NANOMINERALS AND THEIR BEARING
ON METALS UPTAKE BY PLANTS

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Abstract. In the frame of a project aiming at the identification of nanominerals, especially of gold and silver in the waste dumps, two area were selected for the study, i.e. Valea lui Stan ores in the Căpăţâna Mts. (Au- Cu-As) and Bădeanca Valley ores in the Leaota Mts. (Co-Ni-Bi-Ag-U). A combination of optical, chemical (AAS, ICP-AES) and structural methods (NGR, XRD, TEM/SAED) has been proved to be succesfull for such an attempt. New minerals have been identified in the two areas, i.e. uytenbogaardtite, greenockite, maghemite etc. (Valea lui Stan); lavendulan, maghemite, Mn-spinel, ferrihydrite etc. (Bădeanca Valley) not previously known, all of them being at nanometric scale. The presence of silver carbonates at nanometric scale is also worth of mentioning. At the beginning of the experimental uptake of metals by plants, metal-enriched neutral soils have been used. *Zea mays* and *Trifolium repens* seeds were separately planted in Au, U, Cu and As enriched soils ("artificial ores"). Except for As (the concentration given was too high), the other added metals showed different abilities to be absorbed by different parts of the two plants (roots, trunk, leaves). The highest uptake of gold was measured in *Trifolium* leaves, Cd in roots and trunks, and Zn in leaves. At *Zea mays* uptake of gold was observed in roots, and of Cu, Cd and Zn in trunks. These preliminary results have suggested that the attempt is correct and they represent a good control of the phytomining experiment, using waste dump materials with comparable (low) metal concentration. The ultimate scope of the project is to recover precious metals and to collect heavy metals in plants in order to decontaminate the involved soils or waste dumps.

Key words: nanogold, nanominerals, metals uptake by plants, Valea lui Stan, Bădeanca Valley, NGR, XRD, TEM/SAED, AAS, ICP-AES.

Résumé. L'industrie minière en Roumanie, bien développée dans les dernières siècles, a produit des quantités significatifs de métaux et, par conséquence, des larges quantités de déchets minières très dangereux pour l'environnement. Lăzărescu (1983) a estimé que dans 1980 près que 200 mil. m^3 de stériles minières ont été produit, en recouvrant près que 1500 ha de terrain. Il est possible que dans 2008 (quand la plus part des mines ont été fermées) les chiffres auraient été doublés. Les études poursouivries pour identifier les nanominéraux, particulièrement de l'or et de l'argent dans les déchets minières, ont sélectionné deux zones importantes: Valea lui Stan, dans les Monts Căpăţâna (des minerais de Au-Cu-As) et la Vallée de Bădeanca dans les Monts Leaota (des minerais de Co-Ni-Bi-Ag-U). Les études ont utilisé les méthodes optiques, chimiques (AAS, ICP-AES) et structuraux (NGR-Mössbauer, XRD, TEM/SAED). Des investigations antérieures du minerai primaire et des roches ont montré qu'il n'y pas seulement des macro- et microminéraux, mais aussi des infra- et nanominéraux. La présence des infra- et nanominéraux est très importante pour l'objectif du projet : l'absorption des métaux par les plantes. La mobilité des métaux dans le circuit anatomique des plantes est plutôt en fonction des dimensions des métaux, c'est-à-dire métaux á dimensions nanométriques et métaux dans les sels solubles. Les nanominéraux ou nanocomponents ont des propriétés spécifiques, tel qu'une plus grande réactivité, des charges électriques changeantes etc. Udubaşa *et al.* (2008) ont considéré que les dimensions des cristaux ou grains minérales peuvent varier entre 10^2 et 10^{-9} m. Une classification des minéraux à partir des dimensions peut comprendre les catégories suivantes : A) macrominéraux (dimensions 10^2–10^{-3} m) – investigation par méthodes minéralogiques communes ; B) microminéraux (10^{-4}–10^{-6} m) – méthodes d'investigation : minéralogie optique ; C) inframinéraux (10^{-7}–10^{-8} m) – méthodes d'investigation : EPMA, NGR, XRD ; D) nanominéraux (< 10^{-8} m) – méthodes d'investigation : TEM/SAED. Pour les deux zones des nouveau minéraux ont été identifiés :

uytenbogaardtite, greenockite, maghemite (á Valea lui Stan) ; lavendulan, maghemite, Mn-spinel, férrihydrite (à Bădeanca). La présence du carbonate d'argent à l'échelle nanométrique doit être mentionné aussi. Pour la première étape d'expérimentation de l'absorption des métaux par les plantes (phytoextraction), a été utilisé du sol enrichi en certains métaux. Des semences de *Zea mays* et *Trifolium repens* ont été planté séparément dans des pots avec du sol enrichi en Au, U, Cu et As (« minerai artificiel »). Avec une seule exception, l'arsenic (la concentration était trop grande), toutes les autres métaux ont démontrait certaines capacités d'être absorbé par les différents parties des deux plantes (racines, tiges, feuilles). En ce qui concerne le *Trifolium*, la plus grande capacité d'absorption de l'or a été identifié dans les feuilles, pour le Cd dans les racines et tiges et pour le Zn dans les feuilles. Pour *Zea mays* l'absorbtion de l'or a été observé dans les racines et pour les Cu, Cd et Zn dans les tiges. Ces résultats préliminaires suggèrent que l'expériment a été correct et qu'il représente un bon contrôle pour le future expériment de phytoextraction, en utilisant du matériel de déchets minières avec des teneur faibles en métaux. L'objectif final du projet est de récupérer les métaux précieux et de collecter les métaux lourds dans les plantes pour décontaminer le sol ou les haldes minières.

INTRODUCTION

The mining industry in Romania has been well developed in the last centuries producing significant amounts of metals and as a consequence, large waste dumps and tailing ponds, which represent a real or potential danger for environment. Lăzărescu (1983) estimates that in 1980 about 200 mil. m^3 of residual material have been produced, covering some 1,500 hectares of lands. It is likely that in 2008 (when most of the mines were closed) the both figures are at least double.

This is why any attempt to find ways to attenuate the effects of mining activity related waste materials is welcome. Either phytoremediation or phytomining can be applied for metal uptake by plants (Anderson *et al.*, 1999). In the frame of a scientific project aiming at evaluating the possibility of metals uptake by plants, an interdisciplinary team (mineralogists, geochemists, physicists, botanists, materials scientists etc.) has been organized centered on the University of Bucharest. This paper presents some preliminary results of metals uptake by plants in two selected areas in the South Carpathians with quite different ores, i.e. the Valea lui Stan, Căpăţânii Mts., with Au-Cu-As ores and the Bădeanca Valley, Leaota Mts., showing both pentametallic ores (Co-Ni-Ag-Bi-U) and gold ores.

THE STUDY AREAS

A. The Valea lui Stan mines were operative short before and during the World War II. All the mines were closed due to the low Au tenor and to the discontinuous features of ore bodies. In spite of intense exploration by mining works and drillings (in the '60^{ies} and '70^{ies}) no economic ores were further identified. Essential data on geology, petrography and ore characterization are given by Udubaşa & Hann (1978) and Udubaşa S.S. (2004). The last author supplemented much the ore data with EPMA, fluid inclusions measurements and other techniques.

The Valea lui Stan area is located in the South Carpathians (Căpăţânii Mts.) near the Olt river (**Fig. 1**).

The geological structure is extremely complicated involving several metamorphic groups of Precambrian age and sedimentary formations of Permian and Cretaceous ages. Overthrusts of Austrian and Laramian age as well as cross-cutting faults are described in the area.

The dominant rocks are micaschists, red, orthoclase-bearing gneisses, amphibolites, migmatites, limestones and scarcely developed ultramafics. The sedimentary formations are represented mainly by conglomerates.
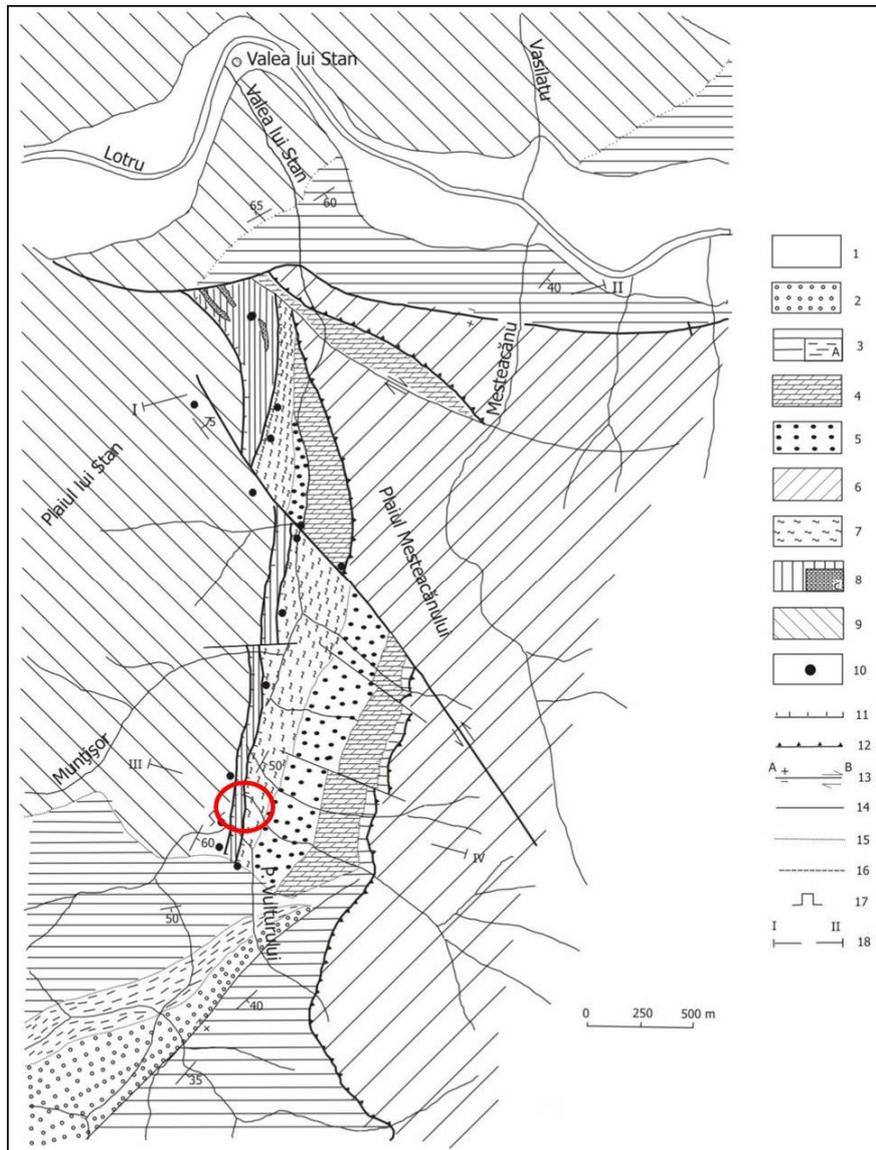
Fig. 1 – Geological sketch map of the Valea lui Stan basin (after Udubasa & Hann, 1988). 1. Holocene; 2. Conglomerates, sandstones, marls (Maastrichtian-Campanian); 3. Conglomerates, marls, sandstones, limestones and clays (a), Coniacian-Santonian; 4. Limestones (Werfenian); 5. Red-violaceous conglomerates (Werfenian-Permian); 6. Cozia augen-gneisses (Cumpana Group); 7. Biotite and muscovite paragneisses with amphibolites levels (Calinesti Formations); 8. Paragneisses, amphibolites, crystalline limestiones (mylonites up to retromylonites), crystalline limestones boudines (c) (Sibisel Group); 9. Paragneisses and migmatites, intensely mylonitized; 10. Gold ores; 11 and 12. Overthrust nappes; 13. vertical fault (a), wrench fault (b); 14. General geological boundary; 15. Transgression boundary; 16. Lithological boundary; 17. Gallery. *Big circle* – location of the studied waste dump.

The ores are shear-zone related and display a typical association of Au-As-Cu. The gold ores have been mined during the XXth century yielding significant waste dumps. The mines are now closed. The minerals encountered in the rocks and ores are given in the **Table 1**, accompanied by the minerals observed under optical microscope in the samples from the waste dumps. The grain size of such material is fine to extremely fine. Due to the long residence on the dumps (more than 75 years) the sulfides have been altered and removed by percolating waters. The still existing ore minerals form fine inclusions in quartz and silicates.

Table 1

Minerals from the Valea lui Stan area, Căpăţânii Mts

Minerals in rocks	*Minerals in ores*	
quartz *	pyrite	quartz
muscovite *	chalcopyrite	calcite
biotite *	arsenopyrite	
orthoclase, microcline *	pyrrhotite	skorodite
plagioclase felspars *	galena	goethite
amphiboles *	sphalerite	hydrogoethite
garnets *	native gold	lepidocrocite
magnetite *	löllingite	chalcocite
ilmenite *	marcasite	covellite
titanite	tetrahedrite	malachite
chlorite *	bornite	cerusite
rutile *		anglesite
zircon		
epidote		clay minerals
Fe-hydroxides *		
graphite		
chalcedony *		
carbonates *		
clay minerals *		
pyrite *		
chalcopyrite *		

* Minerals observed also in the waste dump material.

B. The Leaota Mts. exhibit a mosaic of ore types (being unique in Romania) ranging from pentametallic ores (Co-Ni-Ag-Bi-U), Cu-Bi-pyrite, gold-quartz ores, etc. The epigenetic character of the Leaota ores is advocated by Vlad & Dinică (1983), whereas Udubaşa (2000) collected many arguments in sustaining the shear-zone related nature (several ages!) of the ores, which explain both the heterogeneity of ore composition and the discontinuous development of ore bodies.

The best target for our investigations is the waste dump of the Bădeanca 2 adit, the largest in the area. The ores mined here have had complex compositions, i.e. both pentametallic (Co-Ni-Ag-Bi-U) and common sulphides, as well as gold ores.

The Bădeanca area displays metamorphic rocks of various grades (and ages) in which there are located many ore occurrences related to either shear zones or to faults (**Fig. 2**).

The variety of ore occurrences on an area of restricted size made it ideal loci for experimental attempt to eventually recover the metals by using different plants.

The rocks occurring in the area are mainly micaschists in which intercalations of quartzites, amphibolites, gneisses and scarcely developed eclogites and granites occur in places. Regional retromorphic changes are widespread, on which retrograde transformation on shear planes overlap.

The ore occurrences contain a great number of metals, Au and U included. The minerals so far encountered in the rocks and ores from the investigated area are given in the Table 2. Samples collected from the largest waste dump on Bădeanca Valley have been microscopically investigated. These minerals are also mentioned in the Table 2. Due to the fine grained nature of the material as well as to the long residence (the No. 2 Bădeanca adit was active more than 50 years ago) many primary minerals have been altered (mostly sulfides) and removed by waters percolating the dump.

Fig. 2 – Geological sketch map of the southern part of the Leaota Mts. showing the ore occurrences types. (from Udubaşa, 2000). 1. Quaternary deposits; 2 and 3. Mesozoic sedimentary deposits; 4–7. Leaota metamorphic Group (Late Proterozoic?): Calusu Formation (quartz-chlorite-sericite schists), 5. Leresti Formation (partly retrogressed micaschists ± garnet and albite porphyroblasts, gneisses), 6. Bughea amphibolites and Albesti granite – a rock mixture reminiscent of a pseudo "mini greenstone belt", 7. Voinesti Formation (gneisses, amphibolites ± garnet and pyroxene); 8. Faults. *Big circle* – location of the studied waste dump.

ANALYTICAL METHODS

Earlier investigations of primary ores and rocks have revealed that not only macro- and microminerals do exist, but also infra- and nanominerals. The presence of minerals other than microminerals is of prime importance for the final scope of the project, i.e. the metals uptake by plants. The mobility of the metals in the anatomic circuit of the plants is first of all a function of their size, i.e. of metals being at the nano-size domain as well as of metal bonded in soluble salts. The nanominerals or nanocompounds have specific properties, such as higher reactivity, changing electrical charges etc.

All the samples collected from the waste dump of Bădeanca 2 adit were investigated first by optical microscope. The minerals identified so far are generally the same as compared to the primary rocks and ores (see **Table 2**). Interesting is also the presence of some opaque rings (Plate I), presumably consisting of a Mn-spinel (pointed out by NGR spectra), formed at the expense of spessartine grains, commonly occuring in the host rocks.

Table 2

Minerals from the Bădeanca Valley, Leaota Mts

Minerals in rocks	*Minerals in ores*	
quartz [*] plagioclase felspars [*] muscovite [*] biotite [*] amphiboles garnets [*] rutile ("leucoxene") [*] magnetite [*] hematite ilmenite [*] zircon [*] titanite chlorite [*] carbonates [*] graphite clay minerals [*] hydrogoethite [*] pyrite [*]	pyrite chalcopyrite pyrrhotite galena sphalerite safflorite löllingite molybdenite maucherite wittichenite tetrahedrite marcasite arsenopyrite bismuthinite native bismuth gold uraninite	quartz calcite ankerite barite fluorite erythrite annabergite malachite azurite covellite chalcocite goethite hydrogoethite lepidocrocite clay minerals

[*] Minerals observed also in the waste dump material.

The samples were analysed by the aid of ICP-AES and the results are given in the Table 3. Except for Pb, all the analysed elements show low contents. Although the ores from Bădeanca 2 adit are quite different (Co-Ni-Ag-Bi-U) as compared to the Valea lui Stan ores (Au-As-Cu), the average concentration of the elements are quite similar.

Table 3

ICP-AES analyses on waste dump materials

Sample	Element concentration (%)							
	Cd	Pb	Ag	Co	Bi	Cu	Au	Ni
Valea Badeanca (gal. 2)								
2B1	0.053	0.650	0.085	0.175	0.135	0.055	0.159	0.863
2B2	0.020	0.090	0.027	0.035	0.260	0.016	0.060	6.267
2B3	0.041	0.205	0.102	0.112	0.111	0.051	0.017	3.505
2B4	0.025	0.100	0.031	0.040	0.330	0.017	Nd	1.323
2B5	0.042	0.515	0.082	0.141	0.186	0.141	Nd	0.916
2B6	0.055	0.674	0.092	0.164	0.153	0.043	Nd	1.409
2B7	0.024	0.100	0.026	0.04	0.260	0.016	0.003	1.468
2B8	0.045	0.693	0.085	0.157	0.128	0.044	0.003	0.556
2B9	0.023	0.098	0.025	0.036	0.140	0.015	0.038	0.374
Mean	*0.036*	*0.317*	*0.062*	*0.100*	*0.189*	*0.044*	*0.030*	*1.853*
Valea lui Stan (gal. Stefan)								
VS1	0.042	0.100	0.054	0.038	0.250	0.016	Nd	0.894
VS2	0.060	0.552	0.091	0.156	0.135	0.055	Nd	0.054
VS3	0.080	0.569	0.080	0.163	0.193	0.154	0.004	5.746
VS4	0.131	0.494	0.091	0.220	0.143	0.110	0.003	1.312
Mean	*0.076*	*0.427*	*0.079*	*0.144*	*0.122*	*0.086*	*0.035*	*1.996*

THE NANOMINERALS

It was shown by Udubaşa *et al.* (2008) that the crystal/grain size of minerals varies between 10^2 and 10^{-9} m. A size-related classification/systematics include four categories as presented in Table 4.

Table 4

Size-related systematics of minerals (Udubaşa *et al.*, 2008).

Category	Size range	Methods of investigation
A. Macrominerals	10^2–10^{-3} m	Common macroscopic methods
B. Microminerals	10^{-4}–10^{-6} m	Optical mineralogy
C. Inframinerals	10^{-7}–10^{-8} m	EPMA, NGR, XRD
D. Nanominerals	$< 10^{-8}$ m	TEM/SAED

The category A represents the majority of mineral species known worldwide, i.e. 3500–3800 in number.

The category B of minerals can be detected only under the microscope and occur mainly as inclusions or form fine or very fine aggregates, e.g. clay minerals. Exsolution bodies and the daughter minerals in the fluid inclusions belong hitherto. (Their number is of approx. 300 or less.)

The inframinerals (category C) cannot be seen or cannot be resonably identified under the optical microscope. Such minerals occur as ultrafine inclusions and/or very fine intergrowths, a fact preventing the identification as a result of interfering properties.

The nanominerals (category D) cannot be depicted by usual mineralogical/physical methods; even EPMA seems to be useless in many cases. Their presence can be "seemed"/predicted by NGR and finally visualised and properly identified by TEM/SAED and/or HRTEM.

It is known (Bazin *et al.*, 2006; Waychunas & Zhang, 2008) that the nanoparticles exhibit considerable deviations from the standard properties, e.g. higher reactivity and residual electric charges. In the gold ores from Valea lui Stan area, South Carpathians, there have been identified numerous nanominerals by using NGR and TEM/SAED (Udubaşa *et al.*, 2008). Among them the nanogold is most spectacular, occurring both as individual spherical grains and coral-like aggregates. Such a form of gold presentation may represent an alternative to the "invisible" gold, presumably substituting Fe or As in the structure of some minerals, e.g. arsenopyrite (Cabri *et al.*, 1989; Cathelineau *et al.*, 1989). In the Valea lui Stan ores gold is present in all the categories of Table 4. In addition, several infra- and nanominerals have been also identified by using XRD (uytenbogaardtite), NGR (löllingite, cobaltite etc.), EPMA (greenockite), TEM/SAED (maghemite). Further experiments with the waste dump material from this area have been stopped; relatively high As content prevented the growth of experimentally used plants, i.e. *Zea mays* and *Trifolium repens*. *Equisetum* will be used in the next experiments as this plant seems to selectively concentrate the arsenic.

The waste dump material from the Bădeanca Vally, Leaota Mts., contains also a significant number of infra- and nanominerals such as ferrihydrite, maghemite, plattnerite, cristobalite, lavendulan not previously known, as well as silver carbonates (both α and β forms), representing the first occurrence of such compounds under natural conditions. The (Ag, Au) alloys are relatively frequent and they occur closely associated with maghemite, magnetite, pseudobrookite, SiC and quartz. The silver carbonates are commonly associated with (Ag, Au) alloys (**Fig. 3a** and **3b**).

Some examples are given below, in order to show how the structural techniques contributed to the knowledge of mineralogy of the waste dump materials.
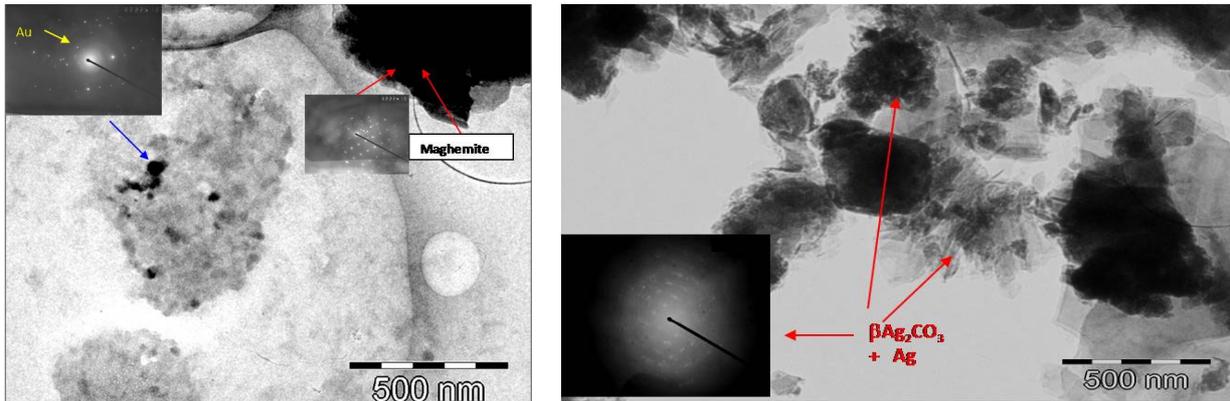
Fig. 3 – TEM/SAED investigatons on Badeanca Valley waste dumps, showing the presence
of Au and maghemite (a) and the association of Ag carbonates with native (Ag, Au) alloy (b).

Mössbauer spectroscopy (NGR). It is mainly dedicated to iron containing minerals and it is
sensitive to both Fe^{2+} and Fe^{3+} ions. A magnetically concentrated sample was thus measured both at
room temperature (RT) and liquid nitrogen temperature (LNT). The spectra are given in the **Figs. 4a** and
4b. Different species of spinels, pyrrhotite, biotite, ferrihydrite, spinel-olivine and a supraparamagnetic
phase (more clearly defined at LNT) have been detected. The significance of this phase will be discussed in
a separate paper. The device and working conditions for the NGR analysis are: standard Promeda
spectrometer with transmision geometry, ^{57}Co:R source, velocity range ± 12 mm/s at RT and LNT.
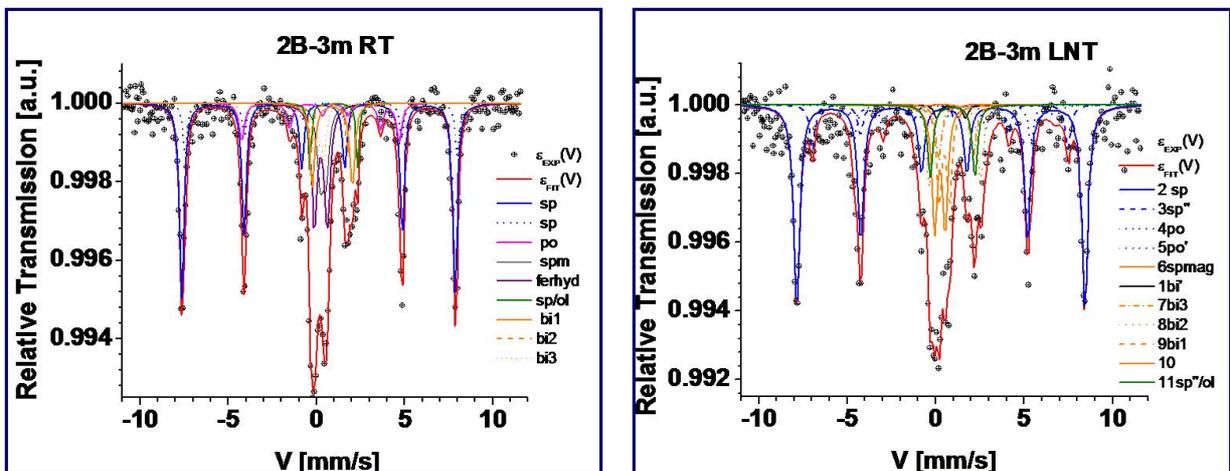
Fig. 4 – The fit of the B-3m RT-spectra (a) and LNT-spectra (b) and the corresponding hyperfine parameters.
Abbreviations: sp = spinel; po = pyrrhotite; spm = magnetic spinel; ferhyd = ferrihydrite; sp/ol = spinel-olivine;
bi = biotite; spmag = superparamagnetic.

X-ray diffraction (XRD). Many minerals have been identified, among them several clay mineral
species (illite, corrensite, kaolinite), ferrihydrite and lavendulan, a complex arseniate, firstly recorded
in the area. Moganite, cattierite, greigite and akanthite are further minerals identified. A typical
diffractogram is given in **Fig. 5**, showing the presence of jacobsite and lavendulan. Device and
working conditions: Bruker D8 Advance Diffractometer, CuKα radiation (λ CuKα = 1.540598 Å).
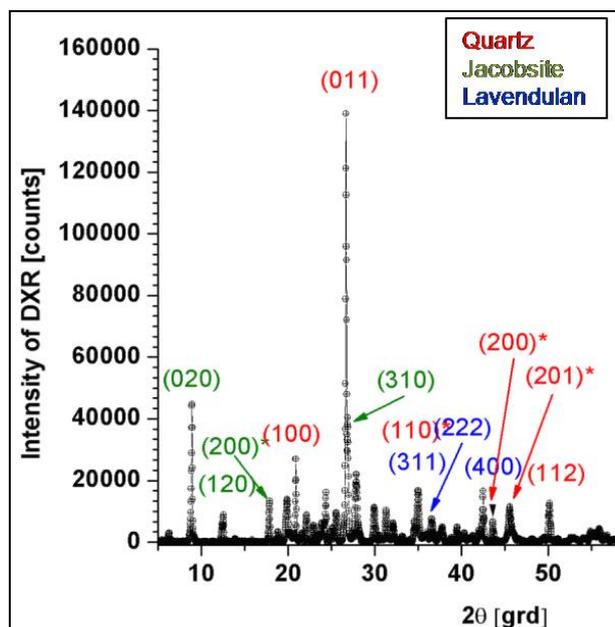
Fig. 5. XRD spectra of Badeanca sample showing
the presence of jacobsite and lavendulan.

Transmission electron microscopy, equipped with selected area electron diffraction device (TEM/SAED). If the above mentioned structural techniques show the presence of minerals at the boundary infra-nano, this method is able to scan all the minerals or compunds down to the nanometric domain. Several pictures are given in the Fig. 3, revealing both the association of gold with maghemite (a) and the presence of the silver carbonate in association with native silver (b). Device and working conditions: JEOL JEM 200Cx transmission electron microscope, accelerating voltage: 80, 100, 120, 160, 200 kV; lattice fringes 0.14 nm; resolution point to point 0.25 nm; magnification: 1000 to 750,000x.

THE RESULTS

For the first stage of investigation the option has been made to use at the beginning neutral soils and adding Au, U, Cu and As solutions of known concentration ("artificial ore" acc. to Anderson *et al.*, 1999). The substances, their concentration, the amounts added on each substratum and the calculated concentration of metals are shown in the Table 5.

Table 5

The calculated concentrations of the added elements

Solution used	Amount	Dilution (distilled water)	Soil weight	Resulted concentration (ppm)	
H(Au Cl)$_4$ H$_2$O	0.5 g	500 ml water	500 g	9.2	Au
UO_2 (NO$_3$)$_2$	0.5 g	500 ml water	500 g	24	U
CuSO$_4$ 5H$_2$O	0.5 g	500 ml water	500 g	0.2	Cu
K$_3$$AsO_4$	0.5 g	500 ml water	500 g	4.6	As

The concentration of metals have been proved to be correct except for As: the plants have not survived in the soils enriched in As. Experiments with such As concentrations will be repeated using other plants, known as As concentrators, e.g. *Equisetum*, or with lower As concentration.

There are several plants known as accumulators or even as hyperaccumulators of metals, e.g. *Brassica juncea*, *Impatiens sp.*, *Hordenum vulgare* etc., either grown on soil or immersed in metal salts (Anderson *et al.*, 1999). We prefered however to use domestic plants such as *Zea mays* and *Trifolium repens*, selected from the database of the Botanical Garden (Faculty of Biology) in Bucharest.

The results of metal enrichment in plants by using neutral soils as well as neutral soils to which solutions containing dissolved metal salts (of Au, U, Cu and As) were added, are given in the **Tables 6** and **7**.

Table 6

The concentrations of different elements in *Zea mays* grown on different kinds of soils

Sample	Element concentration (ppm)							Sample
	Au	Cu	Cd	Co	Ni	Pb	Zn	
Plants grown on neutral soil								
P0	(<0,001)	13,640	(<0,001)	9,054	20,281	53,491	292,095	Soil
P1	0,785	61,709	0,537	(<0,001)	10,195	30,586	614,939	Root
P2	(<0,001)	267,787	0,785	(<0,001)	(<0,001)	59,683	860,688	Trunk
P3	(<0,001)	27,226	0,227	(<0,001)	1,815	26,772	174,925	Leaf
Plants grown on soil enriched in Au								
P4	19,851	14,934	(<0,001)	8,438	18,272	45,438	233,636	Soil
P5	3,440	33,540	(<0,001)	(<0,001)	nd	14,620	303,291	Root
P6	0,537	38,254	(<0,001)	(<0,001)	nd	21,725	361,764	Trunk
P7	(<0,001)	31,061	0,894	(<0,001)	2,011	26,369	206,704	Leaf
Plants grown on soil enriched in U								
P8	(<0,001)	15,853	(<0,001)	8,681	22,364	48,345	285,535	Soil
P9	(<0,001)	29,621	0,267	(<0,001)	(<0,001)	21,882	262,582	Root
P10	(<0,001)	281,840	(<0,001)	(<0,001)	(<0,001)	50,518	913,321	Trunk
P11	(<0,001)	21,742	(<0,001)	(<0,001)	(<0,001)	16,220	167,725	Leaf
Plants grown on soil enriched in Cu								
P12	(<0,001)	173,760	(<0,001)	5,533	15,606	34,070	96,383	Soil
P13	0,384	190,301	4,220	(<0,001)	20,718	37,983	236,341	Root
P14	(<0,001)	91,698	(<0,001)	(<0,001)	(<0,001)	40,949	490,690	Trunk
P15	(<0,001)	32,820	(<0,001)	(<0,001)	0,486	11,183	234,842	Leaf
Plants grown on soil enriched in As								
P16	(<0,001)	14,783	(<0,001)	6,984	20,829	42,399	238,670	Soil
† … no plant survived…								
Clarke	*0,05*	*70*	*0,15*	*23*	*80*	*16*	*132*	*Clarke*

Table 7

The concentrations of different elements in *Trifolium repens* grown on different kinds of soils

Sample	Element concentration (ppm)							Sample
	Au	Cu	Cd	Co	Ni	Pb	Zn	
Plants grown on neutral soil								
P17	(<0,001)	11,347	(<0,001)	5,674	16,620	35,786	184,970	soil
P18-rt	0,604	7,245	0,604	4,830	13,282	19,923	307,293	root + trunk
P18-f	0,682	8,530	0,682	9,554	(<0,001)	70,288	438,106	leaf
Plants grown on soil enriched in Au								
P19	10,741	12,224	(<0,001)	5,830	17,845	38,156	189,144	soil
P20-rt	6,599	11,809	0,695	4,862	7,294	(<0,001)	286,885	root + trunk
P20-f	10,070	8,885	(<0,001)	1,185	(<0,001)	18,363	361,628	leaf

Plants grown on soil enriched in U							
P21	(<0,001)	14,686	(<0,001)	6,205	19,837	41,902	239,808	soil
P22-rt	0,652	5,219	(<0,001)	1,087	6,524	(<0,001)	184,186	root + trunk
P22-f	0,925	0,231	(<0,001)	2,080	0,231	31,666	277,598	leaf
Plants grown on soil enriched in Cu							
P23	(<0,001)	209,940	(<0,001)	5,390	18,731	35,444	193,763	soil
P24-rt	(<0,001)	88,659	0,487	5,846	9,743	(<0,001)	390,199	root + trunk
P24-f	(<0,001)	102,176	(<0,001)	0,000	(<0,001)	33,113	507,096	leaf
Plants grown on soil enriched in As							
P25	(<0,001)	12,411	(<0,001)	5,629	17,205	40,059	179,125	soil
† … no plant survived…							
Clarke	0,05	70	0,15	23	80	16	132	*Clarke*

Figure 6 shows the plants grew on different types of artificial metal enriched soils. Except for Co, Ni and Pb, the other metals analysed (Au, Cu, Cd and Zn) have been significantly enriched in different parts of the *Zea mays* plants. The gold uptake by *Trifolium repens* leaves is the most interesting in soils enriched in U. Although in different manner, the two plants may be regarded as Au accumulator and/or depolutant for other metals: Zn, Cd, Cu (*Zea mays*) and Zn, Pb, Co, Cd (*Trifolium repens*).
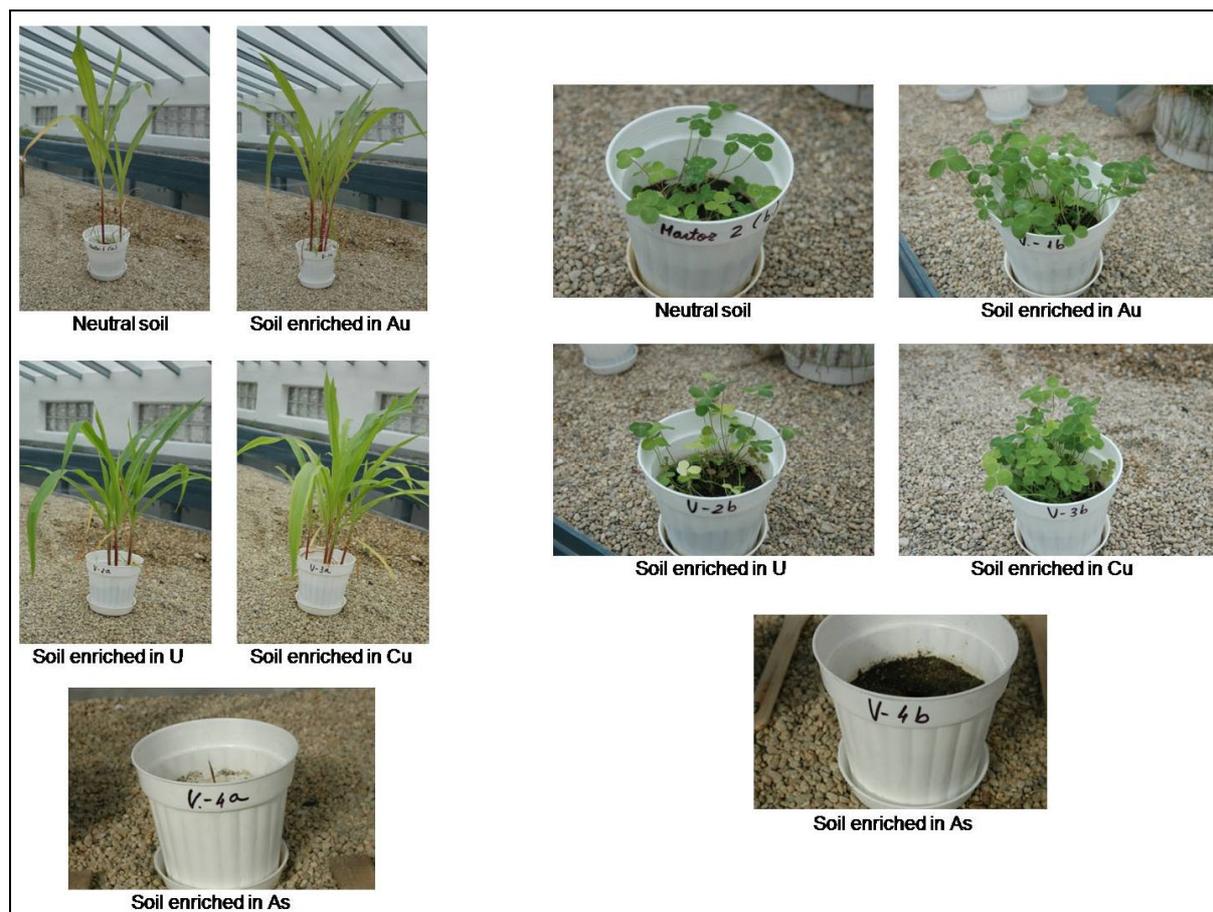
Fig. 6 – The plants developped on different types
of artificial metal enriched soils.

This first step of checking the metal enrichment in plants showed that solutions used (see Table 5) are suitable for experiments, except for As.

CONCLUSIONS

The combination of many methods of analysis seems to be a key to obtain as many information as possible, concerning the state of metals in the waste dump materials. Identification of infra- and especially of nanominerals is of prime importance in understanding the ways some plants may absorb the metals from waste dump materials. For the time being only nanometric gold and/or gold-silver alloys plus silver carbonates may account for direct uptake of the precious metals by plants. Efforts are now made to identify the ways other metals are absorbed (?) by plants, may be via soluble salts.

Identification of nanominerals seems to be a basis for understanding the metal uptake by plants. Good results were obtained for Au, Cu and Zn. For the time being only Au or (Au, Ag) and silver carbonates have been identified at the nanometric scale, together with Fe compounds (magnetite, hematite, wüstite, maghemite), Fe and Ca silicates, SiC, etc.

The capabilities of the plants to absorb metals are as follows:

Zea mays:

– For neutral soil, Au is enriched in roots, Cu in roots and trunks and Cd + Zn in trunks.

– For Au enriched soil, only Cd accumulates in leaves and Zn in trunks.

– For U enriched soil, Cu and Zn accumulate in trunks.

– For Cu enriched soil, Au and Cd accumulate in roots and Zn in trunks. No significant migration has been recorded for Co, Ni and Pb.

Therefore, *Zea mays* can account as depolutant for Cu, Cd and Zn, and partly as gold accumulator.

Trifolium repens – Under same conditions it has been proven to be a better accumulator for all the elements, except Cu and Ni, as follows:

– For neutral soils, the leaves accumulate significant amounts of Au, Cd, Pb and Zn.

– For Au enriched soils, the leaves recovered nearly all the gold added; Cd accumulates in roots+trunks and Zn in leaves.

– For U enriched soil, Au is significantly concentrated in leaves, in a way not completely understod.

– For Cu enriched soil, only Cd, in roots+trunks, and Zn, in leaves, show significant enrichment.

Therefore, *Trifolium repens* seems to be a good solution for Au recovery as well as depolutant for Cd, Pb and Zn. No response has been found for Cu, Co and Ni. Co and Ni are seemingly refractory elements under the conditions investigated.
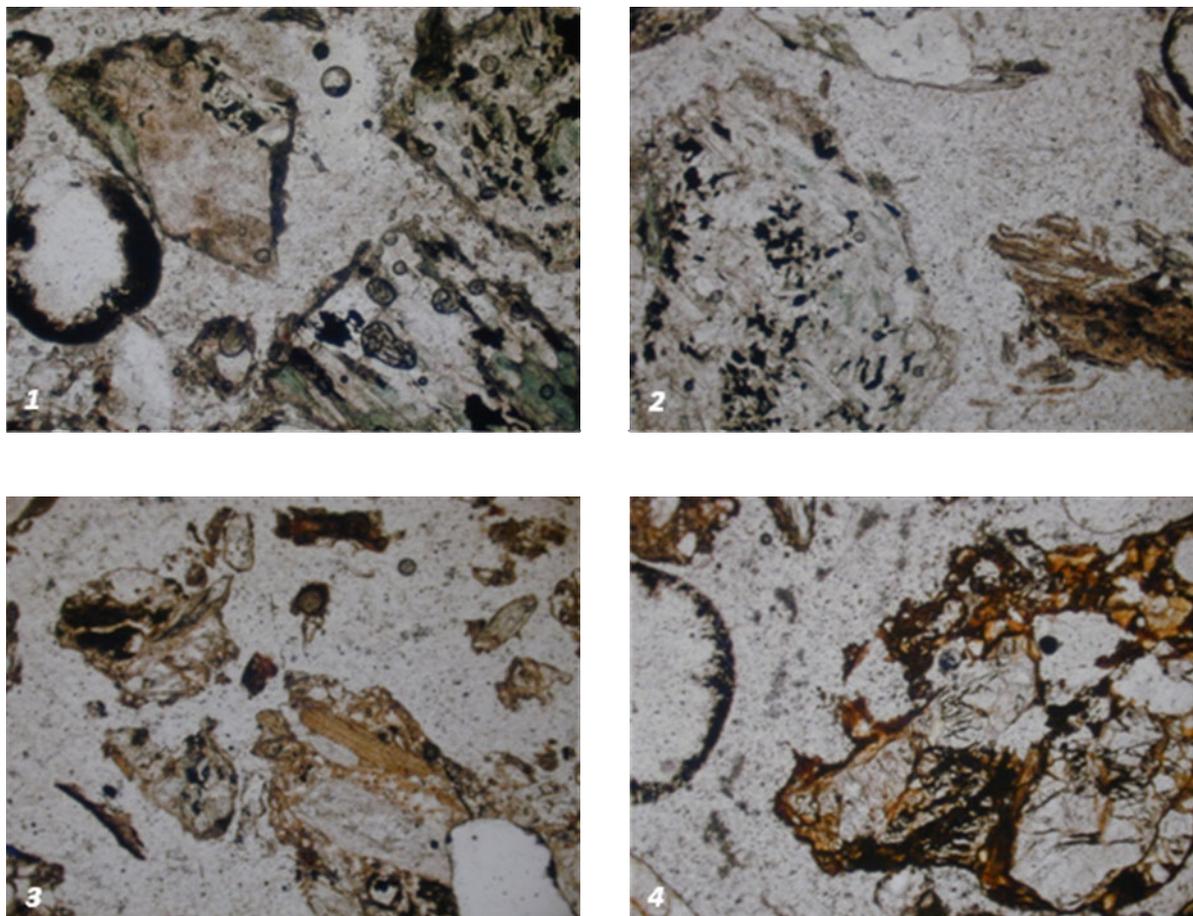
Plate I

Microphotographs of thin sections made on waste dump materials, embeded in epoxy.
The magnification is about 40x, N ||.
Photo 1. Rock fragments with euhedral opaque minerals (black), muscovite (white) and chlorite (green). Left side: a "ghost" of garnet (spessartine?) with black rims, presumably consisting of a Mn-spinel. Badeanca Valey area.
Photo 2. Subhedral opaque minerals (left) in micaschists. Right:
biotite with patches of Fe-hydroxides. Badeanca Valey area.
Photo 3. Biotite (relatively fresh) and opaque minerals (magnetite) and Fe-hydroxides. Valea lui Stan area.
Photo 4. Fine opaque blades (ilmenite), euhedral grains (magnetite) and Fe-hydroxides (yellowish-brown spots).
Left: a garnet (spessartine) "ghost" with opaque rims (similar to Photo 1) Valea lui Stan area.

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