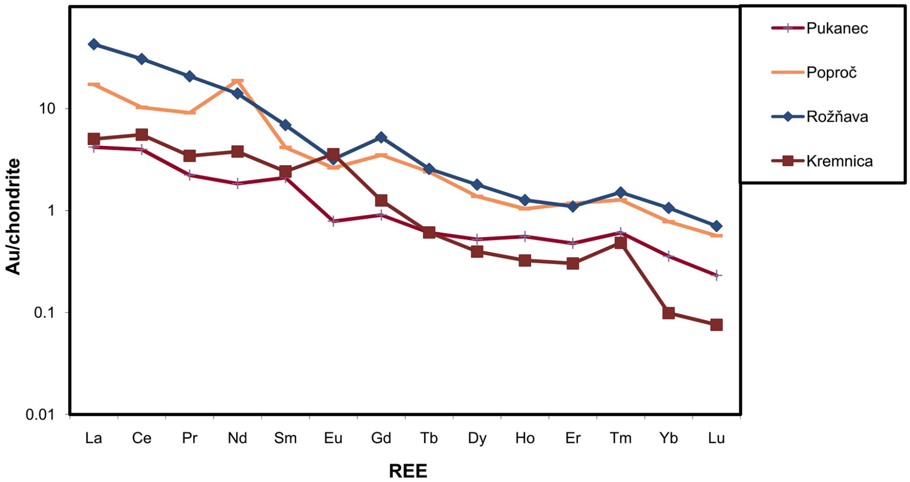

Fig. 6. Comparison of average REE values normalized to chondrite on the localities from the Gemeric tectonic unit and neovolcanics.

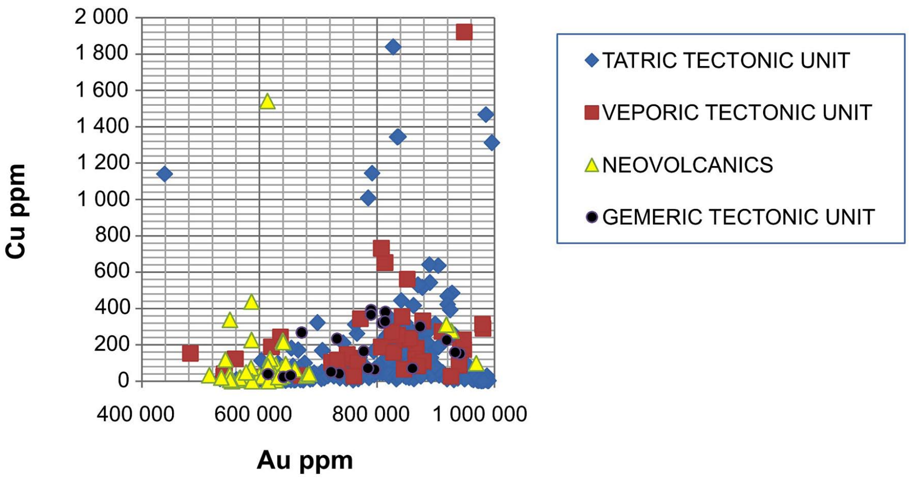

Fig. 7. Relationship between Au and Cu in studied gold samples.

content was identified in the gold samples from Magurka and Pezinok (Fig. 4) contributing 90 % to the overall REE content. The highest overall REE content was identified in gold samples from Hnúšťa (Tab. 3), which contains up to 85.8 ppm REE in average. Chondrite normalized REE patterns of gold from Tatric tectonic unit show positive Nd anomaly on the samples of gold from Boca, Magurka, Pezinok and Kriváň (Fig. 4). Chondrite-normalized REE patterns for gold from Hybe are characterized by positive Tm anomaly and a moderately negative Eu anomaly. Chondrite-normalized REE patterns for gold from neovolcanics are specific. These are typical by a relatively stable trend with not apparent negative Eu anomaly (Fig. 6). Chondrite-normalized REE patterns for gold from the Veporic tectonic unit are very variable (Fig. 5). Positive Nd anomaly and negative Eu anomaly was identified only in gold samples from Hnúšťa. The pattern for Rimavská Baňa locality is very specific and points to a depletion of REE relative to chondrite. Anomalous contents are obvious for Sm, Tb and Tm, which makes this locality different from the other studied localities. LREE/HREE ratio is very low (2.15). Gold from Gemeric tectonic unit is characteristic with high LREE/HREE ratio (Rožňava – 17.32, Poproč 12.3), particularly in the samples where REE content correlates with U, Th, Ti, Zr, Nb, Hf and W, which indicates their origin in the given apatite-U-REE mineralization. In general, if the gold from Gemeric tectonic unit contains U, than LREE/HREE >10, if the content of U is below detection limit, than LREE/HREE <10. Chondrite-normalized REE patterns for cores and gold rich rims have almost similar LREE pattern, the deviations are observed in HREE pattern, where the gold rich rims have a significantly lower HREE content than cores and even lower HREE content than chondrite (Fig. 6).

Base metals

The Cu content of all samples varies in the range from 0 ppm up to 10 990 ppm (average 204 ppm). Significant differences between individual localities and geotectonic units have not been observed (Fig. 7).

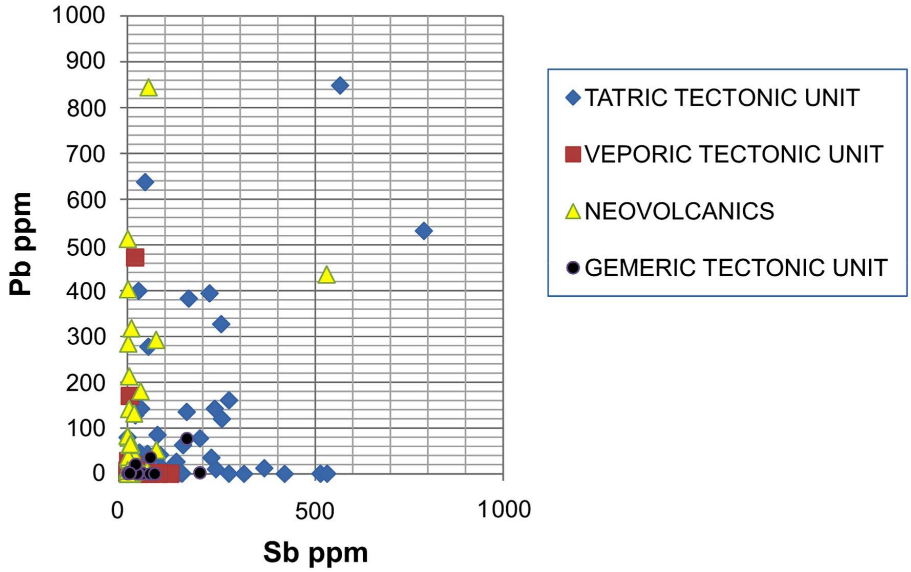

Fig. 8. Relationship between Sb and Pb in studied gold samples.

Increased contents of Cu can be explained as a presence of microinclusions of sulphides and/or sulphosalts. Samples from Zlatníky with increased Cu content (>100 ppm) have moderately high content of Au (794 562 – 931 651 ppm) which indicates part of the primary gold in association with chalcopyrite. Pb content is not systematically increased (Fig. 8), contrary to Cu, and varies within a range 0 – 10 153 ppm, in average 185 ppm. Similar observation has also been made for Zn and Sb respectively. Pb contents up to 1 ppm have been identified in almost 30 % of the assays and a Pb content up to 10 ppm occurred in more than 60 % of the assays. This means, that Pb content is not caused by the presence of microinclusions of minerals. The highest abundance of Pb minerals microinclusions has been identified in gold samples from neovolcanics and from the Tatric unit. Sb content up to 1 ppm has been identified in 24 % of the assays. Sb content up to 10 ppm has been identified in more than 56 % of the assays. Interestingly, positive correlation between Sb and Pb has been observed only in localities in the Tatric and in the part of the localities in the Gemeric tectonic unit (Fig. 8). Sb content varies from 0 ppm up to 19 068 ppm, in average 360 ppm. Anomalous contents of Zn, related to abundant microinclusions of minerals, have been identified at Zlatníky and Pukanec localities.

Elements such as Cr, Ge, Ga, Mo, Cd, etc., occur in low concentrations up to 1 ppm. Rarely increased contents of Sn, Co, Ni in 10 – 100 ppm mostly do not mutually correlate and we did not identify any mutual relationship between them. Contents of V, Ti, Zr, Nb, Rb, Sr mutually correlate and are probably caused by the presence of rock forming accessory minerals.

Tatric tectonic unit

The selected analytical method is very useful for identifying of character of unknown primary source of gold which has not been possible before using the EMPA analysis. E.g. Bakos and Chovan (2006) considered Au--Sb mineralization at Kriváň in the High Tatras Mts. to be primary source of alluvial gold in Hybica creek – Hybe. The results in Tab. 2 indicate, that gold from Hybica creek – Hybe probably has an exotic origin. Compared to other localities in the Tatric tectonic unit this locality shows very low content of As, Sb, Pb, Te, Mn, Fe and the highest contents of Sn from all studied localities in the Western Carpathians. Gold with similar chemical composition has not been identified in this study or in any other geotectonic unit in the Western Carpathians respectively. The footwall of the alluvial sediments of Hybica creek – Hybe is formed by flysch Paleogene sedimentary rocks. Gold from Hybica creek – Hybe could also be sourced from similar source as the gold from Strihov conglomerates in Eastern Slovakian flysch (Maťašovský, 1999).

Comparison of the assays of gold from the localities with similar character of primary source (e.g. Magurka, Boca, Kriváň) shows moderate differences in content of some elements, but contents of accessories are similar in general. The localities Magurka, Boca and Kriváň are typical with high contents of Sb and As (Tab. 2), which are caused by microinclusions of the associated minerals. Pezinok (Bakos et al., 2002a) or Harmanec (Bakos et al., 2004) localities with similar mineralization do not have developed younger sulphidic Sb, Pb, Zn, Cu, Bi mineralization (Bakos et al., 2002b), and therefore the gold samples from these localities have only slightly increased contents of As and Sb. Primary sources of gold at Zlatníky, Malinová had probably only a small proportion of gold related to Sb mineralization stage and Zlatno probably did not have Sb mineralization stages developed. Their character could have been similar to the localities Pezinok or Harmanec. Chemical composition of gold from Pezinok, Malinová, Zlatníky and Zlatno is similar with some analysis of gold from Magurka, Kriváň and Boca with lower content of Sb and As, which did not contain microinclusions of associated minerals. Another explanation of the investigated geostatistical difference could be a higher impact of transport on the alluvial gold (Bahna et al., 2002). Therefore we do not suggest other exotic source of gold from these localities.

The part of the gold flakes from Zlatno locality has significantly higher contents of Fe, Mn and Ba. Increased content of these elements is typical for Uderiná locality with supergene Au mineralization (Maťo and Maťová, 1993) and we assume that higher content of these elements indicates supergene origin of gold. This fact is also supported by previous research of Bakos and Žitňan (2001) concerning the occurrence of supergene Au mineralization in Zobor block of the Tribeč Mts. Gold from Zlatno has unusually high Hg content (avg. 93 654 ppm) compared to other localities in the Tatric tectonic unit and forms the most abundant accessory in alluvial gold from this locality.

Veporic tectonic unit

Two different styles of Au mineralizations can be clearly distinguished in the Veporic tectonic unit by comparison of chemical composition of gold. Kokava nad Rimavicou and Hnúšťa localities situated on Sinec shear zone are typical with Au, Bi-Te mineralization (Ferenc and Bakos, 2006), which was reflected also in the composition of microinclusions. The presence of microinclusions of Bi--Te minerals has been identified also at Rimavská Baňa, where the primary source of gold is unknown. Gold from this locality is also typical with anomalous Pd content (the highest from all studied localities; Tab. 3) and also by significantly lower content of As, Ba, Ni, Fe in comparison with the other localities in the Veporic tectonic unit. Due to close proximity of the Sinec shear zone and an increased content of Bi and Te in gold from Rimavská Baňa, we assume similar character of primary source of gold as in Kokava nad Rimavicou. The difference in the content of Pd, As, Ba, Ni and Fe in comparison with the gold from Kokava nad Rimavicou has not been explained yet. Gold from Hnúšťa locality has similar geochemical features – systematically increased contents of Te and Sb as gold from Rimavská Baňa. Both localities are spatially related to Sinec shear zone. This zone hosts number of sulphidic mineralizations with variable mineral associations and this is reflected in the chemical composition of gold samples in proximity of this zone. Gold from Uderiná and Podrečany has similar geochemical features which are different from other localities in the Veporic tectonic unit. They are characteristic with increased content of Hg, Ba, Mn, Fe and almost do not contain any Bi. Comparing the geochemical features and character of the mineralization at Uderiná (Maťo and Maťová, 1993) and Podrečany we assume supergene origin of gold from Podrečany, too.

Gemeric tectonic unit

Comparison of chemical composition of gold from Rožňava and Poproč provided surprising results. In general we would expect a very similar trace element pattern – high content of Fe, As and Sb from the mineral association of hydrothermal Sb-Au veins. Gold from Poproč shows the trace element pattern typical for gold from Sb-Au veins, while in Rožňava there is typical the presence of gold with increased U, Th, Zr, Nb, Rb, As, etc. and a significantly lower content of Sb (Tab. 4). This confirms that significant amount of gold was sourced out also from the quartz veins with apatite-U-REE mineralization. Presence of gold in U-REE-apatite mineralization was described for the first time by Rojkovič et al. (1997).

Neovolcanics

The comparison of gold from epithermal mineralizations of low sulphidation style at Kremnica (Maťo et al., 1987)

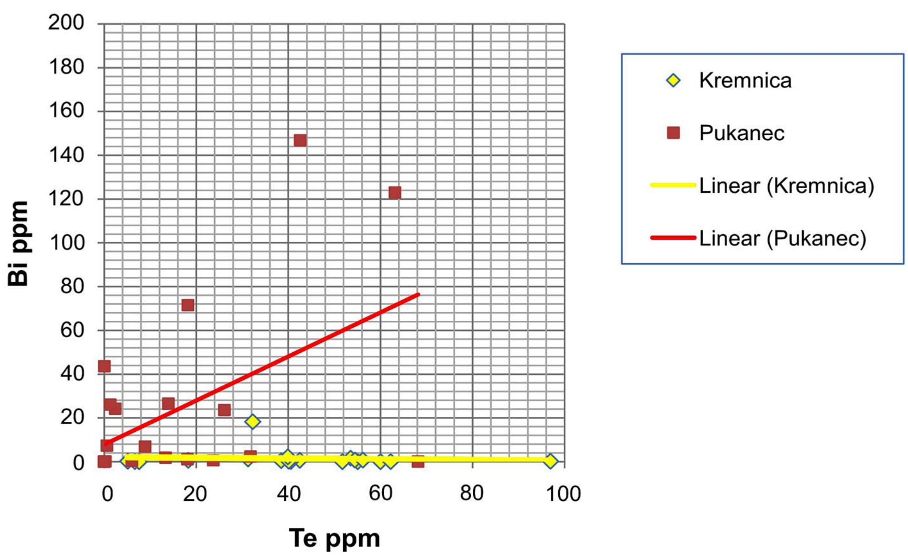

Fig. 9. Relationship between Te and Bi in studied gold samples from Kremnica and Pukanec.

and Pukanec (Bahna and Chovan, 2001) provided very interesting results. The localities have significantly different contents of elements. Kremnica deposit is characteristic by geochemical association Fe, Sb, As, Te (Tab. 6). Maťo et al. (l. c.) describes high proportion of tellurides from Kremnica deposit with typical Ag, Cu, Pb, Zn mineral association. Pukanec has also similar geochemical characteristic with similar association of elements, besides Sb and As. Te content is also in average several times higher, but variable. Kremnica is typical with lower Te content, but this is systematically increased (Fig. 9). Anomalous contents of Se, Te and Bi in one sample of gold from Pukanec indicate the presence of microinclusions of Bi-S-Te-Se minerals, which have not been described on the deposit yet. The presence of supergene gold at the locality cannot be distinguished from the obtained data.

Gold rich rims

Gold rich rims assays interpretation is problematic due to their thickness and used methodology. Even with the beam diameter reduced to 15 μm, we cannot exclude contamination of the assayed material with core material of lower fineness. In spite of this fact the assays of gold rich rims, compared to the cores of the gold samples, have significantly lower content of Ag and Hg. The contents of other assayed elements in the rims were approx. two times lower than those in the cores, besides of Cu, Ba, Ti, V, Co, Ni, Rb and I.

Conclusions

LA-ICP-MS is a very suitable method for trace elements study in the gold samples. For the quantitative assay of Hg it does not provide relevant values yet. Due to the abundance or random distribution of microinclusions of the associated minerals in the gold samples a sufficiently large amount of the measurements is required for statistical processing of the data. The study of microinclusions provides very valuable information to characterize unknown primary source of alluvial gold. The primary source of gold from paleoplacers at Malinová and Zlatníky has probably similar character to quartz veins with low content of Sb, Pb, Zn, Cu and Bi as at Pezinok, Harmanec, etc. A part of gold from Zlatno is probably of supergene origin, and part of the samples cannot be reliably interpreted. The gold from Hybica creek has exotic origin in flysch belt paleoplacers. The gold from Rimavská Baňa shows an association with Te, Bi minerals, which indicate a similar character of mineralization as the Au, Te and Bi mineralization at Kokava nad Rimavicou. Gold from Hnúšťa has probably originated in the sulphidic mineralizations related to Sinec shear zone. The gold from Podrečany placers analogically to Uderiná comes from a supergene Au mineralization. The extension of the statistical data and assays of gold from other localities could help to define other unknown primary sources and would supplement the knowledge about metallogeny of gold.

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Rukopis doručený 1. 2. 2010
Revidovaná verzia doručená 1. 2. 2010
Rukopis akceptovaný red. radou 17. 2. 2010

Význam geochémie aluviálneho zlata pre prieskum – príklady z vybraných rozsypov v Západných Karpatoch

Metóda LA-ICP-MS (laserová ablácia) bola po prvýkrát aplikovaná na analýzu vzoriek zlata zo Západných Karpát. Spolu 377 vzoriek zlata z 19 lokalít zo všetkých hlavných tektonických jednotiek sa analyzovalo na súbor 60 chemických prvkov. Metodika sa ukázala ako veľmi vhodná na identifikáciu genetických typov mineralizácií, ktoré sú primárnym zdrojom rozsypového zlata. Prítomnosť mikroinklúzií asociujúcich minerálov v zlate je nevyhnutná na stanovenie asociácie stopových prvkov. Kvalitatívne a kvantitatívne zatúpenie stopových prvkov nám umožnilo interpretovať charakter primárneho zdroja zlata aj na lokalitách, kde dosiaľ nebol identifikovaný. Veľmi nízky detekčný limit metódy umožnil sledovať zastúpenie prvkov vzácnych zemín (REE) a vypracovať normalizačné diagramy zastúpenia REE vzhľadom na chondrit. Detekčný limit pre Hg je pre použitú metodiku veľmi vysoký a obsah Hg vo vzorkách sa interpretoval iba semikvantitatívne.

Najzaujímavejšie výsledky sa dajú zhrnúť takto: Zlato z potoka Hybica (Hybe) má pravdepodobne exotický pôvod a pochádza z flyšových sedimentov centrálnokarpatského paleogénu. Pre zlato z rozsypov v Nízkych Tatrách je charakteristický zvýšený obsah Fe, As, Sb, Pb a Cu, čo veľmi dobre odráža charakter primárnej mineralizácie. Zlato z lokalít Zlatno v Tribeči a Zlatníky v Považskom Inovci s neznámym primárnym zdrojom má vysokú rýdzosť a nízky obsah stopových prvkov, preto nie je možné odhadnúť charakter primárneho zdroja. Významný podiel zlata z rozsypov v okolí Rožňavy pochádza pravdepodobne z apatitovej U-REE mineralizácie. Supergénne zlato z Uderinej má zvýšený obsah Hg, Ba, Mn a Fe. Podobná asociácia prvkov sa zistila aj v zlate v rozsypoch z okolia Podrečian. To umožňuje predpokladať, že pochádza tiež zo supergénnej mineralizácie. Zlato z Rimavskej Bane má zvýšený obsah Bi a Te. Indikuje to rovnaký pôvod zlata ako na lokalite Kokava nad Rimavicou. Pôvod zlata z okolia Hnúšte je možné hľadať v sulfidických mineralizáciách viazaných na sineckú strižnú zónu. Pre lokalitu Pukanec sú charakteristické zriedkavé mikroinklúzie Te-Bi minerálov, kým v Kremnici sa vyskytujú teluridy bez Bi. Vo vzorkách zlata zo Západných Karpát je všeobecne nízky obsah platinoidov. Použitie metodiky je vzhľadom na priemer lúča a hrúbku vysoko rýdzich lemov problematické. Na základe niekoľkých analýz je však možné konštatovať, že lemy sú ochudobnené oproti jadru zlatiniek o Ag, Hg, Cu, Ba, Ti, V, Co, Ni, Rb a I.

Rozsah štatistických údajov a analýz zlata z iných lokalít by mohol pomôcť pri identifikácii charakteru iných neznámych primárnych zdrojov rozsypového zlata a doplniť informácie o metalogenéze výskytov zlata v Západných Karpatoch.