

Towards mineralogical and geochemical reference groups for some Bronze Age ceramics from Transylvania (Romania)

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ABSTRACT. Based on their chemical composition ceramic shards from three Bronze Age sites in Transylvania, *i.e.*, Copăceni, Derşida and Palatca respectively, were distinguished by major, trace, and RE elements. Within the Copăceni samples, two subgroups (A and B) showing different chemistry and mineralogy were additionally separated out. The link between chemistry and mineralogy showed clearly the important contribution of the temper to the overall chemistry of the ceramic shards. In turn, the chemistry facilitated the provenance study of the raw materials, which were collected in the vicinity of the sites. In combination with the mineralogy of the ceramics, the chemical analyses can serve as a basis for a geochemical reference set used by further studies.

Key words: ancient ceramics, Bronze Age, mineralogy, geochemistry, archaeometry, Romania

INTRODUCTION

Compositionally, the ancient ceramics can be regarded as artificial rocks formed during a short living thermal event from clays mixed with tempering material, *e.g.*, sands, potshards, and others.

The ceramic is a two-component system consisting of a major component, the clay matrix and clasts as the second one. The latter originate mainly from the tempering material added by the potter and partly from the raw clay. The clasts may consist of one or more of the following types: crystalloclasts, lithoclasts, ceramoclasts and bioclasts (Ghergari et al., 1999; Ionescu and Hoeck, 2008). Chemical analyses have been used since several years in archaeometry to group and classify ancient ceramics, and for provenance studies (Yoon et al., 2001; Gliozzo and Memmi Turbanti, 2004; Mirti et al., 2004; Barone et al., 2005; Belfiore et al., 2007).

Taking into account the compositional complexity of the ceramics, the chemical analyses of ceramic shards have to be treated with utmost care in particular for the search of possible sources. The use of chemical data of whole ceramic fragments and their interpretation requires additionally a detailed mineralogical and petrographic study.

The paper presents the results of the first geochemical study on Bronze Age ceramics in Romania done in order to delineate distinctive features for each site as base for future analogies. We will show here that sound results can be achieved provided care is taken in handling the chemical data and connecting with the mineralogy and petrography.

ARCHAEOLOGICAL AND GEOLOGICAL BACKGROUND

In Romania and in particular in Transylvania, several Bronze Age settlements rich in ceramics artefacts, *e.g.* Ilişua, Copăceni, Palatca, Derşida were investigated. So far, only mineralogical-petrographic studies were carried out (Ionescu et al., 2005, 2006, 2007a, b; Precup et al., 2006 a, b; 2007, 2008; Precup, 2008). The present study deals with ceramic potshards from Copăceni, Derşida and Palatca (Fig. 1), provided by the National Museum of History of Transylvania from Cluj-Napoca.



Fig. 1. Location of the Copăceni - Early Bronze Age (1), Derşida - Middle Bronze Age (2) and Palatca - Late Bronze Age (3) sites within the Romanian territory.

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The Copăceni site is located 25 km south of Cluj-Napoca (site 1 in Fig.1) and was dated as Early Bronze in age (~2000 to 1600 B.C.). Small and medium-sized ceramic table ware was found at the site. The high amount and typological diversity of the ceramics remnants, and the finding of similar ware in several archaeological sites in Transylvania supported the outline of the most important cultural phenomenon of the second half of the Early Bronze age, i.e. the „Copăceni-type” (Rotea, 1993, 1997). Geologically, the site is located at the contact of the Transylvanian Depression with the units of the Northern Apuseni Mts. and Southern Apuseni Mts., respectively (Lupu et al., 1967). The Cenozoic sediments of the Transylvanian Depression are represented by Palaeocene continental red clays, Eocene marls, clays, limestones and sandstones, Badenian conglomerates, limestones ± celestine and barite (Imreh and Imreh, 1959; Savul et al., 1964), gypsum, salt, volcanic tuffs and sandstones, Sarmatian marls, sandy marls, sandstones and sands, Upper Pleistocene and Holocene gravels and sands. Lithologically, the units belonging to the Northern Apuseni Mts. (Săndulescu, 1984; Pană et al., 2002; Balintoni et al., 2009) include Palaeozoic and Mesozoic metamorphics (micaschists, quartzites, gneises, granitoids, amphibolites, skarns, marbles) and Late Cretaceous-Early Palaeogene magmatites (granodiorites, dacites, diorites, andesites). The Southern Apuseni Mts. units consists of Late Jurassic Island Arc Volcanics (basaltic andesites to rhyolites, and associated pyroclastics), overlain by Tithonian platform limestones.

The Derșida site is located in western Romania, 90 km in straight line NW of Cluj-Napoca (site 2 in Fig. 1). The ceramic findings consist of various table ware, decorated with incisions and assigned to the „Wietenberg Culture” (Chidioșan, 1980) of Middle Bronze Age (~1600 - 1300 B.C.). Geologically, the area belongs to the eastern part of the Pannonian Basin. Mainly Badenian conglomerates, sandstones, marls and limestones, Sarmatian sandstones, marls, conglomerates and sands, Pannonian clays, marls, sands and gravels, Upper Pleistocene sands, gravels, clays and loess and Holocene gravels and sands occur in the area (Bleahu et al 1966, Giușcă et al., 1967; Răileanu et al., 1967). Towards southeast, in the Meseș Mts. (Northern Apuseni Mts.), the metamorphics consisting of micaschists, garnet-micaschists, amphibolites, quartzites form a fault bounded, NE-SW oriented narrow wedge (Giușcă et al., 1967; Răileanu et al., 1967). Late Cretaceous-Early Paleogene dacitic and Neogene andesitic small bodies can be also found in the Meseș Mts.

The Palatca site is located 30 km in straight line ENE from Cluj-Napoca (site 3 in Fig. 1), in the Transylvanian Basin. The site is dated as Late Bronze Age (~1300 to 1000 B.C.) and several thousands fragments of various decorated pottery were found (Rotea, 1997). Geologically, around the site only sedimentary formations such as Badenian marls, sandstones, salt and volcanic tuffs, and Sarmatian marls, sands and gravel are found. The Holocene sands and gravels fill in the small valleys. Towards west, at 10 km in straight line, the Someș river shows large terraces, covered by Upper Pleistocene sands and gravels (Răileanu et al., 1967). In the Badenian formations the „Dej tuff” level occurs, cropping out west of Palatca (Ciupagea et al., 1970; Szakacs, 2000). In the close vicinity of the site, the Sarmatian formations contain,

intercalated between marls and sands, the „Ghiriș tuff”, compositionally a pyroxene andesite, with a high amount of amphiboles and pyroxenes (Ciupagea et al., 1970).

SAMPLES AND METHODS

For the identification of the mineral phases, 16 thin sections were cut from Copăceni, 22 from Derșida and 28 from Palatca samples respectively, were studied in polarized light. Due to the small size of the shards, only 5 ceramic samples from Derșida, 5 samples from Copăceni and 7 samples from Palatca were chemically analyzed for major, minor, trace and RE elements at the Acme Analytical Laboratories Ltd. Vancouver (Canada). For SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, MnO, TiO₂, P₂O₅, MnO, Cr₂O₃, Ba, Ni, Sc analyses by ICP-ES (Spectro Ciros Vision) and the ICP-MS analyses (Perkin-Elmer-Elan 6000/9000) for REE and incompatible elements were done by LiBO₂/Li₂B₄O₇ fusion in a graphite crucible at 980°C and subsequently dissolution in HNO₃ (5%). This procedure was also applied for Co, Cs, Ga, Hf, Nb, Rb, Sr, Ta, Th, U, V, W, Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The precious and base metals 2+ (Mo, Cu, Pb, Zn, Ni, As) were digested in aqua regia and also analyzed by ICP-MS. Loss of ignition (LOI) was determined by weight loss after ignition at 950°C for 90 minutes. The C_{tot} was determined by a LECO furnace.

RESULTS

Mineralogy and petrography

For a sound interpretation of the geochemistry of the ceramics, a brief presentation of the mineralogy and petrography is necessary.

The Copăceni pottery has red or dark brown colour, either homogeneously distributed across the ceramic body or forming a „sandwich-type” zoning. The observations made on thin sections in polarized light show two main ceramic types:

- Type A ceramics (Fig. 2a), composed of an opaque and more or less isotropic, amorphous clayish matrix. Embedded are mainly clasts of quartz and plagioclase, as well as muscovite. Moreover, biotite, amphiboles, pyroxenes, epidote, allanite(?) and opaque minerals were identified. As lithoclasts, fragments of micaschists, quartzites, skarn-like rocks and granitoids are visible.

- Type B ceramics (Fig. 2b) consists of a translucent, relatively anisotropic matrix. The crystalloclasts are composed of quartz, plagioclase and rare K-feldspar. Muscovite lamellae and rare amphibole can be seen. The lithoclasts consist of fragments of volcanic acidic tuffs, various volcanics (rhyolites, basaltic andesites, dacites) and chert. The texture in either preferentially oriented, parallel to the ceramic wall or shows a random orientation of lamellar phases and pores. One of the main characteristics for this ceramic type is the presence of high amount of plagioclase and volcanic acidic tuff fragments.

The Derșida samples show a wide range of colours, from light brown to dark brown, in general inhomogeneously distributed within the ceramic wall. The mineralogical study revealed a microcrystalline anisotropic

(Fig. 2c), sometimes amorphous isotropic (Fig. 2d) clayish matrix. Small crystalloclasts of quartz, K-feldspar, plagioclase, muscovite, rare amphibole and pyroxene, besides large-sized various lithoclasts are present. The most characteristic are the amphibolitic schists, quartzites, granodiorites and altered andesite fragments. Soil concretions are also identified, as well as rare ceramoclasts. The texture is in general unoriented, with few exceptions when it shows a slight parallel arrangement of lamellar minerals and pores.

The Palatca samples show a highly inhomogeneously coloured ceramic body, ranging from red to almost black. Very often a sandwich-type zoning can be noticed across the ceramic wall. The wide range of compositions do not allow to separate out some mineralogical-petrographic subgroups.

The matrix is either microcrystalline-anisotropic (Fig. 2e, f) or almost amorphous-isotropic. The clasts vary from sample to sample. Quartz, muscovite, K-feldspar and plagioclase (Fig. 2e) and various lithoclasts, such as quartzites, clays, sandstones are common. Andesite and pyroxenes are restricted to two samples (37-1 and 37-14). Ceramoclasts occur frequently (Fig. 2f). Calcite is rare and occurs as burial deposition on fissures and voids.

As a general remark, the ratio between the lutitic/partly silty grain size (matrix) over silt+arenite+rudite grains (clasts) is higher in Copăceni (54%) and Palatca (56%) compared with Derșida (48%). In individual samples this ratio might be reversed. The values are given as arithmetic mean.

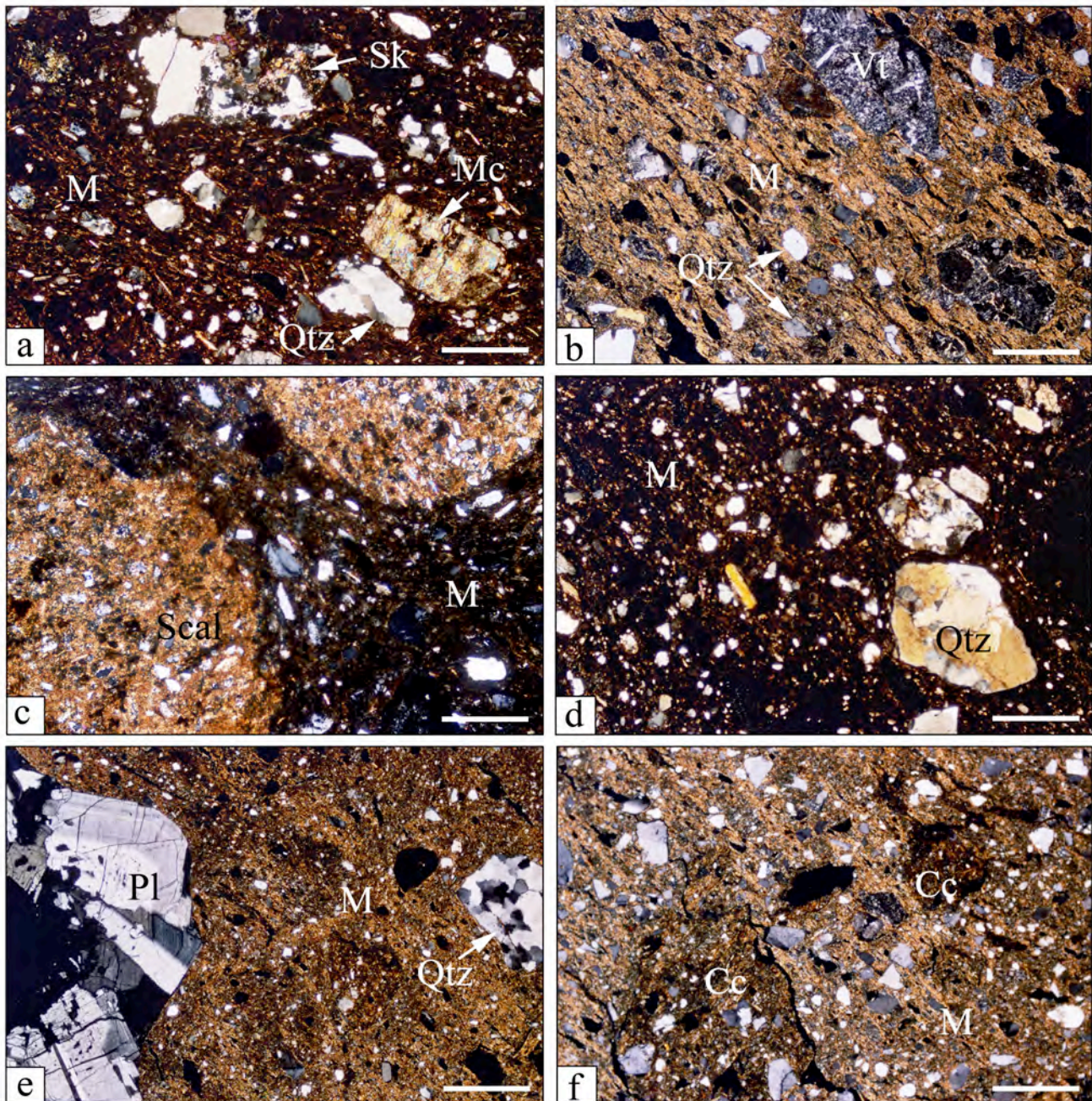


Fig. 2. Microphotographs of thin sections of Bronze Age ceramics (polarized light, crossed polarizers, scale bar = 0.5 mm. a) Sample 36-5 Copăceni A. Almost isotropic matrix (M) comprising clasts of quartzite (Qtz), diopside skarn (Sk) and micaschist (Mc); b) Sample 36-3 Copăceni B. Anisotropic, oriented matrix (M), with small crystalloclasts of quartz (Qtz) and large clasts of volcanic tuffs (Vi); c) Sample 35-1 Derșida. Isotropic matrix (M) enclosing large lithoclasts of calcareous silt (Scal); d) Sample 35-15 Derșida. Small crystalloclasts of quartz and large clasts of quartzites (Qtz) in an isotropic matrix (M); e) Sample 37-14 Palatca. Anisotropic matrix (M) including a very large plagioclase clast (Pl) and a quartzitic lithoclast (Qtz); f) Sample 37-10 Palatca. Quartz crystalloclasts (white and shades of gray in the image) and various ceramoclasts (Cc) embedded in an anisotropic matrix (M).

Geochemistry

The original geochemical analyses for the ceramics including the major, trace and RE elements are listed in Table 1. All samples show, based on SiO₂ content, an intermediate to acidic chemistry. The CaO content, ranging from 1.30% to 3.0%, is relatively low. Some elements *e.g.*, Al and Mg show only little variation. Others, such as K (Figs. 3a-c), Fe (Fig. 3d), Ti, Sr, Zr, Cr and Co show significant variation and can be used for grouping and classification. There is only a weak co-variation among the major elements. A first inspection of the data from all sites *i.e.*, Copăceni, Derşida and Palatca shows that they are spread to a certain extent not only between the groups but also within the groups. Among these, Na, K, Ca and P within the major element group and Ni, Co, Cr, Th, Sc, Zr, or Ce as trace elements respectively, have a certain potential of discrimination. Due to their similar geo-chemical properties many trace elements such as Cr/Ni, Cr/Co (Fig. 4a), La/Ce (Fig. 4b), V/Ti, V/Sc (Fig. 4c), Sc/Ti, Nb/Zr (Fig. 4d), Th/Ta, Zr/Hf and others are positively correlated. For example, the compatible elements such as Cr, Ni and Co are enriched during magmatic processes in minerals such as olivine, pyroxenes, amphiboles or spinels. When used as temper these elements contribute to the overall chemical budget of the ceramics. In a similar way the amount of Sc, V and to some extent Ti in ceramics can increase by adding a temper rich in amphibole, pyroxene, magnetite or ilmenite. The same holds for feldspar in respect to K, Na, Ba, Sr. On the other hand, some elements might be diluted by the frequent addition of quartz or quartzites as temper. Thus, the mineralogy of the temper plays an important role in the chemistry of the ceramics determining the relative enrichment or depletion of an element upon the mixture with the clayish matrix.

For the further discussion of the chemistry, the ceramics were grouped according to their original sites *i.e.* Copăceni, Derşida and Palatca, respectively. The samples from Derşida and Palatca show a considerable spread in major and trace elements, a division in subgroups is not discernable. The five Copăceni samples show a bi-modal element distribution (Table 1). Two shards (36-5 and 36-8) are markedly different from the others in respect to a large number of elements. They are significantly enriched in Fe, Ti, Al, Cr, Ni, Co, Cu, Zn, Sc, Nb, Zr, Y, V, Hf, Cs, and Rb, but relatively depleted in Si, K, and Sr compared to the three other shards (samples 36-1, 36-3, 36-7). Based on the systematic change, we grouped the former as Copăceni A and the rest as Copăceni B. This is in accordance with the mineralogy and petrography of Copăceni as described above. The major difference is the frequent occurrence of biotite, amphibole, pyroxene and metamorphics in the Copăceni A, compared with plagioclase, muscovite, volcanic acidic tuffs and volcanics in the Copăceni B ceramics.

DISCUSSION

The chemical analyses of ceramic shards should serve multiple purposes as: a) a characterization of a certain group of ceramics, b) possible separation between different groups, c) possible classification within one group and d) for provenance studies. Chemistry is not an independent variable, each chemical variation reflects the

differences in the mineralogical composition and the amount of matrix and temper.

Major Elements

The classical K₂O+Na₂O vs. SiO₂ diagram (Fig. 3a) highlights in particular the potential of the alkali elements to separate the groups: the Copăceni samples A and B are nicely separated from the Derşida samples by the significant higher alkali content of the former. The Na₂O vs. K₂O diagram (Fig. 3b) sorts out to a certain extent all three groups. The grouping is not perfect, but the Derşida samples exhibit a slightly higher Na₂O/K₂O ratio than the others. This is due to the low potassium content in the matrix (also shown by the electron microprobe analyses - unpublished data). Copăceni A and B have a tendency towards higher Na₂O and K₂O compared to Palatca.

Several other element ratios have been proposed for characterization of sediments in terms of provenance. For example the Al₂O₃/TiO₂ ratio (Nagarajan et al., 2007) or the K₂O/Al₂O₃ ratio (Fig. 3c, Table 1) and the Index of Compositional Variability (Cox et al., 1995).

The latter, in short ICV, is calculated from (Fe₂O₃+K₂O+Na₂O+CaO+MgO+MnO+TiO₂)/Al₂O₃ and it may range from 0.01 (clay minerals) to 1000 (non-clay silicates); it might well be applied also for ceramics. Values between 0.75 and 0.95 calculated for our samples indicate some contributions from minerals such as muscovite, feldspars and/or amphiboles as observed in the thin sections. The values are not significantly different between the groups (Table 1). The variation within the one group is in the same range. The K₂O/Al₂O₃ ratio (Fig. 3c) is lowest in Derşida (0.13 to 0.16), variable in Palatca and Copăceni A (0.12 to 0.20) but higher in Copăceni B (0.22-0.27). The low K₂O/Al₂O₃ ratio can be explained by the very low K₂O content combined with a relatively high CaO in the matrix (see above). The Al₂O₃/TiO₂ ratio is larger than 30 for Copăceni B (due to the more acidic clasts) and between 16 and 20 for the rest of the samples.

Trace elements

While Copăceni B samples are easily distinguished by some major elements, the other groups are more difficult to be separated out. Copăceni A has the highest Fe₂O₃ content (Fig. 3d) and additionally the highest Co (Fig. 4a) and Ce (Fig. 4b) values as well as high concentrations of Cu, Zn, Ti, V and Sc (Fig. 4c). This is at least partly due to the opaque minerals as well as to the relatively high amount of pyroxene and amphiboles as part of the temper. Both subgroups of Copăceni have one specific characteristic, the high Sr content which is, with 500 to 2000 ppm, a multiple of those from Derşida and Palatca (100-250 ppm). The high Sr content (Fig. 4e) in Copăceni is most likely caused by the specific localization in close vicinity of the site of the celestine-bearing Badenian formations (Imreh and Imreh, 1959; Savul et al., 1964).

The differentiation among Derşida and Palatca is more difficult to obtain. Both groups overlap to a wide extent and are rarely clearly separated. Among the major elements, only the Na₂O/K₂O ratio (Fig. 3b) shows a certain potential for classifying as shown above. In a similar way as the alkalis, the Zr/Nb ratio (Fig. 4d) separates both groups with a value of below 18 for Derşida and above 18 for Palatca.

Table 1. Bulk-rock chemistry for Bronze Age ceramic samples.

Sample	36-5	36-8	36-1	36-3	36-7	35-1	35-8	35-10	35-11	35-12	35-15	37-1	37-10	37-13	37-14	37-16	37-23	37-24	
Site	Copăceni B					Derșida					Palatca								
SiO ₂	58.72	64.81	65.35	66.06	66.83	68.96	66.14	66.32	62.27	69.66	67.39	66.30	69.69	70.60	64.74	60.27	64.59	68.89	
TiO ₂	0.98	0.85	0.38	0.48	0.31	0.73	0.76	0.82	0.68	0.85	0.76	0.79	0.78	0.73	0.92	0.70	0.70	0.76	
Al ₂ O ₃	16.87	17.72	14.71	13.87	14.82	14.83	15.45	14.3	13.41	14.31	14.46	16.43	14.43	13.91	15.92	15.79	14.24	14.53	
Fe ₂ O ₃	7.35	7.08	3.76	4.30	3.78	5.79	5.94	5.13	5.43	5.47	5.4	6.14	4.31	5.13	6.46	6.13	5.58	6.84	
MnO	0.15	0.17	0.04	0.03	0.03	0.12	0.06	0.08	0.07	0.09	0.06	0.12	0.05	0.09	0.07	0.13	0.07	0.13	
MgO	2.04	1.78	1.48	1.66	1.78	1.52	1.34	1.20	1.45	1.36	1.34	1.44	1.21	1.13	1.26	1.56	1.43	1.28	
CaO	2.31	1.48	2.06	2.08	1.72	2.03	2.00	1.92	3.03	1.57	2.00	1.34	1.68	1.29	1.96	2.11	1.58	1.14	
Na ₂ O	1.17	1.20	0.74	1.31	1.33	1.19	1.07	1.01	0.98	1.16	1.08	1.03	0.91	1.10	0.85	0.90	0.80	0.97	
K ₂ O	2.98	2.96	3.99	3.08	3.45	1.90	2.10	2.21	1.87	2.25	2.27	3.21	2.58	2.53	1.86	2.98	2.07	2.89	
P ₂ O ₅	0.19	0.15	0.21	0.14	0.05	0.19	0.34	0.34	0.64	0.23	0.4	0.13	0.23	0.22	0.50	0.52	0.22	0.16	
LOI	7.00	1.60	6.90	6.70	5.60	2.60	4.60	6.60	10.00	2.90	4.80	2.90	3.90	3.10	5.20	8.60	8.50	2.20	
Total	99.76	99.80	99.62	99.71	99.70	99.86	99.80	99.93	99.83	99.85	99.96	99.83	99.77	99.83	99.74	99.78	99.78	99.81	
K ₂ O/Al ₂ O ₃	0.17	0.16	0.27	0.22	0.23	0.13	0.14	0.15	0.14	0.16	0.16	0.20	0.18	0.18	0.12	0.19	0.15	0.20	
ICV	1.0065	0.8758	0.8463	0.9329	0.8367	0.8954	0.8589	0.8650	1.0075	0.8910	0.8928	0.8563	0.7983	0.8627	0.8404	0.9246	0.8588	0.9642	
TOT/IC	0.93	0.34	0.64	0.61	0.26	0.23	0.17	0.83	1.87	0.13	0.76	0.13	0.22	0.70	0.39	1.72	0.79	0.14	
TOT/S	0.01	0.01	<0.02	<0.02	<0.02	0.01	0.03	0.01	0.03	0.03	0.01	0.01	<0.02	0.01	<0.02	0.01	<0.02	<0.02	
Ba	721.4	769.7	1149.1	619	609	508	782	890.6	691	727	592.6	826.2	768	684.4	828	1040.4	684	554	
Mb	1.3	1	0.4	0.2	0.1	0.3	0.2	0.2	0.2	0.2	0.2	0.6	0.6	0.6	0.5	0.5	0.4	1.4	
Cu	32.3	23.2	10	13.8	12.9	13.7	15.4	20.4	24.3	12.5	12	15.8	16.1	17.8	14.2	26.5	21.0	25.6	
Pb	12.2	12.9	17.1	8.0	7.6	9.2	15.1	14	15.2	12.9	11.1	14.7	18.2	13	17.6	16	19.2	21.8	
Zn	89	83	47	43	32	50	67	62	63	52	64	69	68	74	56	88	62	75	
Ni	48.3	43.3	6.6	7.7	6.9	19.2	25.3	27.5	23.7	24.3	20.6	34.8	33.1	36.2	17.4	33.3	31.5	51.3	
Cr	130	116	34	41	27.4	75	75	75	68.5	95.8	89	116	109.5	103	89	116	95.8	109.5	
As	4.7	6.5	3.3	3.6	3.6	3.4	6.4	4.8	6.6	4.1	7	5	4.6	7.7	12.7	17.9	7.3	8.1	
Co	19.3	19.2	7.9	8.0	7.1	16.2	13.6	15.6	14.5	16.2	13.9	14.1	14.5	13.4	16.1	14.4	13.4	17.6	
Sc	18	16	10	11	9	15	15	13	14	14	14	14	13	11	16	14	12	14	
Sr	5.2	7	3.6	3.6	3.2	3.8	4.1	4.4	3.8	4.2	3.6	6	5.7	6	5.9	6.1	6.0	6.2	
Ga	21.3	21.1	14.8	14.6	15.2	15.9	16.0	17.2	14.3	15.5	15.6	18.4	16.0	15.4	17.4	19	16.8	16.9	
Hf	6	6.1	4.2	3.8	4.3	5.4	5.8	7.8	5.7	7.0	6.4	5.8	6.3	5.9	6.6	5.9	4.9	5.8	
Nb	14.3	13.3	11.1	8.7	10.6	9.1	11.8	13	10.1	13.2	10.3	11.7	14.4	11.7	14.7	12.4	13.9	14.0	
Rb	103.8	128.5	83.2	92.2	74.9	68.9	69.7	84.9	71.9	81.3	73.9	106.6	92.2	101	73.8	115.6	102.3	105.1	
Sr	795.8	412.4	2008.4	899.7	1441	165.5	191.9	211.3	224.4	154.9	246.1	123.1	139.2	116.6	181.0	186	146.3	104.9	
Ta	1.2	1	1.2	0.8	1.0	0.7	0.8	1.1	0.8	0.9	0.9	1	1.1	0.9	1.0	1	1.0	1.1	
Th	13.1	12.5	18	11.9	16.1	7.8	9.4	11.1	7.8	11.2	9.6	11.7	11.6	8.9	11.3	12.2	11.6	12.1	
U	2.9	2.9	2.7	2.0	2.7	1.7	2.2	2.5	1.8	2.5	1.8	2.3	2.8	2.2	3.2	2.6	2.2	2.6	
V	144	134	58	61	48	116	108	116	108	103	123	102	96	97	133	120	99	109	
W	2.1	2.1	1.7	1.9	1.3	1.3	1.5	1.6	1.6	1.9	1.4	2.3	2.0	1.8	1.9	2.1	1.9	2.0	
Zr	194	216.8	123.9	139.2	160.9	177.2	215.7	258.7	204.2	257.3	220.3	195.1	231.4	202.1	252.3	203	193.4	197.6	
Y	31.6	35.2	42.1	15.5	16.2	23.8	23.7	32.1	26.0	24.8	28.9	30.6	23.9	24.9	27.1	30.5	22.1	24.3	
La	36.5	37.8	45.5	20.8	24.2	23.4	25.6	31.8	21.9	28.3	27	32.5	29.5	30.4	31.1	35.7	27.5	28.8	
Ce	88.7	90.1	78.6	42.2	50.6	54.3	52.1	75.3	49.5	61.1	63.6	78.7	62.9	75.1	60.5	82.2	59.9	66.1	
Pr	9.27	9.78	11.61	4.82	5.71	6.15	6.52	8.13	6.39	7.21	7.1	8.38	7.42	7.62	7.66	8.66	6.88	7.49	
Nd	34.7	36.9	42.6	19.9	21.9	23.4	26.9	31.1	25.2	29.5	28.2	31.9	30.4	29.2	31.3	32.9	28.2	29.3	
Sm	6.6	6.9	8.9	3.47	3.92	4.6	5.12	5.9	4.84	5.61	5.2	6.1	5.65	5.2	5.88	6.2	5.09	5.51	
Eu	1.3	1.42	1.24	0.67	0.70	0.95	1.18	1.23	1.08	1.20	1.08	1.17	1.16	1.01	1.27	1.15	1.04	1.12	
Gd	5.19	5.86	7.72	2.93	3.33	3.8	4.77	5.23	4.50	4.92	4.5	4.94	4.88	4.4	5.39	5.13	4.51	4.83	
Tb	0.99	1.07	1.45	0.51	0.57	0.75	0.80	0.94	0.77	0.87	0.84	0.95	0.85	0.81	0.91	0.99	0.79	0.80	
Dy	5.1	5.65	7.25	2.81	2.96	3.66	4.30	5.14	4.59	4.62	4.6	5.02	4.63	4.24	4.83	5.19	4.36	4.38	
Ho	1.02	1.05	1.23	0.60	0.61	0.75	0.88	0.95	0.92	0.99	0.86	0.96	0.95	0.82	1.02	0.94	0.89	0.87	
Er	3.12	3.43	3.75	1.84	1.94	2.32	2.52	2.94	2.47	2.90	2.73	3	2.77	2.58	2.97	2.95	2.54	2.48	
Tm	0.47	0.5	0.52	0.29	0.31	0.34	0.41	0.45	0.41	0.44	0.41	0.44	0.43	0.37	0.48	0.43	0.43	0.41	
Yb	2.84	3.03	3.38	1.94	1.98	2.02	2.50	2.77	2.50	2.63	2.57	2.76	2.63	2.34	2.98	2.76	2.58	2.42	
Lu	0.41	0.44	0.49	0.30	0.30	0.34	0.38	0.42	0.39	0.40	0.39	0.43	0.41	0.36	0.45	0.41	0.38	0.36	

*Major elements in %, minor, trace and RE elements in ppm. Ferric as Fe₂O₃. Index of Compositional Variability (ICV) = (Fe₂O₃+K₂O+Na₂O+CaO+MgO+MnO+TiO₂)/Al₂O₃.

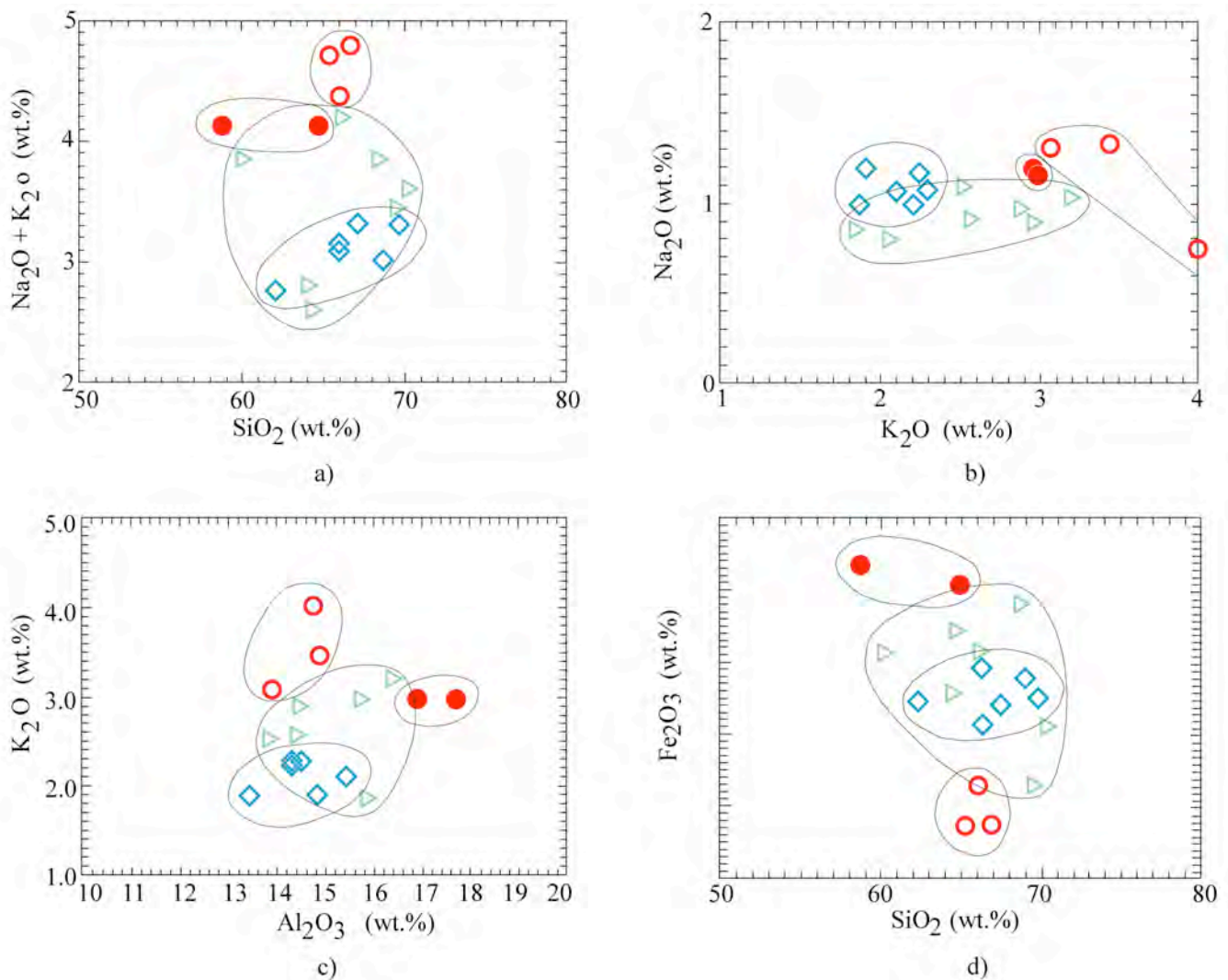


Fig. 3. Plot of the ceramics composition in the a) SiO_2 vs. $\text{Na}_2\text{O} + \text{K}_2\text{O}$, b) K_2O vs. Na_2O , c) Al_2O_3 vs. K_2O and d) SiO_2 vs. Fe_2O_3 diagrams. Legend: full red circles - Copăceni A, empty red circles - Copăceni B, blue diamonds - Derșida, green triangles - Palatca.

Furthermore, there is also a tendency for lower Cr and Ni values in Derșida but again not clear separation. A distinct separation among both groups is shown only by the Cs content (Fig. 4f), with about 6 ppm in Palatca and 4 ppm in Derșida.

The accuracy and the precision of the Cs determination is in the range of 0.4 ppm and 0.2 ppm respectively, which allows for a clear separation. In the ceramics, Cs can have two sources: either from the matrix clay (silt) and/or from the temper minerals. According to Cullers (1994) shales and clays can incorporate up to 30 ppm Cs, silts and sands less up to 9 and 7 ppm Cs respectively. On the other hand, Cs can be included in the K-bearing minerals (compare Murariu, 2002) such as feldspar (up to 30 ppm), muscovite (approx. 20 ppm) and particular in biotite (up to 200 ppm). Minor amounts of Cs also occur in amphiboles. The temper clasts from Derșida are derived mainly from metamorphics from the Northern Apuseni Mts. and contain frequently biotite, muscovite, amphiboles and to a lesser extent K-feldspar. These minerals can contribute significantly to the overall Cs concentration in these samples. The Palatca clastics are derived from the Neogene volcanics, with plagioclase, K-feldspar and rare biotite.

Despite the higher amount of potential Cs-bearing minerals, the Derșida samples show consistently lower Cs value than Palatca, where such minerals are rare. This argues in turn for already different Cs levels in the matrix clays (silts) between Derșida and Palatca.

REE and Spider diagrams (Figs. 5a-f and 6a-f). The normalisation of the REE and other trace elements against those from mantle, crust or MORB is a powerful tool in magmatic petrology to infer magmatic processes. This approach may be also used in interpreting ancient ceramics. Normalizing the REE against various average shales such as North American Shale Composite (NASC; Gromet et al., 1984), Post Archean Australian Shale (PAAS; Taylor and McLennan 1985; Nagarajan et al., 2007) or European Shale (ES; Haskin and Haskin, 1966), similar patterns appear for all samples (Copăceni – Fig. 5a, Derșida – Fig. 5c, Palatca – Fig. 5e), consistent with the results for other trace elements. For simplicity only the NASC normalized patterns are shown.

Generally, the REE concentration of the ceramics normalized against NASC is slightly below 1, varying from 0.6 to 1. Few samples are above 1 for the LREE. The overall pattern is almost flat with a minor variation, as for example a small relative enrichment of Ce or a small depletion of Er. Normalized with NASC, a negative Eu

anomaly is observed in Copăceni B samples and to a lesser extent in Copăceni A.

The Upper Continental Crust (UCC; Rudnik and Gao, 2003) normalized patterns are close to unity, with the MREE and the HREE slightly above (Figs. 5 b,d,f). The low concentration of REE in the ceramics compared with the shales is probably due to the temper but it brings at the same time the ceramics close to the average upper

continental crust. It should be noted here that the (La/Yb)_N ratio is >1 for NASC and <1 for the UCC normalization. The Copăceni A group has a higher REE content than Copăceni B except for the sample 36-1 which exhibits the highest REE concentration in particular for Sm, Gd, Tb, Dy, due to a singular occurrence of a REE-bearing mineral, probably allanite. In 36-1 Ce and Eu values are lower than for Copăceni A.

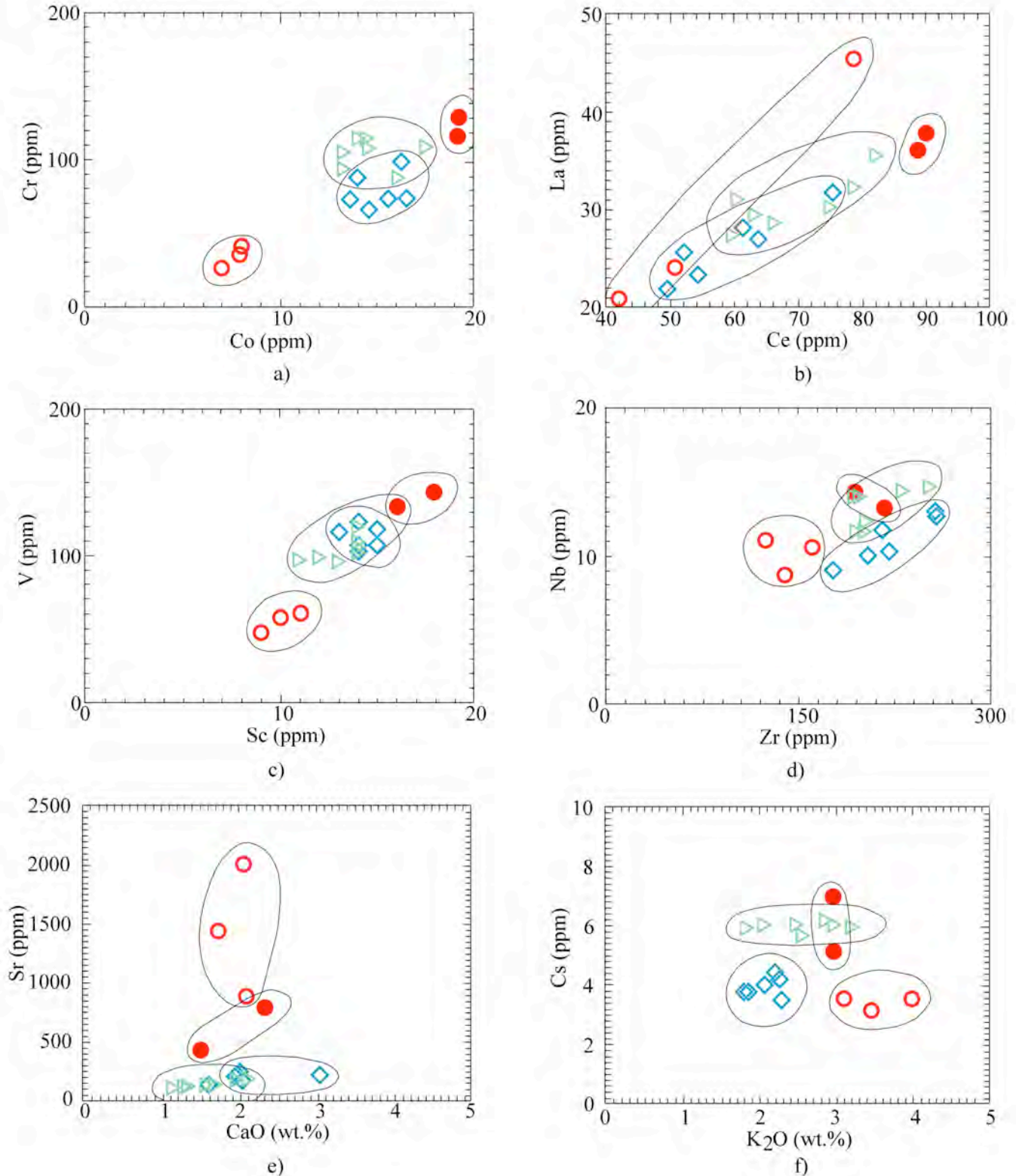


Fig. 4. Plot of the ceramics composition in the a) Co/Cr, b) Ce/La, c) Sc/V, d) Zr/Nb, e) CaO/Sr and f) K₂O/Cs diagrams. Legend: full red circles – Copăceni A, empty red circles – Copăceni B, blue diamonds - Derșida, green triangles - Palatca.

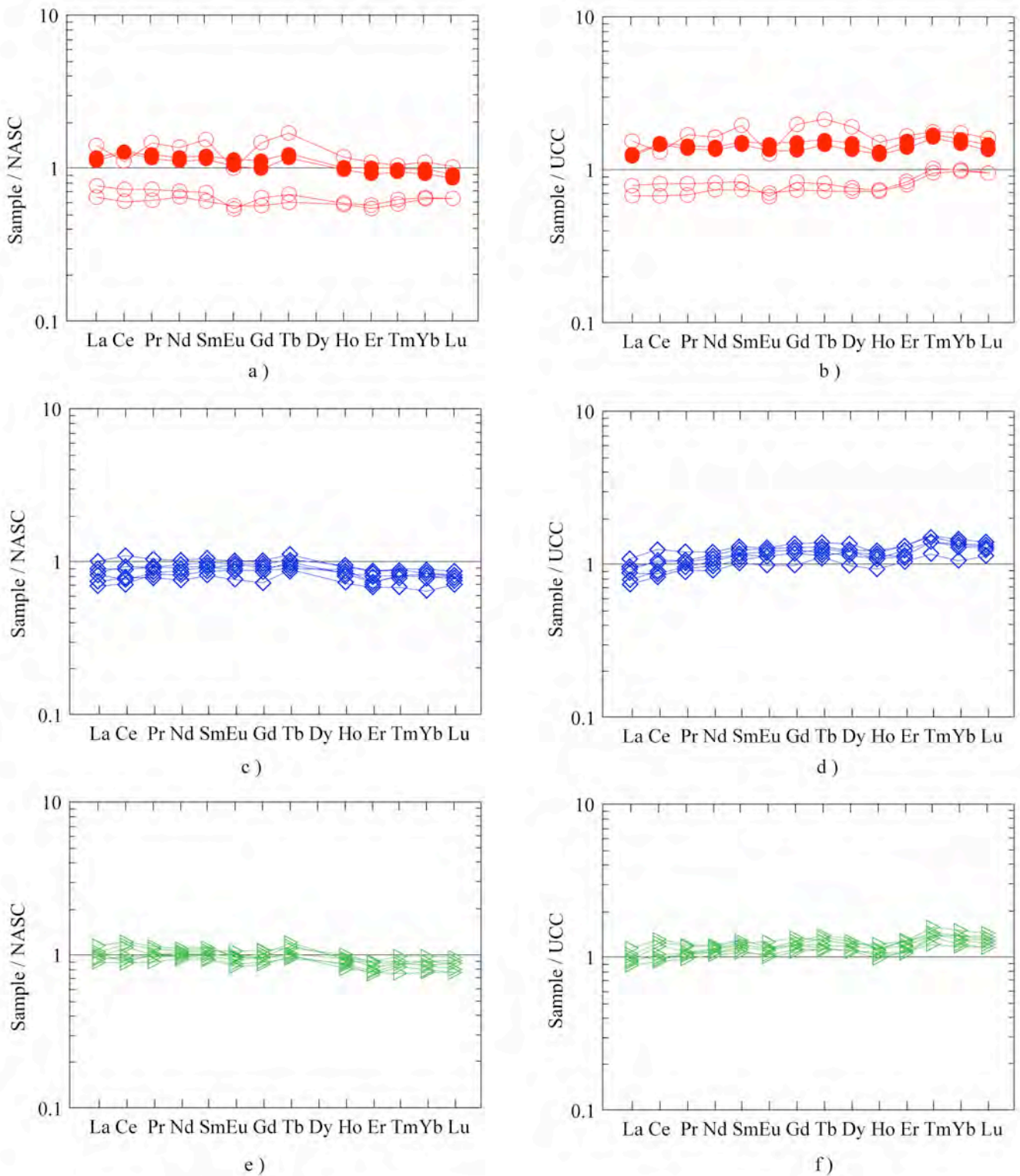


Fig. 5. REE diagrams for Copăceni (a, b), Derșida (c, d) and Palatca (e, f) samples, normalized to NASC (Gromet et al., 1984) (a, c, e) and UCC (Rudnik and Gao, 2003) (b, d, f). Legend: full red circles - Copăceni A, empty red circles - Copăceni B, blue diamonds - Derșida, green triangles - Palatca.

The spider diagrams (Figs. 6a-f) normalized against NASC display similar results (Figs. 6 a, c, e). The patterns are slightly below unity with some irregularities. Rb, is low in all groups, K in Copăceni A, Derșida and Palatca, Ti only in Copăceni B and Cs in Derșida. Ba and Y are high in all samples, Th only in the Copăceni groups. The positive Sr anomaly in Copăceni (Fig. 6a) is clearly visible. Additionally, Derșida exhibits a small positive Sr anomaly (Fig. 6c) which is not seen in Palatca (Fig. 6e). Sample 36-1 from Copăceni B is highest in the REE, Y, Studia UBB, Geologia, 2009, **54** (2), 41 – 51

Ba, and Th but low in the other elements. Normalized against the UCC, the pattern is more close to 1, only the elements between Zr and Yb are slightly above (Fig. 6b). As a whole, the it is more smooth except for Sr, with a positive anomaly for Copăceni A and B, but contrast to the NASC normalization with a negative anomaly for Derșida and Palatca, which is due to the high Sr values of UCC. The low Ti (due to low Ti content of the acidic volcanics - derived temper) values remain for the Copăceni B samples (Fig. 6a).

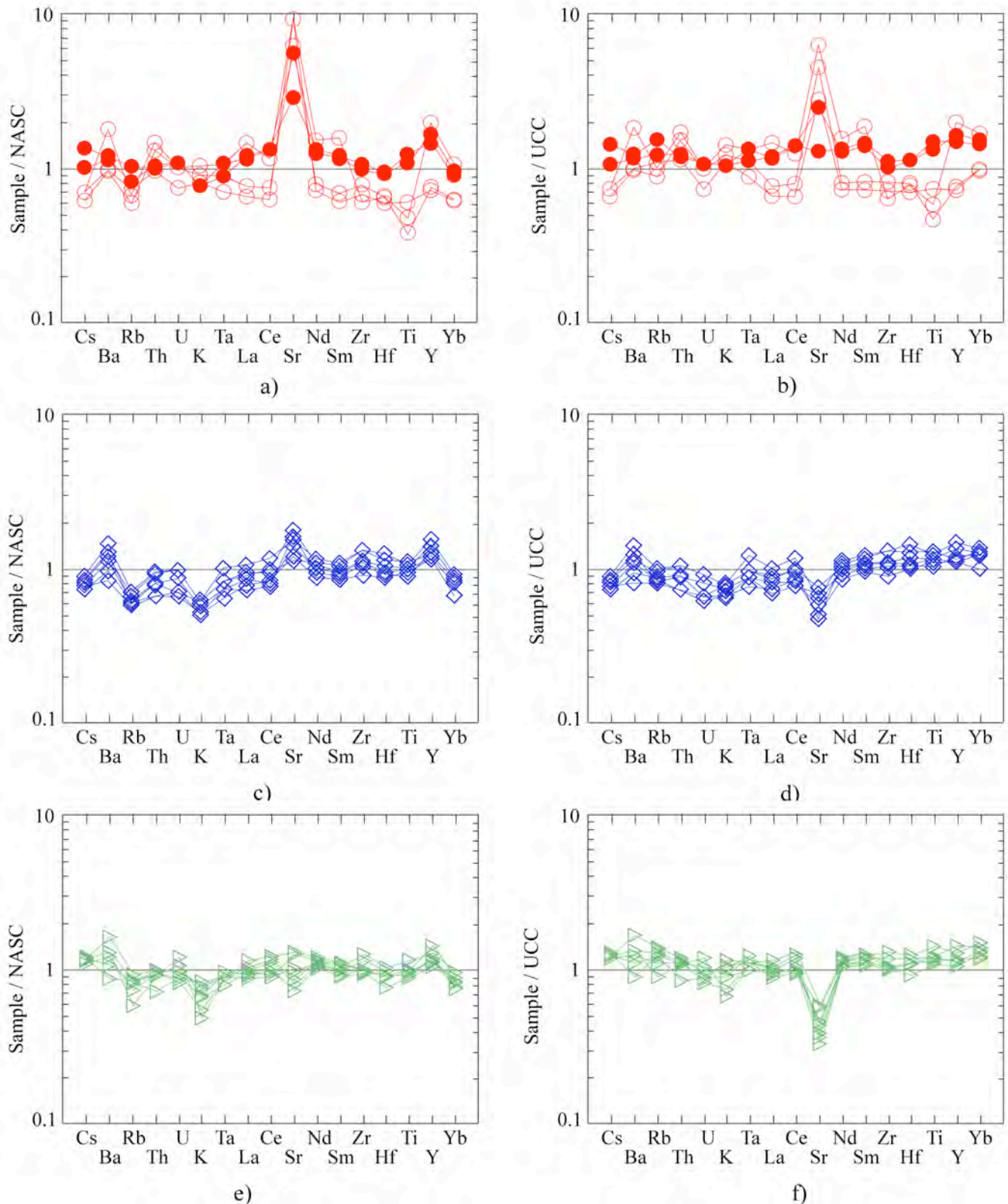


Fig. 6. Spider diagrams for Copăceni (a, b), Derșița (c, d) and Palatca (e, f) samples normalized to NASC (Gromet et al., 1984) (a, c, e) and UCC (Rudnik and Gao, 2003) (b, d, f). Legend: full red circles - Copăceni A, empty red circles - Copăceni B, blue diamonds - Derșița, green triangles - Palatca.

Like the bivariate diagrams, the REE normalized and the spider diagrams also sort out clearly Copăceni B from the rest. Both Copăceni groups are distinct in their anomalous high Sr content (Figs. 6 a, b). Derșița (Figs. 6 c, d) and Palatca (Figs. 6 e, f) samples overlap largely, the former showing a trend to lower normalized

values. The shale normalized patterns, as shortly discussed above, are below 1 regarding mainly REE and spider diagrams equally. For the interpretation, the nature of the temper minerals is important. Pyroxene, amphibole, biotite, muscovite and opaque minerals contribute to the REE and partly to several other trace elements in Copăceni

A and Derşida. The acidic volcanic fragments, quartz and feldspars forming almost exclusively the temper in Copăceni B and Palatca cause more likely a dilution of the total REE budget. This difference is well visible within the both Copăceni groups, but not discernable between Palatca and Derşida. Most likely the clays were already variably depleted in respect to the REE and trace elements such as Ti, U, Pb, Nb, and Cs concentration. The (La/Yb)_N ratios point in the same direction. They are, depending on the norm values, similar for all groups despite the highly variable temper material suggesting also differences in the REE content in the raw clays.

CONCLUSIONS

The discussion of the chemical data and their interpretation, in terms of mineralogy, showed that the variability of the chemistry is to a considerable part determined by minerals such as quartz, feldspars, pyroxene, amphibole, micas, opaque minerals and the according lithoclasts including metamorphics, acidic or basic volcanics and plutonics.

Despite the relative small database, a careful analysis of the chemistry combined with the mineralogy, allows to characterize the Bronze Age ceramics from the three locations and to separate out the subgroups A and B for Copăceni. Based on major elements, such as Al₂O₃, TiO₂ and K₂O, the Copăceni B subgroup could be sorted out not only from Copăceni A but also from Derşida in a relatively simple way. The exceptional REE concentrations of sample 36-1 from Copăceni B are probable due to the presence of allanite. Derşida is well separated from both Copăceni groups in terms of major and trace elements. Due to their wide spread element concentration compared with the other groups the Palatca samples overlap to a certain extent with Copăceni A, the distinction from Copăceni B is more clear. The most difficult is the distinction between Derşida and Palatca. Both groups are sorted out - not always accurately - by their Na₂O/K₂O, Zr/Nb ratios and the Cs content.

The chemistry contributes also to the identification of raw material sources, in particular the temper. Copăceni A was separated out, among other elements, by the positive Sr anomaly. It is an excellent evidence that the Copăceni raw material was mined at a close distance from the Badenian celestine-bearing sediments. Whereas Copăceni A has an important contribution from the metamorphic basement of the Northern Apuseni units, with acidic and basic rock fragments and minerals, including opaque phases, the mineralogy in Copăceni B is documented by intermediate and acidic volcanics derived from the Jurassic Island Arc Volcanics. This difference in mineralogy is clearly reflected in the chemistry of the ceramics. The temper material for the first group were most likely alluvial sediments of the Hășdate brook. These alluvias contain fragments of the Apuseni metamorphics showing basic and acidic composition. For Copăceni B the most probable source is then the Racilor creek, NNW of Copăceni.

The temper material was collected in relatively close vicinity of the sites. This is in particularly true for the Copăceni, with a strong Sr anomaly indicating the Badenian source. In Derşida, metamorphic rocks and to a

smaller extent intermediate and acidic volcanics were collected as temper from the Crasna Mare river sediments nearby. This river has its springs in the metamorphic rocks of the Northern Apuseni units (Meseş Mts.). Besides the metamorphic material it also takes some Neogene volcanics downhill. More complicated is the situation in Palatca, located in the Transylvanian Basin. Chemistry and mineralogy indicate intermediate to acidic volcanics together with some metamorphics as major temper material. Presently, there is no river catchment which could collect such material from either the Eastern Carpathians or the Apuseni Mts., but the Sarmatian sediments include clastic sequences with volcanic and metamorphic clasts, which could be derived from the geological surroundings of the Transylvanian Basin, probably from the NE in the Sarmatian times. In the absence of an appropriate stream catchment we suppose that the raw materials of the ceramics were collected from outcrops of Sarmatian silts and sands.

The geochemical analyses from three sites assigned to the Bronze Age contain data including major elements, trace elements and REE. They are the first complete data set on Bronze Age ceramics in Romania and were linked with their mineralogical composition. Although the quantity of analyses is not too large they can serve as a basis for a geochemical reference set used by further studies.

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