PRELIMINARY DATA ABOUT THE CHEMICAL COMPOSITION OF ALLUVIAL GOLD FROM PIANU VALLEY (SEBEŞ MOUNTAINS, SOUTHERN CARPATHIANS, ROMANIA)

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This paper shows the first geochemical data about the alluvial gold grains of Pianu Valley (northern slope of Sebeş Mts., Southern Carpathians), realized by means of electron microscopy (SEM, EDS) and chemical (ICP-MS) methodologies.
The EDS microanalyses provide information about the chemical composition of the associated minerals sporadically present on the gold grain surface, mainly represented by quartz, feldspars and goethite.
The chemical analyses provide (1) the gold and silver contents from two selected populations of gold particles with different grain size, (2) the estimation of their gold fineness (G.F.) (ranging between 961 and 969) and (3) the composition of the mineral associations in the gold grains.

Key words: Alluvial gold; Gold fineness; SEM; EDS; ICP-MS; Southern Carpathians; Romania.

INTRODUCTION

Pianu Valley gold placer is a well known locality of southern Carpathians, closely related to the gold exploitation since the Roman times to the XXth century (Fig. 1).

The Pianu Valley area is characterized by widespread outcrops of kyanite-bearing micaschists, gneisses and amphibolites belonging to the Getic Realm, which are affected by a wide shear zone and are intruded by various granitoid bodies and, locally, overlaid by Upper Cretaceous to Middle Miocene sedimentary successions. In the northern sector these Getic Units are also covered by Quaternary piedmont sedimentary deposits, located very closely to the above mentioned tectonic contact and including the gold placers of Pianu Valley [12,13].

The catchments area of the Pianu Valley consists of metamorphic rocks whereas the drainage basin is formed by sedimentary deposits. Large alluvial deposits are present in the lower course of Pianu Valley. The gold alluvial samples have been collected from the sedimentary deposits (cobbles and gravels) of both actual tributaries and ancient placers of Pianu Valley during the regional geological survey carried out for gold exploration in the Sebeş Mountains area [9].

The 66 spots of panning were located on the main tributaries of Pianu Valley. Panning allows the visual detection of native gold grains directly in the field. Gold concentrations were obtained only in six samples of heavy mineral fractions, with a population of gold grains ranging between 2 and 50. The two richest gold concentrations are located on "Valea de Sebeş", a right tributary, which crosses sedimentary rocks and the tectonic contact with the metamorphic rocks.

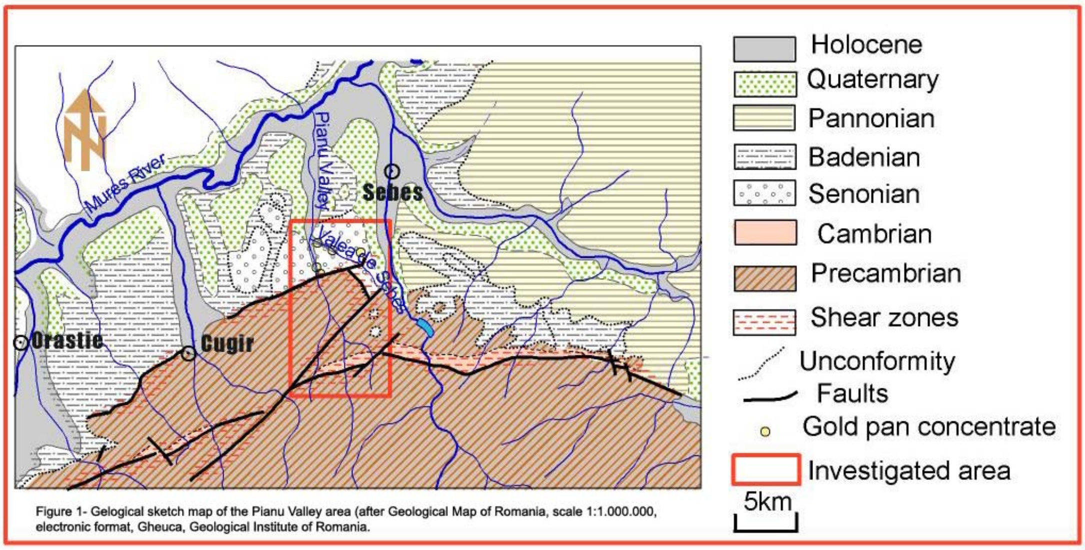

Fig. 1. Geological sketch map of the Pianu Valley area (after Geological Map of Romania, scale 1:1.000.000, electronic format, Gheuca, Geological Institute of Romania).

SEDIMENTOLOGICAL AND MINERALOGICAL FEATURES OF THE PIANU VALLEY GOLD GRAINS

Chemical and physical processes affect the gold grains all over their way from the lode source to the placer deposit. Silver is commonly leached from the surface of the gold grains, leaving Au-enriched rim and Au-Ag-unchanged core [1, 2, 10].

Thus, thickness and/or chemistry of the leached zone are proportional to the distance from the source and, as consequence the fineness of alluvial gold is greater than that of the lode gold of the district eroded. The explanation of this fact is that silver is more soluble in the meteoric waters than gold and is leached, resulting a relative enrichment of gold. Ramdohr (1965) for the first time described the silver depletion process on the gold grains from Rhine Valley by observing in polished section the gold grain core unaltered and surrounded by leached rims.

The morphology of the gold particles from Pianu seems to be closely related to the distance from the source. The mechanical weathering linked to the flowing surface waters is responsible for flattening, rounding, abrasion and folding on the gold particles. Flattening requires a relatively long transport; whereas moderate to well rounded gold particles can be found after short transports [3, 4, 11].

The gold grains from Pianu Valley present different morphological characteristics:

– irregular shapes with rounded contours and irregular topography of the surface, strongly marked by the presence of cavities, frequently filled with associated minerals (Fig. 2b, c, f);

– rounded and oval shapes with smooth contours and regular surface topography characterized by folded edges (Fig. 2 a, d).

The mechanical incorporation of minerals on the surface of the gold grains during transport in the Pianu alluvial environment is frequent and mainly represented by quartz and feldspar (Fig.2a, c), whose occurrence has been emphasized by the SEM and EDS analyses, as described below.

CHEMICAL COMPOSITION OF GOLD GRAINS

Two gold-bearing grain populations (1.00–2.00 mm and 0.25–1.00 mm; labeled A and B, weighting 0.0125 g and 0.0158 g, respectively) were selected under the stereoscopic microscope and used for chemical analyses (Table 1).

The analyses were performed at the Geological Analysis Laboratory of the S. C. Prospecțiuni S. A. (Bucharest) by inductively coupled plasma-mass spectrometry method (X7-ICP-MS-Thermo Elemental, UK-2002).

After treatments with *aqua regia* and HCl solution, the A-population has been totally dissolved, whereas the B-population has been partially dissolved. For this reason a process of inquartation was needed, alloying with an amount of silver (Ag/Au ratio = 4/1) being necessary for the amount of undissolved gold.

Both the analyzed populations show high values of gold (93.50 and 93.00 %) and low percentages of silver (3.77 and 2.95 %, see Table I.

The chemical analysis shows the existence of other chemical elements present in both the A and B gold populations, with the frequency of 2.73% and 4.05%, respectively. The elements like **Ca**, **Mg**, **Al**, **Fe, Sn**, **Zn** have significant values, which can be related to the presence of the associated minerals and the opaque inclusions within the gold grains (Table 1).

Table 1

ICP-MS analysis of gold-bearing grains

Precious metals (%)			**Other elements (p. p. m.)**			
Sampl	**A**	**B**	**Sam**	**A**	**B**	***d. l.***
Au	**93.5**	**93.00**	**Fe**	147	1354	
Ag	**3.77**	**2.95**	**Ti**	42	38	
G. F.	**961**	**969**	**Al**	174	1514	
G. F.: gold fineness = =[Au/ (Au +Ag)] × 1000			**Mg**	246	2072	
			Ca	335	2105	
			Mn	67	56	
			K	215	203	
			Na	29	27	
			Li	4.3	3.4	*0.2*
			Be	0.07	0.05	*0.2*
			V	258	199	*1*
			Cr	76	54	*1*
			Co	1.4	1.3	*0.5*
			Ni	47	39	*0.5*
			Cu	335	408	*1*
			Zn	120	987	*1*
			Ga	0.8	0.7	*1*
			As	17	17	*1*
			Rb	2	2	*0.1*
d.l.= detection limit;			**Sr**	121	110	*1*
			Y	17	12	*0.1*
			Zr	15	13	*1*
			Mo	10	6	*0.1*
			Cd	3.4	2.8	*0.1*
			Sn	292	1446	*0.4*
			Sb	17	10	*0.5*
			Te	1	1	*0.01*
			Cs	0.2	0.1	*0.1*
			Ba	27	35	*1*
			W	0.7	0.7	*0.25*
			Pb	52	44	*1*
			Bi	5.2	4.6	*0.04*
			Th	6.9	6.0	*0.05*
			U	0.4	0.2	*0.01*
			Hg	59	37	

SCANNING ELECTRON MICROSCOPY (SEM) AND MICROANALYSIS (EDS)

The SEM and EDS investigation* has been performed on four alluvial gold- bearing grains (Figure 2, d, e) in order (1) to examine the morphological characters, (2) to identify weathered zones, leached rims, internal structure and other shape characteristics and, finally, (3) to obtain the chemical composition of selected surfaces. The results are given in the Table 2.

Table 2

Element concentration (wt. %) of the composite gold bearing grains, performed by EDS microanalysis

Gold bearing grains	**1**		**2**	**3**	**4**			
	A	**B**			**A**	**B**	**C**	**D**
Al	15.92	1.06	2.01	2.49	20.82	1.40	2.53	4.77
Si	50.14	1.95	2.74	3.57	41.60	93.52	3.12	9.83
K	21.52	0.90	0.82	0.76	2.15	0.98	0.79	0.50
Ca	–	–	–	–	27.54	–	–	2.97
Ti	–	–	–	–	2.00	–	–	0.30
Fe	1.96	0.54	1.84	1.51	3.37	1.67	1.32	0.97
Au	10.47	95.55	92.60	91.67	2.52	2.44	92.24	80.67
	100.01	**100.00**	**100.01**	**100.00**	**100.00**	**100.01**	**100.00**	**100.01**

The element concentrations were normalized by using the ZAF method; A-to-D represent the selected surfaces where the analyses have been performed.

* Analyses of the gold grains and their inclusions have been performed by a Philips XL20 SEM, equipped with an EDS X-ray Microanalysis System (Laboratory of the Dipartimento di Fisica e Ingegneria dei Materiali e Territorio, Università Politecnica delle Marche Ancona, Italy).

The first grain (1) was analyzed in two spots:

A–the high values of **Si** (50.14 %), **K** (21.52 %) and **Al** (15.92 %) and the low contents of **Au** (10.47 %) and **Fe** (1.96 %) can be related to the presence of associated minerals, such as silicates (orthoclase) and accessory goethite;

B–high value of **Au** (95.55%) and low contents of **Si**, **Al**, **K** and **Fe** testifies the presence of small amounts of minerals mechanically added on the surface of the gold particle, probably represented by silicates and goethite.

The second (2) and third (3) gold grains, both analyzed in only one spot, show high value of **Au** (92.60 % and 91.67 %, respectively) and low contents of **Si**, **Al**, **K** and **Fe**.

The fourth (4) composite grain was analyzed in four spots (A, B, C and D, shown in Figure 2e and in Table 2):

A–high values of **Si** (41.60 %), **Ca** (27.54 %), **Al** (20.82 %) and **Fe** (3.37 %) and low contents of **Au** (2.52 %), **K** (2.15 %) and **Ti** (2.00 %), which can be related to the presence of silicates (plagioclase), too small to be specifically identified;

B–high value of **Si** (93.52 %) and low contents of **Al**, **K**, **Au** (2.44 %), **Fe**, probably related to the presence of abundant quartz and traces of other accessory silicate minerals;

C, D–these spots show high values of **Au** (92.24 % and 80.67 %, respectively) and low contents of impurities, such as **Si**, **Al**, **Ca**, **K**, **Fe** and **Ti**, commonly occurring in the detrital gold grains.

Thus, the **Au** contents are highly variable in the four apparently homogeneous gold-bearing grains analyzed, according to the presence of mineral inclusions, probably embedded into gold grains during transport. These associated minerals can be attributed to orthoclase (1/A), plagioclase (4/A), quartz (4/B) and goethite, minerals which abundantly occur in the catchments area of the Pianu Valley.

Figure 2f shows the **Au** and **Si** distribution map in the forth composite gold grain, closely related to the occurrence of numerous inclusions of silica-bearing minerals, only partly visible in the SEM photographs.

DISCUSSIONS

The gold fineness obtained for the alluvial gold from Pianu Valley by using the ICP analysis is ranging between 961 and 969 for the coarse- and fine-grained population, respectively (A and B populations). So, considering that both the analyzed populations have approximately the same weight (0.0125 g and 0.0158 g), the slightly different values of gold fineness seem to be mainly linked to the grain size of the A- and B-populations (*i.e.* gold fineness could be inverse-proportionally to the size of the particles of the analyzed population). Anyway, even if the size of the gold grains could have indirectly influenced the gold fineness, the difference of the values obtained is low and both are specific for alluvial gold.

These results seem to be in agreement with the McLaren's statement (1908) regarding the alluvial gold particles that ascribes the highest values of gold fineness to the most fine-grained particles, presented in Table 1.

Moreover, according to the Morrison's *et al.* (1991) criteria discriminating different classes of gold deposits on the basis of the fineness, the high gold fineness values obtained for the alluvial gold particles from Pianu Valley could be tentatively related to the primary gold occurrences from the Southern Carpathians.

In the Central Southern Carpathians multiple sources have been suggested to explain the gold alluvial concentrations, identified with protores (*i.e.* retrogressed rocks such as blastomylonites) and with kyanite-micaschists with titanian hematite nests in quartz lenses. The paleosutures containing anisofacial rocks, such as eclogites, granulites and ultrabasites, partially healing the shear zones supplement the possible gold sources [12, 13].

The ICP analyses show high gold contents (93.5 % and 93 %) and low percentages of silver (3.77 % and 2.95 %), coupled with discrete amounts of other chemical elements (2.73 % and 4.05 %). Some of these (**Ca**, **Al**, **K** and **Fe**) can be interpreted as elements linked to the associated minerals, as orthoclase and plagioclase, which are incorporated in alluvial gold grains, as testified by the EDS method too. The other ones (**Mg**, **Sn**, **Zn** and **Cu**), evidenced only by ICP analyses, are linked to the presence of opaque mineral inclusions in the gold grains. Finally, the EDS analysis also evidenced the presence of quartz inclusions at the surface of the gold grains.

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