

# Petrological and Geochemical Features of the Neogene Volcanites of the Osogovo Mountains, Eastern Macedonia

## Petrološke in geokemične značilnosti neogenskih vulkanskih kamnin Osogovskih planin (vzhodna Makedonija)

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**Abstract:** The subject of the presented study was the petrological and geochemical characterization of the Neogene volcanic rocks from the Osogovo Mountains. In this paper we present new results of petrological and geochemical analyses of igneous rocks, mostly from Sasa, Toranica and Ruen. The mineralogical and geochemical characteristics of the studied rocks confirmed the results of some previous investigations that indicated that the exposed lithologies are mostly dacites, quartzlatites, trachyandesites, lamprophyres and rhyolites. An absolute age determination using a standard K-Ar method gives ages between  $31.16 \pm 1.40$  and  $14.0 \pm 3.0$  m.y., and also confirmed their proposed Oligocene-Miocene age. The parent material of these rocks is supposed to originate from the contact zone between the lower crust and upper mantle. A possible assimilation of crustal material during magma formation was also suggested. This supposition was further confirmed by the results of the strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) ratios, which are in the range from 0.70954 to 0.71126, as well as by other geochemical characteristics.

**Izvleček:** Članek obravnava petrološke in geokemične značilnosti neogenskih vulkanskih kamnin na območju Osogovskih planin v vzhodni Makedoniji. Podani so najnovejši rezultati geokemičnih analiz in izotopske sestave stroncija ter podatki o njihovi absolutni starosti, dobljeni na podlagi konvencionalne K-Ar metode. Na podlagi mineralne sestave in geokemičnih značilnosti uvrščamo raziskane kamnine med riolite, kremenove latite, trahiandezite in lamprofirске žilnine. Ti različki so bili ugotovljeni tudi v okviru prejšnjih, zvečine petroloških raziskav. Kamnine so oligocensko-miocenske starosti. Glede na podatke o absolutni starosti, dobljeni na podlagi K-Ar metode, lahko rečemo, da so nastale v razponu od pred  $31.16 \pm 1.40$  do  $14.0 \pm 3.0$  milijonov let. Izotopska sestava stroncija in nekatere geokemične značilnosti kažejo, da je magma, iz katere so kristalizirale, najverjetneje izvirala iz kontaktne cone med spodnjim delom zemeljske skorje in zgornjim plaščem. Pri tem dopuščamo tudi možnost njene delne kontaminacije z materialom zemeljske skorje.

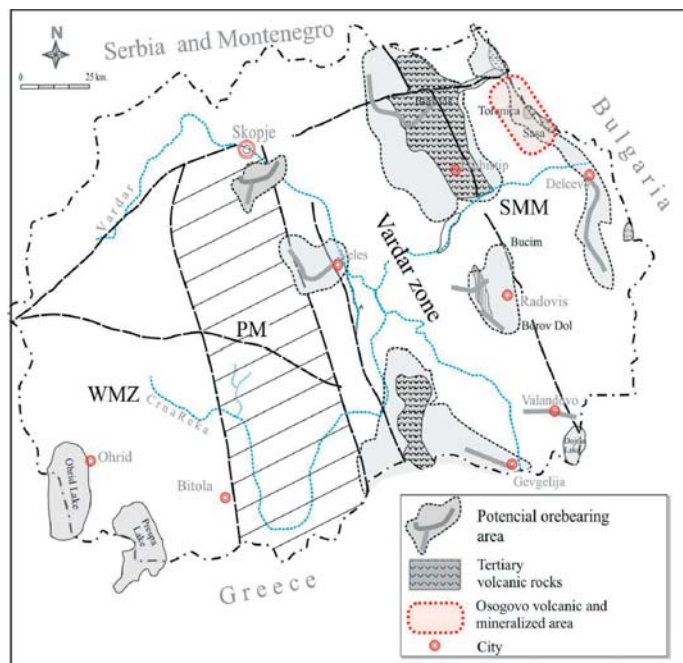
**Key words:** Osogovo mountains, volcanic rocks, absolute age, magma origin, Neogene volcanism

**Ključne besede:** Osogovske planine, vulkanske kamnine, absolutna starost, izvor magme, neogeni vulkanizem

## INTRODUCTION

Volcanic and volcano-intrusive rocks of the Osogovo volcanic and ore-bearing district are a part of a greater metallogenic unit known as the Besna Kobila-Osogovo-Tasos metallogenic zone. The zone has a northwest direction and a total length of 100 km, and is extended on both sides of the Macedonia-Bulgaria border (BOGOEVSKI, 1965; SERAFIMOVSKI, 1990; SERAFIMOVSKI, 1993; ALEXANDROV, 1992; JANKOVIĆ ET AL., 1995). Volcanic rocks in the zone have similar morphological, petrological and geochemical features, and all of them are of Tertiary age. In Macedonia they were found in the northeastern part on the border with Bulgaria (Fig. 1). It should be mentioned that volcanic rocks of similar composition were also found in Bulgaria.

The volcanic rocks in the investigated area occur as elongated dykes with a northwestern direction, a thickness of 50 m and an azimuth of  $260^\circ$ . From the Osogovo to the Besna Kobila Mountains volcanic rocks are represented by pyroclastites, volcanic domas, dykes, necks and veins. In the Osogovo-Besna Kobila mountains they cut the Paleozoic and Riphean-Cambrian metamorphic and igneous rocks and/or cover the older sedimentary rocks of the Upper Eocene age. In the vicinity of the Sasa and Toranica Pb-Zn ore deposits they are represented mostly by dacitic tuffs, dacites, quartzlatites, rhyolites, trachyandesites, andesite-latites and occasionally by lamprophyre veins.



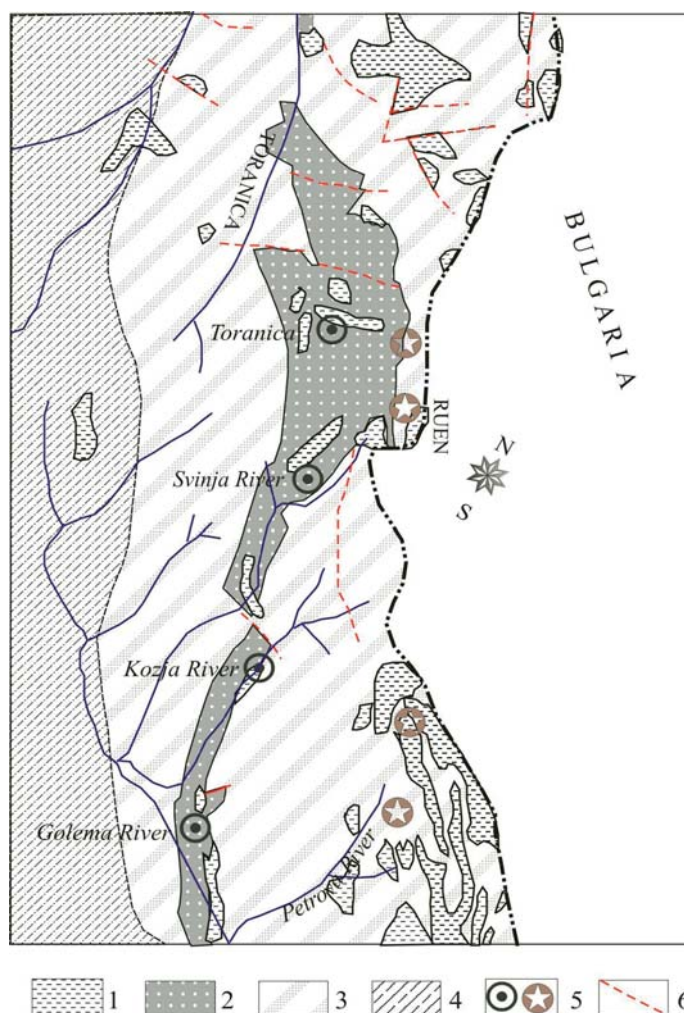
**Figure 1.** Distribution of the Tertiary magmatism in Macedonia.

**Slika 1.** Geografska razprostranjenost terciarnega magmatizma v Republiki Makedoniji.

## GEOLOGICAL SETTING

A detailed description of the major lithologies exposed in the investigated area is summarized by BOGOEVSKI (1965), SERAFIMOVSKI (1990), SERAFIMOVSKI (1993), ALEXANDROV (1992), JANKOVIĆ ET AL. (1995). Large areas of the Osogovo Mountains are

covered by various rocks of different origin. Metamorphic rocks such as two mica-type gneisses and quartz graphite schists are the most abundant. These rocks belong to the crystalline basement of the Serbo-Macedonian Massif (SMM). Quartz graphite schists are of special importance, because they are one of the most important host rocks



**Figure 2.** Geologic setting of the Sasa-Toranica ore district. 1) Quartzlatites, 2) Quartz graphite schists, 3) Sericite-chlorite schists, 4) Gneiss, 5) Lead-zinc deposits and occurrences, 6) Faults.  
**Slika 2.** Geološka zgradba rudonosnega območja Sasa-Toranica. 1) kremenovi latiti, 2) kremenovo-grafitni skrilavci, 3) sericitno-kloritni skrilavci, 4) gnajsi, 5) svinčevo-cinkovo orudjenje in mineralizacija, 6) prelomi.

for the Pb-Zn mineralization. They are usually interbedded with cipolin marbles, which are also very favorable for metasomatic Pb-Zn mineralization. The geological composition of the area is further comprised of quartzlatite, trachyandesite, dacite, trachydacite dykes and necks, which cut older lithological formations. Small lamprophyre dykes and veinlets were also observed (Fig. 2).

The most characteristic tectonic features of the investigated area are the plicative and disjunctive structures. Plicative structures are represented by different scale-size folds observed in quartz graphite schists. The disjunctive - fault structures are the most abundant in the Sasa and Toranica ore deposits. The productive Pb-Zn mineralizations have been found in different ore deposits and mineralizations. The most important deposits are Sasa, Toranica and Ruen. The detailed geological investigations revealed that the ore mineralization is closely related to the Neogene volcanism.

## MATERIALS AND METHODS

For the purpose of this study various igneous, metamorphic and sedimentary rock and ore samples were collected in the field and in the Pb-Zn ore deposits Sasa and Toranica according to the sampling programme designed at the Faculty of Mining and Geology in Štip.

All samples were evaluated by petrographic methods to assess their mineralogical characteristics, ore genesis and hydrothermal alterations. For further geochemical and geochronological analyses unweathered and

hydrothermally unaltered or only slightly altered samples were chosen. They were then ground in a mechanical agate grinder to a fine powder for further analyses. Major, minor and trace element analyses were performed in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd.) by ICP-MS. Rock reference samples JR-2 (rhyolite) and JA-2 (andesite) were used to validate the analytical procedure. Major and minor elements were also determined by XRF at the Laboratories of the Geological Department of the University of Padova, Italy. The determination of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios by TIMS on ten selected volcanic bulk rock samples was made in the Geology Department, Royal Holloway University of London, U.K. Conventional K-Ar dating was performed on seven volcanic bulk rock samples at the Geological Institute in Budapest, Hungary. The accuracy and precision of the analyses were acceptable. The details of the geochemical and isotopic analyses as well as of age determination analyses can be found in BOEV ET AL. (1997) AND TASEV (2003).

## RESULTS AND DISCUSSION

### Petrography

The results of the microscopic study revealed that the dacites in the Luke-Kiselica area, which extend from the Karamanica Mountain to the southeast of the Osogovo mountains (SERAFIPOVSKI AND ALEXANDROV, 1995) are characterized by plagioclase phenocrystals with approximately 37 % An content followed by a small amount of orthoclase, quartz, biotite and amphiboles. Their matrix is holocrystalline to

hypocrystalline with glassy remains. Accessory minerals, such as apatite, sphene and zircon, were found only in traces, while sericite, chlorite, kaolinite, carbonates and ore minerals are of secondary origin.

Quartzlatites were found near the springs of the river Lucka and Kuprina Padina as dykes, and at Samar and Karamanica as dykes and/or volcanic flows (Samar and Crchorija) which cover the underlying volcano-sedimentary rocks. They are characterized by a coarse grained porphyric structure due to the presence of sanidine and plagioclase phenocrysts with approximately 35-40 % An content. Amphiboles and augite were also found as phenocrysts. The accessory minerals are sphene and zircon. These rocks were also mineralized.

Hyalandesites appear as necks and lava flows over the Upper Pliocene sediments at Gradeška mountain. These rocks are of porphyry-vitrophyric structure with plagioclase phenocrysts containing about 37 % An component, followed by more or less well developed biotite, amphibole and augite crystals, and accessory apatite and zircon grains.

At the Sasa-Toranica ore district prevail the volcanic rocks, such as dacite and quartzlatite of hypoabyssal and subvolcanic characteristics. In the whole district these volcanites are hydrothermally altered. Dacites exhibit a holocrystalline structure with about 30 % of the andesine phenocrysts containing 5-16% of An component. Next abundant are the feldspar minerals (13-20 %) followed by quartz (2-3 %) and a small amount of orthoclase, mainly replaced by epidote, chlorite and carbonates. Hydrothermal alte-

rations of the andesites were of various character; illitization, sericitization and propylitization are the most abundant. Apatite, zircon, sphene and magnetite are accessory minerals, while pyrite, chalcopyrite, sphalerite and galena are ore minerals related to mineralization of hydrothermal origin.

The most abundant rocks in the investigated area are represented by quartzlatites. They occur as elongated dykes a few kilometers long. These rocks are characterized by large phenocrysts, mostly sanidine, andesine and feldspar minerals such as biotite, amphiboles and rarely augite. The sanidine crystals are fresh and large; they are up to 6 cm long. Quartzlatites were also considerably hydrothermally altered. Transition rocks, from quartzlatites to rhyolites, were also found in few locations at the Osogovo Mountains. They are slightly more acidic and are exposed near the Sekirica Tower close to the Macedonian-Bulgarian border. The rocks were intensively propylitized.

The volcanic rocks from the Kozja and Svinja River (Sasa mining district) are mainly represented by dacites and quartzlatites. They are highly propylitized and hydrothermally altered. These rocks also contain ore minerals such as pyrite, galena, sphalerite and others.

Trachyandesites of the Sasa-Toranica and broader area form smaller bodies at subvolcanic-volcanic levels. They are characterized by a porphyry structure (fine-grained porphyry) and a crystallized microlitic or microtrachytic matrix. The phenocrysts are up to 3 mm long, and are represented by andesine, sanidine, biotite, augite and hornblende euhedral grains. Apatite, sphene and

zircon occur as accessory minerals. In comparison to the quartzlatites, trachyandesites are depleted in  $\text{SiO}_2$  content. Similar rocks are also exposed in Pečovska Mala in the Osogovo Mountains in Bulgaria.

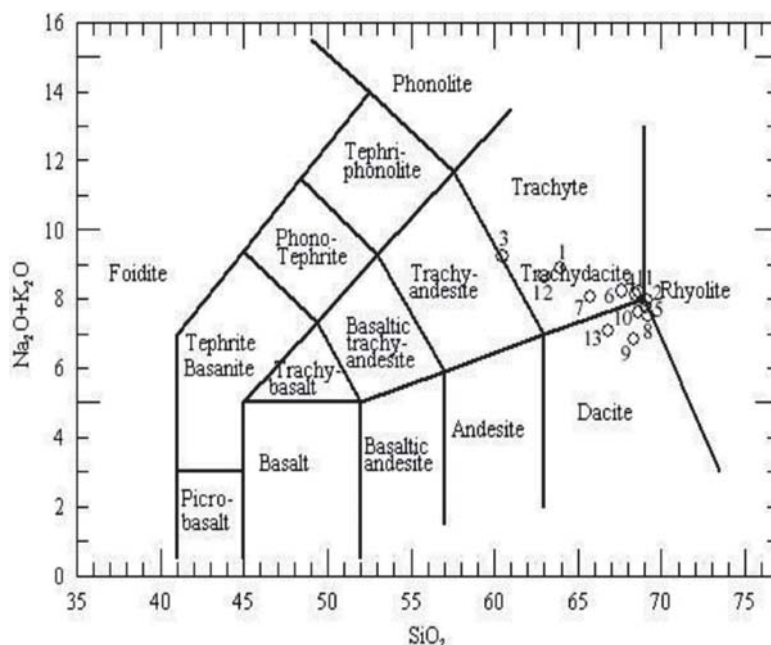
Lamprophyres occur as small dykes near Sredno Brdo and Toranica. They are dark gray to brown with a fine-grained porphyry structure and a glassy matrix. The phenocrysts are pyroxenes, amphiboles and biotite. Accessory minerals are represented by apatite, sphene and zircon.

### Geochemistry

Major, minor and selected trace elemental compositions of the most important volcanic rocks of the Sasa-Toranica ore district are

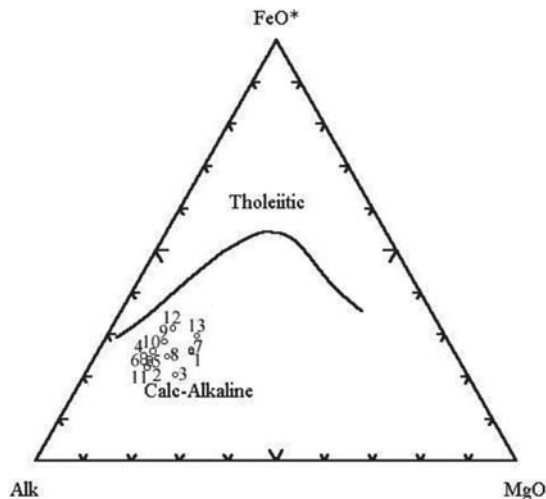
presented in Table 1, while Table 2 shows the results of the REE analyses. In Figure 3 the Total Alkali Silica diagram (LE MAITRE ET AL., 1989) with the position of the analyzed samples is shown. The Figure 4 represents the IRVING AND BARAGAR (1971) classification for volcanic rocks.

From Figures 3 and 4 it is clear that the investigated volcanites mostly plot in the fields that define dacites, trachydacites and rhyolites. Only sample 3, with the highest  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  content, plots in the border between the trachydacite and trachyandesite fields. Furthermore, a classification according to IRVING AND BARAGAR (1971) revealed that the volcanites from the Sasa-Toranica ore district are of calcalkaline rock suites. The whole rock C1 chondrite



**Figure 3.** Chemical classification and nomenclature of the volcanic rocks in the Sasa-Toranica ore region, using diagram total alkalis vs. silica (LE MAITRE ET AL., 1989).

**Slika 3.** Klasifikacija vulkanskih kamnin rudonosnega območja Sasa-Toranica na podlagi vsebnosti alkalij in kremenice (TAS) (LE MAITRE ET AL., 1989).

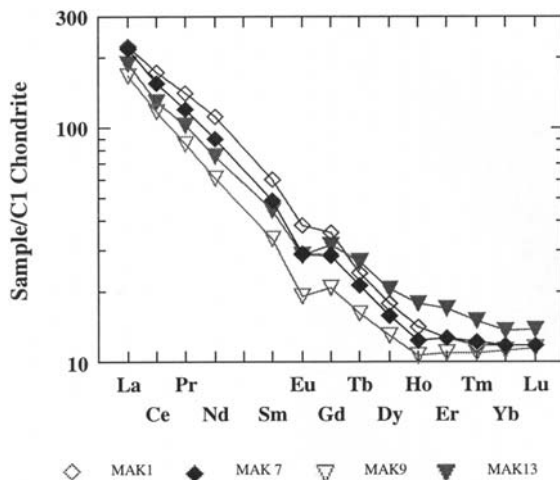


**Figure 4.** Classification of volcanic rocks from the Sasa-Toranica ore region ( $\text{Alk} = \text{Na}_2\text{O} + \text{K}_2\text{O}$ ;  $\text{FeO}^* = \text{FeO} + 0.8998 \times \text{Fe}_2\text{O}_3$  (IRVING AND BARAGAR, 1971).

**Slika 4.** Klasifikacija vulkanskih kamnin rudonosnega območja Sasa-Toranica po IRVINGU IN BARAGARJU (1971); ( $\text{Alk} = \text{Na}_2\text{O} + \text{K}_2\text{O}$ ;  $\text{FeO}^* = \text{FeO} + 0.8998 \times \text{Fe}_2\text{O}_3$ ).

normalized REE patterns (Fig. 5) show a strong LREE enrichment above the average continental crust and moderate negative europium anomalies with  $\text{Eu}/\text{Eu}^*$  values between 0.728 and 0.829 (Table 2). Such a

strong LREE enrichment could be related to crystal fractionation and/or assimilation of the LREE-enriched continental material or a combination of the two mechanisms (DRAUT ET AL., 2002).



**Figure 5.** Rare-earth element patterns normalized to C1 chondrite for the volcanic rocks from the Sasa-Toranica ore region.

**Slika 5.** Vzorec redkih zemelj za vulkanske kamnine rudonosnega območja Sasa-Toranica normaliziran na C1 hondrit.

**Table 1.** Chemical composition of the volcanic rocks in the Sasa-Toranica ore region (major oxides in %), trace elements in ppm).

**Tabela 1.** Kemična sestava vulkanskih kamnin iz rudonosnega območja Sasa-Toranica (glavni oksidi v %, sledne prvine v ppm).

| Elem.                          | M1    | M2    | M3    | M4    | M5    | M6    | M7    | M8    | M9    | M10   | M11   | M12   | M13   |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>               | 63.93 | 69.10 | 60.48 | 68.46 | 69.09 | 67.62 | 65.73 | 69.19 | 68.35 | 68.59 | 68.65 | 63.00 | 66.83 |
| TiO <sub>2</sub>               | 0.65  | 0.43  | 0.54  | 0.44  | 0.44  | 0.46  | 0.63  | 0.40  | 0.41  | 0.42  | 0.40  | 0.52  | 0.56  |
| Al <sub>2</sub> O <sub>3</sub> | 14.35 | 14.92 | 16.43 | 15.47 | 15.00 | 15.53 | 14.94 | 14.72 | 15.15 | 15.29 | 15.29 | 16.24 | 15.52 |
| Fe <sub>2</sub> O <sub>3</sub> | 1.29  | 0.67  | 0.81  | 0.57  | 0.82  | 0.92  | 0.91  | 0.67  | 0.73  | 0.53  | 0.58  | 2.31  | 0.61  |
| FeO                            | 3.05  | 2.37  | 2.37  | 2.58  | 2.20  | 2.19  | 3.07  | 2.49  | 2.62  | 2.69  | 2.44  | 2.81  | 3.53  |
| FeOt                           | 4.43  | 3.11  | 3.22  | 3.26  | 3.07  | 3.17  | 4.04  | 3.22  | 3.50  | 3.31  | 3.09  | 5.17  | 4.33  |
| MnO                            | 0.11  | 0.08  | 0.10  | 0.08  | 0.10  | 0.07  | 0.09  | 0.31  | 0.34  | 0.30  | 0.24  | 0.10  | 0.40  |
| MgO                            | 3.15  | 1.38  | 2.86  | 1.24  | 1.40  | 1.42  | 2.86  | 1.87  | 1.46  | 1.38  | 1.32  | 2.00  | 2.58  |
| CaO                            | 3.91  | 2.78  | 6.85  | 2.69  | 2.89  | 3.27  | 3.14  | 2.51  | 3.70  | 2.85  | 2.55  | 4.04  | 2.47  |
| Na <sub>2</sub> O              | 2.56  | 3.38  | 3.67  | 2.66  | 3.40  | 3.24  | 2.88  | 1.58  | 1.46  | 1.95  | 2.85  | 3.28  | 2.43  |
| K <sub>2</sub> O               | 6.32  | 4.58  | 5.57  | 5.47  | 4.37  | 4.98  | 5.19  | 5.93  | 5.37  | 5.66  | 5.35  | 5.36  | 4.66  |
| P <sub>2</sub> O <sub>5</sub>  | 0.60  | 0.24  | 0.28  | 0.23  | 0.24  | 0.24  | 0.49  | 0.27  | 0.25  | 0.24  | 0.24  | 0.28  | 0.21  |
| LOI                            | 3.96  | 3.43  | 3.05  | 4.03  | 4.06  | 3.87  | 3.69  | 2.77  | 5.31  | 4.33  | 3.56  | 4.96  | 4.93  |
| Cr                             | 50    | 27    | 27    | 38    | 24    | 14    | 69    | 71    | 50    | 30    | 27    | 17    | 73    |
| Ni                             | 30    | 32    | 34    | 49    | 18    | 16    | 46    | 52    | 45    | 29    | 37    | 12    | 61    |
| Ba                             | 2339  | 1236  | 1586  | 1199  | 1151  | 1336  | 1587  | 2290  | 1873  | 1900  | 2550  | 1297  | 2722  |
| Rb                             | 247   | 211   | 137   | 270   | 214   | 224   | 213   | 218   | 236   | 242   | 191   | 165   | 196   |
| Sr                             | 964   | 499   | 1216  | 415   | 464   | 555   | 580   | 408   | 268   | 347   | 460   | 664   | 314   |
| La                             | 59    | 59    | 52    | 57    | 71    | 66    | 39    | 56    | 48    | 47    | 59    | 95    | 53    |
| Ce                             | 106   | 71    | 110   | 98    | 63    | 78    | 95    | 62    | 84    | 66    | 62    | 139   | 58    |
| Nd                             | 29    | 16    | 31    | 9     | 26    | 24    | 29    | 16    | 7     | 0     | 0     | 38    | 5     |
| Zr                             | 297   | 186   | 135   | 195   | 199   | 195   | 221   | 251   | 189   | 200   | 181   | 163   | 173   |
| Y                              | 22    | 21    | 24    | 19    | 19    | 19    | 22    | 23    | 19    | 22    | 22    | 24    | 32    |
| Nb                             | 15    | 11    | 10    | 12    | 12    | 10    | 13    | 12    | 11    | 12    | 10    | 10    | 11    |
| Th                             | 44    | 31    | 34    | 30    | 34    | 30    | 34    | 49    | 33    | 39    | 40    | 49    | 37    |
| U                              | 9     | 7     | 5     | 9     | 7     | 8     | 7     | 8     | 8     | 9     | 7     | 6     | 7     |

**Legend:** 1. M-1 Trachydacite; 2. M-2 Trachyte-rhyolite-dacite; 3. M-3 Trachyandesite-trachydacite; 4. M-4 Trachydacite; 5. M-5 Dacite; 6. M-6 Trachydacite; 7. M-7 Trachydacite; 8. M-8 Dacite; 9. M-9 Dacite; 10. M-10 Dacite; 11. M-11 Trachydacite; 12. M-12 Trachydacite; 13. M-13 Dacite.

**Legenda:** 1. M-1 trahidacit; 2. M-2 trahit-riolit-dacit; 3. M-3 trahiandezit-trahidacit; 4. M-4 trahidacit; 5. M-5 dacit; 6. M-6 trahidacit; 7. M-7 6 trahidacit; 8. M-8 dacit; 9. M-9 dacit; 10. M-10 dacit; 11. M-11 6 trahidacit; 12. M-12 6 trahidacit; 13. M-13 dacit.

**Table 2.** Rare-earth elements content (in ppm) in the volcanic rocks from the Sasa-Toranica ore region.**Tabela 2.** Vsebnost REE (v ppm) v vulkanskih kamninah iz rudonosnega območja Sasa-Toranica.

| Elem. | MAK1 I | MAK7 I | MAK9 II | MAK13 II |
|-------|--------|--------|---------|----------|
| La    | 53.10  | 52.00  | 39.60   | 44.90    |
| Ce    | 106.00 | 95.40  | 72.10   | 79.30    |
| Pr    | 13.30  | 11.40  | 8.08    | 9.72     |
| Nd    | 52.50  | 42.10  | 28.30   | 35.20    |
| Sm    | 9.20   | 7.50   | 5.10    | 6.80     |
| Eu    | 2.22   | 1.68   | 1.11    | 1.65     |
| Gd    | 7.30   | 5.90   | 4.30    | 6.50     |
| Tb    | 0.90   | 0.80   | 0.60    | 1.00     |
| Dy    | 4.50   | 4.00   | 3.30    | 5.20     |
| Ho    | 0.80   | 0.70   | 0.60    | 1.00     |
| Er    | 2.10   | 2.10   | 1.80    | 2.80     |
| Tm    | 0.30   | 0.31   | 0.28    | 0.38     |
| Yb    | 2.00   | 2.00   | 1.90    | 2.30     |
| Lu    | 0.30   | 0.30   | 0.29    | 0.35     |
| Eu*   | 0.83   | 0.77   | 0.73    | 0.76     |

**Legend:** MAK-1I Trachydacite; MAK-7I Trachydacite; MAK-9II Dacite; MAK-13II Dacite

**Legenda:** 1. MAK-1I trahidacit; MAK-7I trahidacit; MAK-9II dacit; MAK-13II dacit

The Eu anomaly is mainly controlled by the presence of feldspars.  $\text{Eu}^{2+}$  is compatible in plagioclase and K-feldspar, relative to the  $\text{Eu}^{3+}$  that is incompatible. Thus the removal of feldspar from a felsic melt by crystal fractionation or partial melting of a rock

containing K-feldspars gave rise to a negative Eu anomaly in the melt. A crystal fractionation and/or partial melting of the continental material could thus explain a negative europium anomaly in the investigated samples (DRAUT ET AL., 2002).

**Table 3.**  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the volcanic rocks from the Osogovo mountain.**Tabela 3.** Izotopsko razmerje  $^{87}\text{Sr}/^{86}\text{Sr}$  v vulkanskih kamninah Osogovskih planin

| No. | Locality                         | Rock type       | $^{87}\text{Sr}/^{86}\text{Sr}$ |
|-----|----------------------------------|-----------------|---------------------------------|
| 1.  | Golema R.950, Sasa               | Quartzlatite    | 0.71051                         |
| 2.  | Kozja R. IV <sub>o</sub> , Sasa  | Quartzlatite    | 0.70994                         |
| 3.  | Svinja R. IV <sub>o</sub> , Sasa | Quartzlatite    | 0.71126                         |
| 4.  | Toranica – 2                     | Quartzlatite    | 0.71016                         |
| 5.  | Toranica, TO-1                   | /               | 0.70979                         |
| 6.  | Sasa                             | Andesite-latite | 0.71064                         |
| 7.  | Sasa                             | Quartzlatite    | 0.71024                         |
| 8.  | Sasa, SA-2                       | /               | 0.70954                         |
| 9.  | Toranica, MK-1                   | Trahydacite     | 0.71055                         |
| 10. | Sasa, MK-9                       | Dacite          | 0.71096                         |

(1-8) BOEV ET AL. (1997), (9-10) TASEV (2003).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  initial ratios of the analysed rocks are reported in Table 3. Their isotopic results range from 0.70954 to 0.71125. These values are mostly in the range of the igneous rocks of the crustal origin, and are somewhat higher than the values commonly found in the andesites (0.703 – 0.708) and the plutons aligned along the continental margins (CARMICHAEL ET AL., 1974). Such values also suggest that the magma that has produced Neogene igneous complexes at the Osogovo mountains is a product of the primary magmatic melt that originated from the border zone between the upper mantle and the continental crust where processes of mixing and the contamination of primary magma occurred. This is also supported by strontium isotope data for the Upper Tertiary calc-alkaline complexes of the Serbo-Macedonian metallogenic province and Kožuf Mountain ( $^{87}\text{Sr}/^{86}\text{Sr}$  is in the range from 0.7088 to 0.7090) as well as by those for volcanic rocks from the Rogozna, where the initial range of  $^{87}\text{Sr}/^{86}\text{Sr}$  is between 0.7074 and 0.7085 (SERAFIPOVSKI, 1990).

The above mentioned magmatic activity was related to the processes that took place after the closure of the Tethys Ocean and subduction of the oceanic plate under

the SMM (Serbo-Macedonian masif - Cretaceous), due to the collision of the African plate with the Euroasian plate. The collision of these two continental segments produced the calc-alkaline magmatism during the Middle and Upper Jurassic. The collision also resulted in thickening of the continental crust and in isostatic uplifting. Due to discontinued compression, temporal, partial melting of the basal parts of the continental parts took place. The pulsations of the tectono-magmatic activities were repeated many times during the Oligocene, Miocene and Pliocene (KARAMATA, 1982; SERAFIPOVSKI AND TASEV, 2002). From the metallogenic point of view, of special interest is the zone of deep fractures along the west margin of the SMM, which represents the active continental margin. The fractures served as feeding channels for the uplifting of calc-alkaline magmas and hydrothermal ore bearing solutions (JANKOVIĆ ET AL., 1997).

Nevertheless, some other authors (BOEV AND YANEV, 2001) relate these magmatic and hydrothermal activities to Late Tertiary Aegean subduction, referred to active continental margin of the Andean type. They supposed that the Macedonian igneous rocks were formed by mildly alkaline magmas

**Table 4.** Absolute age determination of the volcanic rocks in the Sasa-Toranica ore region by the K/Ar method (TASEV, 2003).

**Tabela 4.** Absolutna starost vulkanskih kamnin iz rudonosnega območja Sasa-Toranica, določena na podlagi K/Ar metode (TASEV, 2003).

| No. | Locality         | Rock type       | K-Ar age (m.y.) |
|-----|------------------|-----------------|-----------------|
| 1.  | Mal Ruen         | Quartzlatite    | 28.38±1.09      |
| 2.  | Toranica-I       | Quartzlatite    | 28.36±1.09      |
| 3.  | Sasa (Kozja R.)  | Quartzlatite    | 30.72±1.19      |
| 4.  | Sasa (Kozja R.)  | Andesite        | 29.25±1.13      |
| 5.  | Sasa (Crvena R.) | Granodiorite    | 31.16±1.40      |
| 6.  | Sasa             | Andesite-latite | 14.0±3.0        |
| 7.  | Sasa             | Quartzlatite    | 24.0±3.0        |

originating from the upper part of the supra-subduction area. The subduction process in the Miocene and Pliocene moved to the south and southwest, probably due to the extension in the north Aegean region (GAUTIER ET AL., 1999) causing migration of the volcanic activity in Macedonia in the same direction, from the Kratovo-Zletovo to the Kožuf area.

Tertiary igneous rocks from the Osogovo mountains are characterized by an unusual distribution of the Pb, Ba, Sr, Rb, Li, Cs and Be contents. They exhibit relative to the Clark background values elevated concentrations of Pb, Ba, Sr and Be and similar contents of Li, Rb and Cs. During the magmatic processes the increase in the concentrations of Li, Pb, Cs, Be, Rb and Ba was observed from fine-grained porphyry quartzlatites to coarse-grained porphyry quartzlatites (SERAFIMOVSKI, 1993A; SERAFIMOVSKI ET AL., 2003). The observed distribution of trace elements most probably indicates that the igneous rocks were formed of magma from the same magmatic chamber, which in different time intervals produced different rock types.

The age of the volcanic rocks of the Sasa-Toranica ore district according to the standard K/Ar method is in the range from  $31.16 \pm 1.13$  to  $14.0 \pm 3.0$  m. y. (Table 4). This range is of the Oligocene-Miocene age, and was also confirmed by other methods.

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## CONCLUSIONS

The presented study of the volcanic rocks from the Sasa-Toranica ore district revealed very different granitoid lithologies, such as rhyolites, dacites, trachydacites and trachyandesites of the Oligocene-Miocene age. According to the standard K/Ar method the age of those rocks range from  $31.16 \pm 1.40$  to  $14.0 \pm 3.0$  m.y. The volcanic rocks display a relatively large range in Sr isotopic ratios. This could be interpreted as a result of fractional crystallization processes occurring at the contact zone between the lower continental crust and the upper mantle, and associated with a possible assimilation of crustal material.

## Acknowledgement

For all his efforts during the field sampling of the Sasa-Golema River, Sasa-Kozja River, Sasa-Petrova River and Ruen volcanites as well as for help with the laboratory analysis, we express our sincere gratitude to our colleague Prof. Dr. Giuliano Bellieni from the Department of Mineralogy and Petrology, University of Padova, Italy. We would also like to thank our colleague Dr. Petra Souvent from the Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia, for help during the fieldwork. Thanks to Dr. Paul McGuinness for linguistic corrections.

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## New data concerning the major ore minerals and sulphosalts from the Pb-Zn Zletovo Mine, Macedonia

### Novi podatki o glavnih rudnih mineralih in sulfosoleh iz Pb-Zn rudišča Zletovo (Republika Makedonija)

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**Abstract:** Based on its mineral content (around 40 minerals) and certain solid solution mineral phases, Zletovo has been classified as a subvolcanic hydrothermal Pb-Zn ore deposit. The main ore minerals are galena and sphalerite. They occur in very characteristic structures, microstructures and textures, which often enclose sulphosalt mineral phases. The most common sulphosalts are bournonite, boulangerite, proustite and luzonite. So far the sulphosalt minerals and their solid solution phases from the Zletovo ore deposit have not been studied in detail. This paper presents the results of a detailed study of ore samples from different levels of the Zletovo mine based on electron microprobe analysis. In the already known mineral assemblage, which is composed mainly of galena, sphalerite, pyrite, chalcopyrite, and siderite, the sulphosalts series, which includes tetrahedrite-tennantite, luzonite, stibioluzonite and pearceite, was distinguished. The composition of the tetrahedrite-tennantite solid solution ranges from pure tetrahedrite to pure tennantite, with the presence of minerals that are representatives of the processes of the intermixing of solid solutions. The compositions of the determined pearceites and luzonites almost match the compositions of the standards for these minerals.

**Izvleček:** Glede na pestro mineralno paragenezo (okrog 40 mineralov) in določene mineralne faze uvrščamo rudišče Zletovo med subvulkanska hidrotermalna Pb-Zn rudišča. Glavna rudna minerala sta galenit in sfalerit, ki kažeta značilne strukture, mikrostrukture in teksture, značilne za hidrotermalna rudišča. Zelo pogosto ju obdajajajo minerali iz skupine sulfosoli. Najbolj pogosto gre za bournonit, boulangerit, proustit in luzonit. Do sedaj minerali sulfosoli iz rudišča Zletovo podrobno niso bili raziskani. V okviru te študije smo z detajlno raziskavo rudnih vzorcev iz različnih obzorij s pomočjo elektronskega mikroanalizatorja poleg glavnih rudnih mineralov kot so galenit, sfalerit, pirit halkopirit in siderit našli še nekatere nove minerale iz skupine sulfosoli. Gre za trde raztopine sistema tetradrit-tenantit, mineral pearceit ter že prej poznani luzonit, ki zaenkrat še ni bil podrobneje raziskan. Sestava pearceita in luzonita se v glavnem ujema s standardno sestavo teh mineralov.

**Key words:** Zletovo Mine, mineral paragenesis, ore minerals, sulphosalts

**Ključne besede:** Rudnik Zletovo, mineralna parageneza, rudni minerali, sulfosoli

## INTRODUCTION

The Zletovo Pb-Zn ore deposit is situated along the active continental margin and is intimately associated with Tertiary volcanism and related hydrothermal activity. The Zletovo Mine is located in the eastern part of the Kratovo-Zletovo volcanic complex. It lies about 5 km NW of the Zletovo village and about 7 km from the town of Probištip.

The first detailed exploration was started in 1928 by the English Selection Mines Limited company and was finished in 1939 when the Zletovo deposit was prepared for exploitation with an annual capacity of 120 000 t of raw ore. Exploitation of the Zletovo Mine have began again during the Second World War with an annual capacity of 400 000 t. The mine is still active up to date and produces lead-zinc concentrates. During the long history of the exploration and exploitation of the Zletovo ore deposit several contributions concerning the origin and the genetic characteristic were published (CISSARZ AND RAKIĆ, 1956; RADUSINOVIĆ, 1961; PANTIĆ ET AL., 1973; DENKOVSKI, 1974; RAKIĆ, 1978; BLEČIĆ, 1981, 1983; PETKOVIĆ, 1982; ZARIĆ, 1982; SERAFIMOVSKI, 1990, 1993; EFREMOV, 1993; SERAFIMOVSKI AND BOEV, 1996; SERAFIMOVSKI AND TASEV, 2003).

There are also a lot of bibliographic materials and annual reports that have resulted from the exploration of the Zletovo Mine concerning the domain of the volcanic rocks, the fault structures, the mineralogical and the genetical features of the deposit. These can be found in the Zletovo Mine's library, the library of the Geoinstitute-Skopje, and in the Ministry of the Economy of the Republic of Macedonia.

## GEOLOGICAL SETTING

The major lithologies in the area are related to Tertiary volcanism, and are represented by andesites, dacites, dacitic ignimbrites and volcanic tuffs (SERA FIMOVSKI, 1990; SERAFIMOVSKI AND ALEXANDROV, 1995; TASEV, 2003, etc.). Dacitic ignimbrites are the most common volcanic rocks in the mining area. Pb-Zn mineralization is spatially and genetically related to fracture and brecciated zones trending NW-SE, NNW-SSE and ENE-WSW. These structures served as conduits and/or depositional sites for ore and gangue minerals, precipitating from the circulating hydrothermal fluids. Ore also occurred as a metasomatic replacement of the wall rocks by ore minerals. Numerous veins and the associated stockwork mineralization thus represent the ore bodies; their thickness ranges from a few centimetres up to 2 m. The veins generally dip from 40° to vertical, averaging about 60°. They are usually more than 1 km long, the exception is ore vein No.10, which is more than 10 km long and reaches the area of the Plavica polymetallic ore deposit (Fig. 1). A total of 16 ore veins have been found in the Zletovo Mine.

Some ore veins are characterized by apophyses, which are shorter and thinner than the main veins. It should be pointed out that the host rock of the ore veins is very often hydrothermally altered. The alteration is mostly represented by kaolinitization and/or silicification. The hydrothermally altered zones around the ore veins are usually barren or poorly impregnated with ore minerals. Mineral vein paragenesis is represented by galena which is the main ore mineral and sphalerite with subordinate pyrite, a lesser amount of siderite and chalcopyrite as well

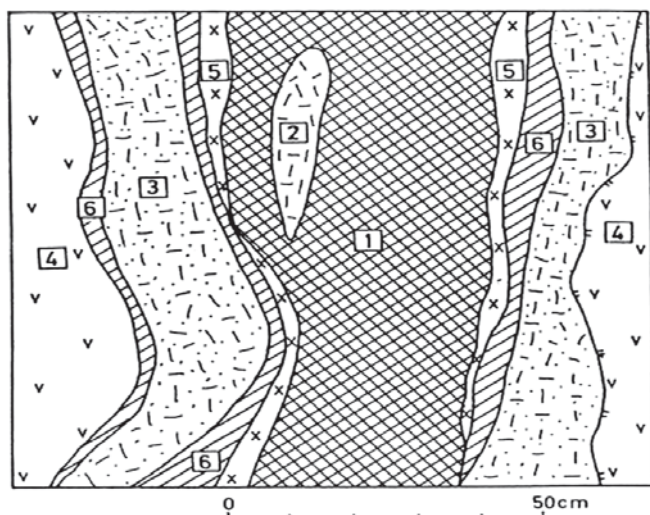


**Figure 1.** Geological map and cross section of the Pb-Zn Zletovo ore deposit (SERAFIMOVSKI, 1990)

1) Hydrothermally altered andesite, 2) Hydrothermally altered dacite, 3) Hydrothermally altered and silicified ignimbrite, 4) Stratified tuff, 5) Hydrothermally altered dacite-andesite, 6) Ignimbrite, 7) Ore veins

**Slika 1.** Geološka karta in profil Pb-Zn rudišča Zletovo (Serafimovski, 1990)

1) hidrotermalno spremenjeni andezit, 2) hidrotermalno spremenjeni dacit, 3) hidrotermalno spremenjeni ignimbrit, 4) plastoviti tuf, 5) hidrotermalno spremenjeni dacit-andezit, 6) ignimbrit, 7) rudne žile



**Figure 2.** Detail of ore vein No. 10, Zletovo ore deposit

1) Pb-Zn ore, 2) Dacito-andesitic ignimbrite (slightly kaolinized), 3) Dacito-andesitic ignimbrite (intensively kaolinized), 4) Dacito-andesitic ignimbrite (unaltered), 5) Siderite, 6) Dacito-andesitic ignimbrite, with galena impregnations

**Slika 2.** Detalj rudne žile št. 10, rudišče Zletovo

1) Pb-Zn ruda, 2) slabo kaoliniziran dacitsko-andezitski ignimbrit, 3) močno kaoliniziran dacitsko-andezitski ignimbrit, 4) nespremenjen dacitsko-andezitski ignimbrit, 5) siderit, 6) dacitsko-andezitski ignimbrit z impregnacijami galenita

as with pyrrhotite, marcasite and magnetite, which were found only sporadically. Minor occurrences of U-mineralisation represented by pitchblende have also been observed.

The morphological and geological characteristics of the ore veins from the Zletovo Mine are in general represented by the main characteristics of the ore vein No. 10 which was studied in detail (Fig. 2). From Figure 2 it is clearly evident that the central parts of the vein are composed of massive ore while the outer parts are hydrothermally altered and only slightly impregnated by ore minerals. Hydrothermal alterations are mostly silicification and kaolinitization. The concentration of ore minerals in the central part is more than 20 % Pb+Zn, while the altered mineralised vein zones exhibit a considerably lower Pb+Zn content of about 3 %.

## MATERIALS AND METHODS

For the purpose of this study the hydrothermal ore veins in the Zletovo Mine were sampled at different levels. The sampling was possible because the exploitation of the mine was in progress. During the field work representative samples for ore microscopy and for further electron microprobe analysis of sulphides and sulphosalts were taken. All the samples were macroscopically selected for the polished sections. Polished sections of the ore samples were first examined under a ZEISS Axiolab Polarizing Microscope equipped with a photographic camera. After this the selected samples of ore minerals and sulphosalts were analyzed for their S, Fe, Co, Cu, Zn, Ge, As, Ag, Cd, In, Sn, Hg, Pb and Bi contents by WDS electron microprobe using a CAMECA/CAMEBAX equipment.

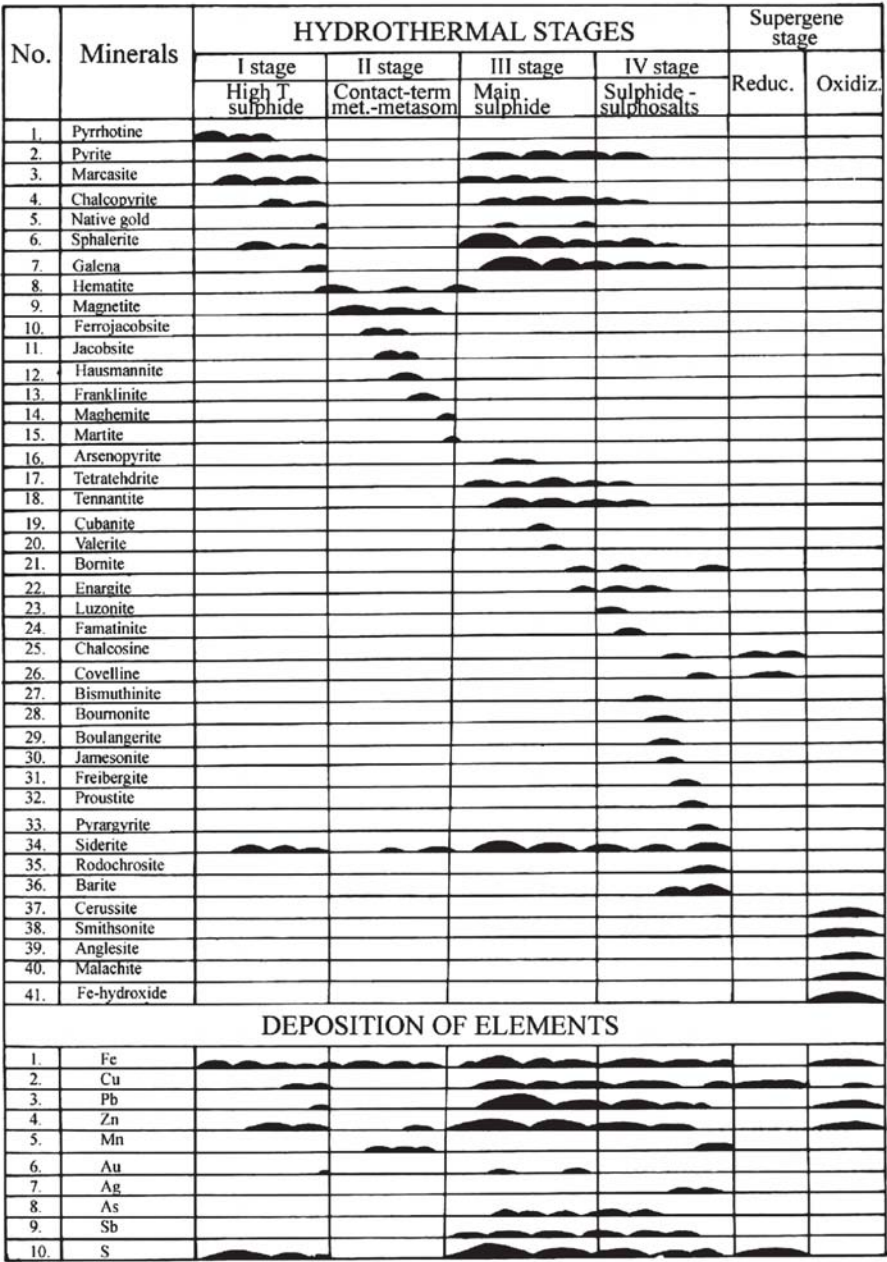


Figure 3. Paragenetic sequences in the Zletovo ore deposit (SERAFIMOVSKI, 1990)  
Slika 3. Paragenetsko zaporedje mineralov v rudišču Zletovo (SERAFIMOVSKI, 1990)

The analytical precision for Sb, Zn, As, and Ag was 1–3 %, 3–10 %, 10–15 % and 10–15 %; however, it was somewhat lower for Pb, Cd, In and Sn, i.e. 2–5 %, 5–15 %, 15–30 % and 15–25 %, respectively. Detectable concentrations of Sn and In were only found in some tetrahedrites, while the Co, Ge, Hg and Bi contents in the tetrahedrites were always below the detection limits of the instrument. The detection limits for Hg and Bi were very high, and usually between 0.4 and 0.6 %. This is most probably due to the interference between the different element's X-ray spectra. As and Pb were also characterized by high detection limits, usually of 0.25 %, relative to those for the other elements such as Fe (0.05 %), Co and Cu (0.07 %) as well as for Zn, Ag, In, Sn, Cd and Ge with detection limits between 0.1 and 0.13 %.

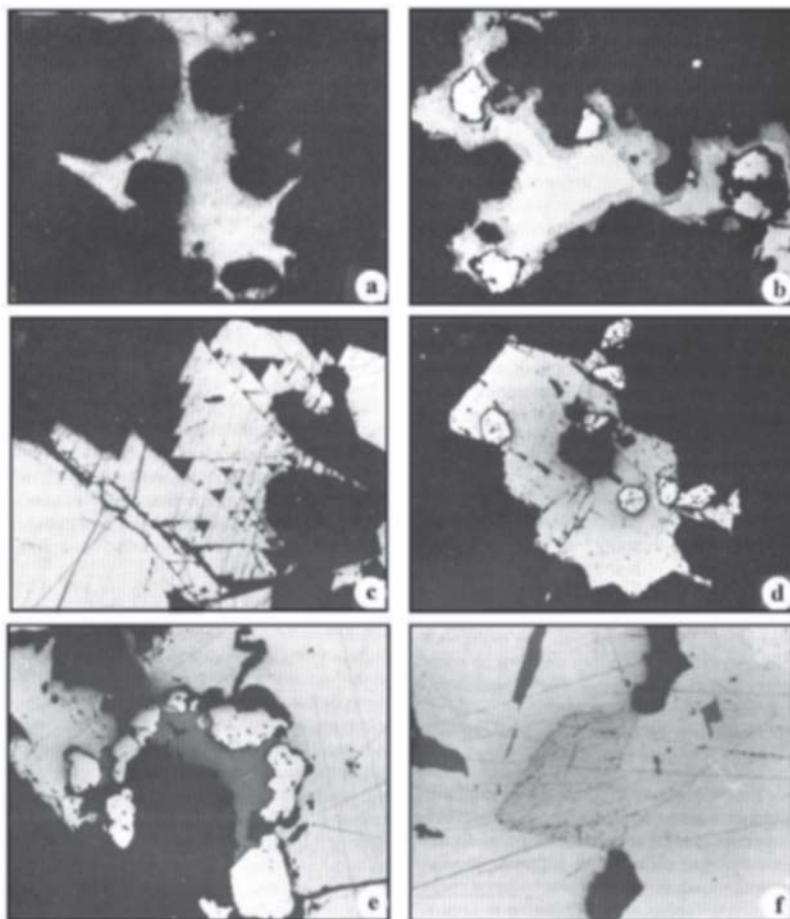
## RESULTS AND DISCUSSION

The results of previous investigations together with the results of the presented study confirm the complex mineral composition of the Pb-Zn mineralization in the Zletovo ore deposit. More than 40 ore bearing and gangue minerals were identified. All of them were crystallized successively from the ore bearing hydrothermal solutions during a few ore bearing stages, thus building complex paragenetic relations. An overview of ore minerals and their sequence of deposition in the frame of the ore forming stages are given in Figure 3. The micro-morphological characteristics and the appearance of the main ore minerals, their relations and the relations of some other minerals are presented in Figure 4.

### Major ore bearing minerals

Galena and sphalerite are the main and the most important ore minerals in the Zletovo Pb-Zn ore deposit, followed by pyrite, chalcopryrite, tetrahedrite, tennantite, marcasite, siderite and partially barite, pyrrhotite, enargite, bornite, arsenopyrite and chalcocite. Magnetite, jacobsonite, hematite, hausmannite and others occur only sporadically. All other ore minerals not mentioned here were mostly found in trace amounts and have no economic importance. It should be pointed out that in some ore veins the quantitative ratios of the main ore minerals are changeable. For example, in ore vein No. 1 galena and sphalerite prevail, while the next most common mineral is siderite. On the other hand in ore vein No. 10 pyrite is the main ore mineral, followed by other sulphides. However, in general, galena and sphalerite are the most common and the most important ore minerals even if they were deposited in different morpho-logical types of mineralization.

Sphalerite was only found in few generations, and in some of them it shows exsolved structures of chalcopryrite due to the decomposition of solid solution sphalerite-chalcopryrite. Most often it is metacolloidal to collomorph with zonal patterns and internal reflections. The crystal forms are very rare. More often it is found in over-growth with galena, chalcopryrite and tennantite. Sometimes it metasomatically replaces galena, although in some places it looks like to be suppressed by them. Here and there sphalerite is cataclastic and interstitially replaced by quartz, galena, tennantite and other minerals. Sphalerite is also myrmekitically interlocked with galena, chalcopryrite, tetrahedrite and other ore minerals.



**Figure 4.** Micro-morphologic shapes and the occurrence modes of galena in the Zletovo ore deposit (SERAFIMOVSKI, 1990): **a)** Metasomatic replacement of galena (white) by well developed quartz crystals (dark). Reflected polarized light, 100x; **b)** Corrosion of chalcopyrite (white) by galena (grey-white) along intestices and the replacement of galena (white grey) by quartz (dark). In the galena there are remains of pyrite (light), while along its borders there is tennantite (grey). Reflected polarized light, 100x; **c)** Cataclized galena crystal (white) suppressed by quartz (dark). Reflected polarized light, 100x; **d)** Pyrite remains (white) in galena (white grey) with the presence of quartz (dark) of metasomatic origin. Reflected polarized light, 100x; **e)** Corrosion of galena (white grey) by tennantite (dark grey) and tennantite by quartz (dark). At the contact between the galena and tennantite are the remains of ring forms of pyrite. Reflected polarized light, 100x; **f)** Hypidiomorphic grain of bournonite (dark grey) in massive galena (grey). Reflected polarized light, 100x.

**Slika 4.** Mikromorfološke značilnosti galenita iz rudišča Zletovo (SERAFIMOVSKI, 1990): **a)** metasomatsko nadomeščanje galenita (belo) s kremenom (temno), odsevna polarizirana svetloba, 100x, **b)** nadomeščanje halkopirita (belo) z galenitom (svetlosivo) in galenita (svetlosivo) s kremenom (temno), odsevna polarizirana svetloba, 100x, **c)** kataklazirana galenitova zrna (belo) cementira in nadomešča kremen (temno), odsevna polarizirana svetloba, 100x, **d)** ostanki pirita (belo) in galenita (svetlosivo) ter metasomatski kremen (temno), odsevna polarizirana svetloba, 100x, **e)** nadomeščanje galenita (svetlosivo) s tennantitom (temnosivo) in tennantita s kremenom (temno). Na stiku med galenitom in tennantitom so ostanki pirita obročaste oblike, odsevna polarizirana svetloba, 100x, **f)** hipidiomorfno zrno bournonita (temnosivo) in masivni galenit (sivo), odsevna polarizirana svetloba, 100x.

**Table 1.** Results of electron microprobe analyses of sphalerite (1-10), pyrite (11, 12), arsenopyrite (13) and galena (14, 15) from the Zletovo ore deposit (in %)

**Tabela 1.** Rezultati geokemične analize rudnih mineralov iz rudišča Zletovo z elektronskim mikroanalizatorjem: (1-10) sfalerit, (11,12) pirit, (13) arzenopirit, (14, 15) galenit). Elementna sestava je v %.

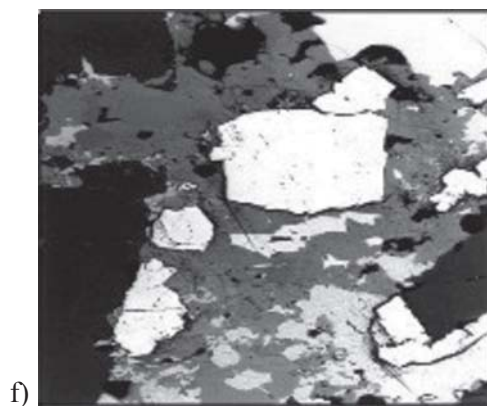
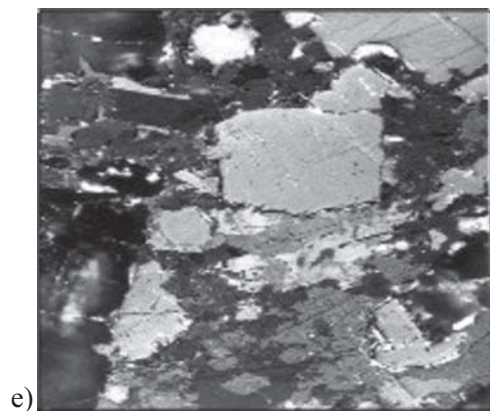
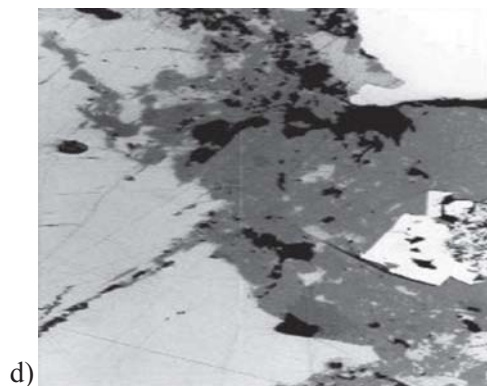
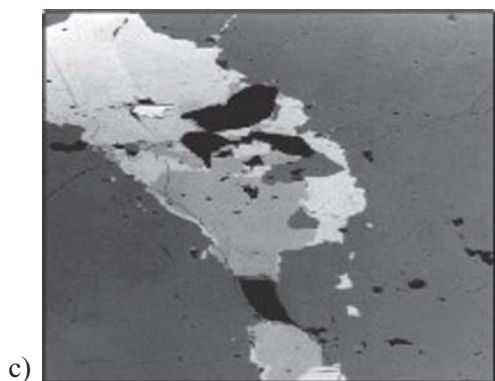
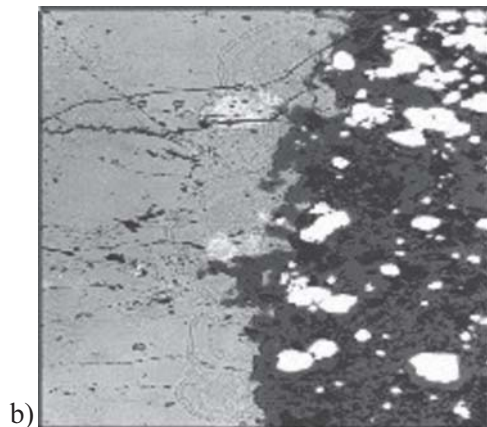
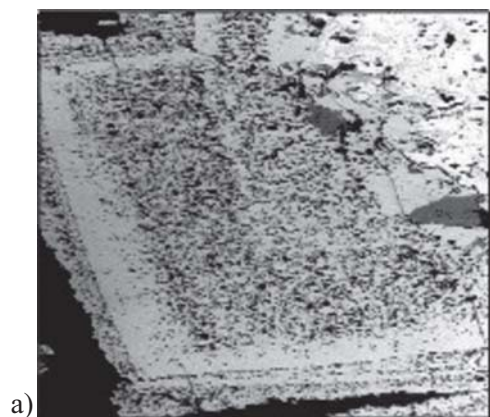
| Elements | S    | Mn  | Fe   | Cu  | Zn   | Ga  | As   | Cd  | Sb  | Pb   |       |
|----------|------|-----|------|-----|------|-----|------|-----|-----|------|-------|
| 1        | 30,5 | 0,0 | 0,3  | 0,0 | 68,7 | 0,0 | 0,0  | 0,5 | 0,0 | -    | 100,0 |
| 2        | 31,0 | 0,0 | 0,4  | 0,0 | 67,8 | 0,3 | 0,0  | 0,5 | 0,0 | -    | 100,0 |
| 3        | 30,3 | 0,0 | 0,6  | 0,0 | 68,0 | 0,0 | 0,0  | 0,0 | 0,1 | -    | 100,0 |
| 4        | 30,4 | 0,0 | 6,5  | 0,0 | 69,1 | 0,0 | 0,0  | 0,0 | 0,0 | -    | 100,0 |
| 5        | 34,2 | 0,1 | 0,4  | 0,0 | 65,3 | 0,0 | 0,0  | 0,0 | 0,0 | -    | 100,0 |
| 6        | 38,5 | 0,2 | 0,8  | 0,0 | 58,8 | 0,0 | 0,8  | 0,4 | 0,0 | -    | 100,1 |
| 7        | 40,4 | 0,0 | 0,6  | 0,0 | 59,6 | 0,0 | 0,0  | 0,0 | 0,0 | -    | 100,1 |
| 8        | 30,7 | 0,0 | 0,5  | 0,0 | 58,5 | 0,0 | 0,0  | 0,3 | 0,1 | -    | 100,1 |
| 9        | 35,0 | 0,0 | 0,0  | 0,0 | 64,7 | 0,0 | 0,0  | 0,3 | 0,0 | -    | 100,0 |
| 10       | 30,7 | 0,0 | 2,8  | 3,7 | 62,7 | 0,0 | 0,0  | 0,0 | 0,1 | -    | 100,1 |
| 11       | 51,8 | 0,0 | 47,5 | 0,2 | 0,4  | 0,0 | 0,0  | 0,2 | 0,0 | -    | 100,1 |
| 12       | 49,2 | 0,0 | 50,2 | 0,0 | 0,0  | 0,0 | 0,7  | 0,0 | 0,0 | -    | 100,1 |
| 13       | 23,1 | 0,0 | 37,1 | 0,2 | 4,1  | 0,0 | 35,0 | 0,0 | 0,6 | -    | 100,1 |
| 14       | 20,5 | -   | -    | -   | 1,0  | -   | -    | -   | -   | 78,6 | 100,1 |
| 15       | 20,5 | -   | -    | -   | 1,1  | -   | -    | -   | -   | 78,6 | 100,1 |

**Figure 5. (next page)** Microphotographs of sulphides and sulphosalts from the Zletovo ore deposit (ore vein No.10) analyzed by electron microprobe: **a)** Late generation of zoned galena crystal rich in quartz inclusions. Earlier generation of galena-sphalerite-pyrite-tetrahedrite ore minerals are the background where the galena crystal was growing. Reflected polarized light, 67x; **b)** Contact between intensively pyritized volcanic rock fragment and massive sphalerite (gray). Reaction with hypochloric NaOH at the borderline confirmed the presence of zinc sulphide with zoned composition. Reflected polarized light, 67x; **c)** Sphalerite cutting by the vein containing galena (light gray), tetrahedrite (gray), chalcopyrite (medium gray, upper part), quartz and traces of pyrite. Reflected polarized light, 270 x; **d)** Ore composed of pyrite (white), chalcopyrite (light gray, left part), tennantite (gray in lower and central part) with inclusions of galena (light gray) and luzonite-stibiolumonite (dark gray, lower central part). Reflected polarized light, oil immersion, 430 x; **e)** Complex mixture of pyrite (white), sphalerite (dark gray), galena (white, irregular shapes), chalcopyrite (light gray, center) tennantite (middle to dark gray, central area) and luzonite-stibiolumonite (dark gray, strongly pleochroic, central part). Reflected polarized light, oil immersion, 430x; **f)** Partially crossed nicols. Note the lamellar twinning in one direction of the luzonite-stibiolumonite (light to middle gray, central and lower part), and the “flashy” internal reflections of tennantite (dark gray, left part).

**Slika 5. (naslednja stran)** Slike sulfidov in sulfosolov iz rudne žile št. 10, analiziranih z elektronskim mikroanalizatorjem, rudišče Zletovo: **a)** Mlajša generacija conarnega galenita z vključki kremenca. Osnovo v kateri je kristal raste predstavlja starejša mineralna parageneza galenit-sfalerit-pirit, odsevna polarizirana svetloba, 67x, **b)** stik med odlomkom močno piritizirane vulkanske kamnine in masivnim sfaleritom (sivo). strukturno jedkanje je odkrilo na stiku conarno zgradbo sfalerita, odsevna polarizirana svetloba, 67x, **c)** sfaleritno polje seka žilica, ki vsebuje galenit (svetlosivo), tetraedrit (sivo), halkopirit (srednje sivo), kremen (temno) in sledove pirit, odsevna polarizirana svetloba, 270x, **d)** poliminerhalno polje sestavljeno iz pirit (belo), halkopirita (svetlo sivo), levi del slike), tennantita (sivo, spodnji in osrednji del slike) z vključki galenita (svetlo sivo) in luzonit-stibiolumonitom (temno sivo, spodnji osrednji del slike), odsevna polarizirana svetloba, oljna imerzija, 430x, **e)** poliminerhalna ruda sestavljena iz pirit (belo), sfalerita (temno sivo) galenita (belo), halkopirita (svetlo sivo, osrednji del slike) tennantita (srednje do temno sivo) in luzonita-stibiolumonita (temno sivo, močno pleohroično, srednji del slike), odsevna polarizirana svetloba, oljna imerzija, 270x, **f)** ista slika, ne povsem + nikoli. Opazne so dvojčične lamele luzonita-stibiolumonita potekajoče v eni smeri (srednji in spodnji del slike) in notranji refleksi v tennantitu (temno sivo, levi rob slike), odsevna polarizirana svetloba, oljna imerzija, 270x.

The composition of the sphalerite in the Zletovo deposit is close to the normal values of the theoretically determined values for sphalerite (CRIDDLE AND STANLEY, 1986). The

exception is the Fe content, which in some sphalerites is up to 6.5 % (Table 1). In addition to Fe, sphalerites also contain small quantities of Mn and Cd.



Galena was also found in a few generations. In contrast to sphalerite it shows a high degree of crystallinity and very often well-developed crystals. The most beautiful crystal forms of galena can be found in the open veins and vugs as well as in the fracture zones. Here and there the galena crystals are cataclastized and exhibit well developed cleavages and extensive replacement with quartz (Fig. 4). The extend of galena replacement by quartz is sometimes so large that only some remains are left of the primary galena grains. In some places the galena develops along the interstices with pyrite and encloses the pyrite remains, while at other locations it is intensively overgrown with bournonite and other sulphosalts.

Galena is usually suppressed by sphalerite, chalcopyrite, tetrahedrite and tennantite, but with these minerals it is also myrmekitically interlocked and forms emulsions. Sometimes dispersive entrapment of pyrite, arsenopyrite and other sulphides can be observed. The elemental composition of galena in the Zletovo Mine is very close to the theoretical values. Microprobe analyses also showed the presence of Zn and Ag in the galena structure (Table 1).

### **Sulphosalts and ore bearing minerals from vein No. 10**

The already known mineral assemblage composed mainly of galena, sphalerite, pyrite, chalcopyrite, siderite and other ore and gangue minerals is supplemented with sulphosalts. During this study special attention was given to ore vein No. 10. From this ore vein five representative samples for ore microscopy and further electron microprobe analyses were taken. Microscopic and

electron microprobe analyses revealed tetrahedrite-tennantite solid solution compositions as well as sulphosalt minerals such as luzonite, stibioluzonite and pearceite (Fig. 5). The composition of particular minerals and the phases of interest found during this study are presented in Table 2 and 3. Their main characteristics are given below:

#### **Luzonite $\text{Cu}_3\text{AsS}_4$**

Luzonite was found in samples Z-3 and Z-5. The luzonite from samples Z-3 is slightly more Fe rich (0.15–0.66 %) and contains less Sb (0.17–2.5 %) relative to the luzonite from samples Z-5, which has only up to 0.14 % Fe and 1.7–3.8 % Sb. The luzonite from samples Z-3 also contains a minor amount of Zn ( $\leq 0.26$  %), Ag ( $\leq 0.17$  %) and Cd ( $\leq 0.15$  %). These elements in the luzonite from samples Z-5 are absent or found in lower concentrations. The elemental composition close to the standard values for luzonite was obtained for the luzonite from sample Z-5-3 Lu2 (Table 2).

#### **Pearceite $\text{Ag}_{13-11}\text{Cu}_{3-5}\text{As}_2\text{S}_{11}$**

Pearceite with 59 % Ag and a ratio  $\text{Sb}/(\text{Sb}+\text{As})_{\text{mol}} = 0.14$  was found in sample Z-5 as rare, small grains associated with Luz+Ten+Gal+Py+Cp. The closest composition to the standard values for this mineral was obtained for the pearceite from sample Z-5-2 Pea3 (Table 2).

#### **Tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ – Tennantite $\text{Cu}_{12}\text{As}_4\text{S}_{13}$**

The tetrahedrites from Zletovo are members of the tetrahedrite-tennantite solid solution [ $\text{Sb}/(\text{Sb}+\text{As})_{\text{mol}} = 0.04 - 0.94$ ]. They are

**Table 2.** Results of electron microprobe analyses of pearceite (Pea) and luzonite (Lu); ore vein No. 10, Zletovo ore deposit (in %)**Tabela 2.** Rezultati geokemične analize pearceita (Pea) in luzonita (Lu) z elektronskim mikroanalizatorjem. Rudišče Zletovo, rudna žila št. 10. Elementna sestava je v %.

| Element | Z-5-<br>2Pea3 | Z-5-<br>2Lu3 | Z-5-<br>2Lu4 | Z-5-<br>3Lu2 | Z-3-<br>5Lu | Z-3-<br>5Lu | Z-3-<br>1Lu6 | Z-3-<br>1Lu7 |
|---------|---------------|--------------|--------------|--------------|-------------|-------------|--------------|--------------|
| S       | 17.41         | 32.04        | 31.84        | 32.62        | 32.29       | 32.55       | 32.87        | 32.68        |
| Fe      | 0.03          | 0.05         | 0.14         | 0.01         | 0.53        | 0.66        | 0.15         | 0.19         |
| Co      | 0.00          | 0.00         | 0.00         | 0.00         | 0.00        | 0.03        | 0.00         | 0.02         |
| Cu      | 15.18         | 47.24        | 46.74        | 48.00        | 46.97       | 47.23       | 47.86        | 47.59        |
| Zn      | 0.03          | 0.03         | 0.14         | 0.00         | 0.04        | 0.12        | 0.23         | 0.26         |
| Ge      | 0.09          | 0.00         | 0.03         | 0.01         | 0.00        | 0.00        | 0.01         | 0.06         |
| As      | 6.31          | 16.67        | 16.21        | 17.79        | 17.50       | 18.92       | 18.27        | 18.03        |
| Ag      | 58.63         | 0.03         | 0.08         | 0.03         | 0.17        | 0.15        | 0.03         | 0.09         |
| Cd      | 0.34          | 0.00         | 0.03         | 0.00         | 0.01        | 0.15        | 0.01         | 0.02         |
| In      | 0.00          | 0.03         | 0.00         | 0.00         | 0.00        | 0.03        | 0.00         | 0.03         |
| Sn      | 0.00          | 0.00         | 0.00         | 0.00         | 0.02        | 0.00        | 0.03         | 0.01         |
| Sb      | 1.64          | 3.12         | 3.77         | 1.67         | 2.48        | 0.17        | 0.75         | 0.67         |
| Hg      | 0.05          | 0.00         | 0.17         | 0.00         | 0.12        | 0.00        | 0.00         | 0.15         |
| Pb      | 0.18          | 0.00         | 0.10         | 0.00         | 0.15        | 0.14        | 0.00         | 0.07         |
| Bi      | 0.29          | 0.00         | 0.00         | 0.20         | 0.00        | 0.00        | 0.00         | 0.00         |
| Sum     | 100.17        | 99.20        | 99.25        | 100.33       | 100.27      | 100.14      | 100.21       | 99.87        |

enriched in Zn, usually 7 - 8 %, and Ag the concentration of which is up to 5.5 % (Table 3). The Fe content is always relatively low, and usually below 1 %. Within the individual samples, elevated concentrations of Ag were found in the more Sb-rich grains or in clusters of grains, and this decreases in the more tennantitic-rich solid solutions. The highest Ag contents are found in small, few micrometers thick droplet-like inclusions of tetrahedrite inside the galena crystals from Gal+Sph+Pyr±Tet/Ten veinlets. These inclusions seem to represent the main Ag reservoir of the previously reported Ag-bearing Zletovo galenas with up to 1250 ppm Ag (MUDRINIĆ AND PETKOVIĆ, 1982). The Cd content in the investigated droplets is usually below 0.3 %, although some of them exhibit considerably higher concentrations of up to 1.1 %. One of the droplets also had a detectable content of about 0.15 %. The Sn concentrations are just above the detection

limit (0.10–0.12 %) and were found only in the more Sb-rich compositions. In samples with a coarser texture the tetrahedrite–tennantite composition is characterized by an intermediate  $\text{Sb}/(\text{Sb}+\text{As})_{\text{mol}}$  ratio of 0.44. The contamination due to an overlap with neighbouring phases may have affected the analysis of the fine grained tetrahedrites, reflected in locally very high Pb contents (up to 0.4 %). The closest composition to the standard values is shown in an analysis of tetrahedrite from the sample Z-3-5Tet2 (Table 3).

Tennantites, as the other end-member of the tetrahedrite–tennantite solid solution series, exhibit elevated concentrations of Zn (1.72–8.33 %) and Sb (1.32–7.38 %) and a relatively low Fe content (0.1–3.06 %). Within different tennantite grains, the amount Ag decreases toward the more tennantitic compositions. The Cd content can also be

**Table 3.** Results of electron microprobe analyses of tennantite (Ten) and tetrahedrite (Tet), ore vein No. 10, Zletovo ore deposit (in %)

**Tabela 3.** Rezultati geokemične analize tennantita (Ten) in tetrahedrita (Tet), z elektronskim mikroanalizatorjem. Rudišče Zletovo, rudna žila št. 10. Elementna sestava je v %.

| Element | Z-3-4<br>Ten | Z-3-1 Ten<br>4 | Z-5-2 Ten<br>2 | Z-5-2<br>Ten 3 | Z-3-5<br>Tet 1 | Z-3-5<br>Tet 2 | Z-3-4<br>Tet |
|---------|--------------|----------------|----------------|----------------|----------------|----------------|--------------|
| S       | 27.27        | 28.00          | 28.04          | 28.03          | 25.16          | 26.48          | 26.48        |
| Fe      | 0.10         | 0.36           | 0.22           | 3.06           | 0.37           | 0.17           | 0.05         |
| Co      | 0.01         | 0.00           | 0.02           | 0.03           | 0.00           | 0.01           | 0.00         |
| Cu      | 40.74        | 41.73          | 42.26          | 45.37          | 35.42          | 37.97          | 38.92        |
| Zn      | 8.31         | 8.33           | 8.13           | 1.72           | 7.37           | 7.81           | 8.20         |
| Ge      | 0.00         | 0.00           | 0.05           | 0.04           | 0.04           | 0.06           | 0.08         |
| As      | 14.94        | 18.86          | 18.06          | 17.85          | 3.59           | 9.35           | 9.53         |
| Ag      | 0.49         | 0.44           | 0.03           | 0.15           | 1.89           | 1.15           | 1.13         |
| Cd      | 0.24         | 0.17           | 0.18           | 0.61           | 0.30           | 0.24           | 0.12         |
| In      | 0.00         | 0.07           | 0.01           | 0.00           | 0.02           | 0.01           | 0.04         |
| Sn      | 0.00         | 0.01           | 0.00           | 0.05           | 0.11           | 0.10           | 0.10         |
| Sb      | 7.38         | 1.32           | 2.56           | 2.55           | 24.52          | 15.98          | 15.55        |
| Hg      | 0.14         | 0.14           | 0.07           | 0.10           | 0.14           | 0.02           | 0.00         |
| Pb      | 0.08         | 0.38           | 0.17           | 0.21           | 0.48           | 0.09           | 0.00         |
| Bi      | 0.00         | 0.00           | 0.00           | 0.00           | 0.16           | 0.33           | 0.00         |
| Sum     | 99.68        | 99.81          | 99.77          | 99.77          | 99.56          | 99.75          | 100.20       |

significant, with concentrations between 0.17 and 0.61 %. In was only detected in concentrations of 0.01 and 0.07 %. The Sn content is only slightly above the detection limit (0.01-0.05 %). The closest composition to the standard values was found for an analysis of sample Z-5-2 Ten2 (Table 3).

### Galena

Galena is almost pure PbS. Elevated concentrations of Cu ( $\leq 0.7$  %), Zn ( $< 0.4$  %), Fe (0.16 %) and possibly Cd ( $\leq 0.16$  %) were found only in some samples. These elements could be related to fine inclusions of unresolved sulphides.

### Sphalerite

Sphalerite is characterized by low Fe contents (usually  $\leq 1$  %). Higher Fe concentrations were measured only in

samples Z-3 ( $\leq 6$  %) and Z-5 ( $\leq 2$  %). Grain-to-grain and within-grain variations in Fe concentrations show no clear textural dependence. The highest Fe contents are typically associated with the lowest Cd concentrations which are in sphalerite, with a minimum Fe content between 0.5 - 0.8 %. Minor amounts of Cu, Sb and Pb were also detected in some sphalerites. The late generations of sphalerite, for example, schalenblende in sample #3, are distinctly cathodoluminescent and represent almost pure sphalerite with only a detectable As content (0.3 %) and low Cd concentrations (0.15 %).

### Chalcopyrite

Chalkopyrite is very pure  $\text{CuFeS}_2$  with trace elements content below the detection limits of the equipment.

## Pyrite

All the analyzed generations of pyrite are considerably enriched in As. This enrichment could be related to very fine unresolved intergrowth textures with arsenopyrite, as suggested by the crystal chemical formulae ( $S+As=Fe$ ). Minor contents of Cu ( $\leq 0.7\%$ ) were only measured in late generations of euhedral and/or partially corroded pyrite grains from  $Gal \pm Sph \pm Tet \pm Ten \pm Luz + Pyr$  mineral assemblages. Pyrite grains related to an early pyritization stage are virtually Cu free. An exception are samples Z-5 in which pyrite revealed an elevated Cu content of about 0.36 % and high As concentrations around 4.4 %. Detectable Pb ( $\leq 0.26\%$ ) and Zn concentrations ( $\leq 0.4\%$ ) were occasionally found both in early and in late generations of pyrite as well as in partially resorbed pyrite grains. More information about the mineral parageneses and geochemical features of the major minerals in ore veins can be found in MUDRINIĆ AND SERAFIMOVSKI (1990; 1991) AND SERAFIMOVSKI AND TASEV (2003).

## CONCLUSIONS

The results from the latest field and laboratory studies of samples from different ore veins confirmed the mineral paragenesis characteristic for hydrothermal conditions of origin and revealed the very complex polymetallic characteristics of the Zletovo Pb-Zn mine. A detailed study of ore vein

No. 10 and its border parts indicated that the main ore minerals are represented by the prevailing galena and sphalerite followed by tetrahedrite, tennantite, pyrite, chalcopyrite, quartz, calcite, siderite as well as other less important ore and gangue minerals. The electron microprobe analyses of the galena and sphalerite showed that their compositions mostly exhibit the theoretical values for those minerals (with minor impurities related to some characteristic trace elements). A detailed study by electron microprobe further revealed that the tetrahedrite and tennantite form solid solution phases with compositions ranging from pure tetrahedrites, through mixed solid phases to pure tennantites. This phenomenon was for the first time found in the Zletovo mine during this study and deserves further investigation. A detailed study of the sulphosalts confirmed the presence of luzonites and pearceites, while some separate phases looked like seligmannite. Our intention to determine silver sulphosalts was not successful; however we will make this the subject of future studies.

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# General Chemistry of Bottled Waters on the Slovene Market

## Splošne kemijske karakteristike ustekleničenih vod na slovenskem tržišču

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**Abstract:** Consumption of bottled waters and soft drinks similar to water is increasing every day. General overview of the market shows big differences among brands. During the consumption of these drinks several questions about their origin and chemical composition arose. In the article research results of 58 bottled waters and soft drinks similar to water bought on Slovene market in September 2004 are presented. Sampling was performed according to unbalanced hierarchical analysis of variance. Chemical analyses included determination of concentration of 67 elements by ICP-MS, anions by ion chromatography and isotopic composition of hydrogen, oxygen and dissolved inorganic carbon by mass spectrometry. Samples were classified into four groups (waters, soft drinks, carbonated and non-carbonated drinks). Nearly all elements are present in investigated samples, however their concentrations vary considerably. Results indicate different natural origin and geochemical processes as well as influence of industrial treatment and flavours on chemical composition of waters and drinks.

**Izvleček:** Potrošnja ustekleničenih voda in pijač, ki so podobne vodam narašča iz dneva v dan. Že bežen pregled tržišča pokaže, da se te pijače med seboj zelo razlikujejo. Pri potrošnji teh pijač se pogosto zastavljajo številna vprašanja o njihovem izvoru ter kemizmu. V članku so predstavljeni rezultati raziskav 58 ustekleničenih voda in pijač podobnih vodi, kupljenih na slovenskem tržišču septembra 2004. Vzorčenje je potekalo po shemi neuravnotežene analize variance. Analiza vzorcev je zajemala določitev koncentracije 67 elementov z ICP-MS, anionov z ionsko kromatografijo in izotopske sestave vodika, kisika in raztopljenega anorganskega ogljika z masno spektrometrijo. Vzorce smo razdelili na štiri skupine (vode in pijače ter gazirane in negazirane vode). V analiziranih vzorcih so prisotni skoraj vsi elementi, vendar v zelo različnih koncentracijah. Rezultati tudi nakazujejo različen naravni izvor in vpliv geokemijskih procesov kot tudi vpliv industrijske priprave in dodatkov na kemijsko sestavo vod in pijač.

**Key words:** bottled water, mineral water, spring water, soft drinks, water chemistry, stable isotopes.

**Ključne besede:** ustekleničene vode, mineralne vode, izvirske vode, pijače, kemija vode, stabilni izotopi.

## INTRODUCTION

The total world production of bottled waters is over  $7 \times 10^{10}$  L annually (ROWLANDS, 2001). The biggest consumers of bottled waters in the world are western countries. Each year, consumption in Germany, France, Switzerland, Italy and Belgium is over 100 L per capita. In new European countries the consumption of bottled waters is lower and big potential for market growing exist. This conclusion is in the agreement with Slovene bottled waters market status. In the year 1998 consumption of bottled waters in Slovenia was 34.4 L per capita (HRIBAR, 2000) and in year 2004 58 L per capita (GIDER, 2005). From these data it is evident that Slovene bottled water market will become larger in future.

Bottled waters market in Slovenia is increasing each year and more and more brands of bottled waters and soft drinks similar to water appear in shopping centers. Bottles available on the market are labeled with many names, classifications and advertisements. Prices for bottled waters are very different and do not resemble the quality and legislative status of particular brand. In spite of relatively strict European and Slovene legislation we can find out disorder in the market. The consumers' behavior shows uncritical relation to waters available on the market and ignorance to present knowledge about water. A main criterion for purchasing bottled water is its price. The bottled waters market status and consumers' behavior shows that a lot of open questions, problems and controversies about drinking and bottled waters exist. This is the reason why more knowledge about bottled waters is needed.

In the present study the hydrochemical overview of most bottled waters available on the Slovene market is given. Therefore, it is not our intention to check the bottled water market status and to control whether the sampled bottles are in the agreement with legislation demands. All brands available on the market were treated on equal terms and no discrimination between domestic and foreign brands was made. Results are given as aggregate values without connection to their brand names.

According to the authors' knowledge all bottled waters and water for soft drinks that are similar to water available on the Slovene market have their source in the groundwater. As a consequence the present analysis gives also opportunity to check what type of groundwater is filled in the bottles. The available data set gives also possibility to develop general procedures for controlling water brands agreement with legislation demands.

## SAMPLING AND METHODOLOGY

Sampling of bottled waters and soft drinks similar to water was made in several steps:

- a) Overview of bottled waters on the market,
- b) Sampling plan,
- c) Purchasing of bottled waters on the market,
- d) Samples preparation,
- e) Transport to laboratories.

During first step of sampling survey of mainly all big shopping centers in Ljubljana and its vicinity was performed. Based on this survey the list of all available brands of

bottled waters and soft drinks similar to water was made. We believe that with this procedure nearly all brands available in the Slovene market on September 2004 were included. Altogether 58 different brands were found, among them 34 are waters and the other 24 are soft drinks similar to water. The later are mixtures of water and some flavours such are aromatic flavours, organic acids or flavours based on sugars. Among all brands 16 are carbonated and other 42 are non-carbonated. None of the soft drinks was carbonated. Most bought brands were stored in plastic bottles and only 3 were in glass bottles.

During the second step it was decided to sample waters from the list according to unbalanced hierarchical analysis of variance. According to this analysis 9 brands and 7 bottles among all are repeated.

During the third step purchasing of brands was performed. By chance one of the big shopping centers was chosen. All available brands in the shop were bought according to the sampling plan prepared before. But not all waters were available in this shop. This was the reason for new shopping in the second shop. The procedure was repeated also in the third shop where the list was completed. The bottles from the shop shelves or package on the floor of the shop were taken incidentally without any prejudice.

After the shopping was complete all bottles were taken to the laboratory where the preparation of samples began. All plastic flasks and seals, except for anions, were washed with diluted  $\text{HNO}_3$  and after that washed off with distilled water. After washing they were air-dried. Before filling

with the sample plastic flasks were washed off also with the same brand, as it was latter filled into the flask. When sampling begin first all plastic flasks were filled with samples. After that pH and electrical conductivity was measured. Conductivity was referred to the 20 °C. Samples for anion determination were filed into 1 L plastic flasks, samples for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  into 100 ml plastic flasks, for  $\delta^{13}\text{C}$  determination in dissolved inorganic carbon (DIC) into 12 mL glass exeteiners and for multielement analyses into 100 mL plastic flasks. Samples for multielemental analysis were acidified with Suprapur®  $\text{HNO}_3$  produced by Merck. To control accuracy of the analytical procedures 5 samples of standard fresh water NIST 1643e were added to the whole set of samples and also four samples of very pure MilliQ® water were added as a blank.

The final step of sampling is represented by transport. Samples for multielement analyses were send by the carrier overseas. Other samples were carried by car into the laboratories. Before transport all samples were stored in the refrigerator at 4 °C.

Multielement analysis was performed by ICP-MS at ActivatedLab in Canada. The accuracy and precision of multielemental analysis were determined as reasonable. The concentration of  $\text{NH}_4^+$  was determined by SIST ISO 7150-1 method, concentration of  $\text{NO}_2^-$  by SM 4500- $\text{NO}_2\text{B}$  method,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  by SIST EN ISO 10304-1 method,  $\text{F}^-$  by method SIST EN ISO 10304-2,  $\text{PO}_4^{3-}$  by SM 4500P-C method,  $\text{HCO}_3^-$  was determined by titration, and  $\text{Cl}^-$  was determined by gas chromatography. All anions, except  $\text{Cl}^-$  were determined at chemical laboratory of Ljubljana waterworks.

**Table 1.** Averages and number of samples (N) with values greater than detection limit of different waters and soft drinks classifications – multielemental and anion analyses.**Tabela 1.** Povprečja in število vzorcev z vrednostmi višjimi od detekcijske meje glede na različne skupine vod in pijač podobnim vodam - multielementne in anionske analize.

| Parameter | DL1  | DL2   | All samples |    | Waters  |    | Soft drinks |    | Non-carbonated |    | Carbonated |    |
|-----------|------|-------|-------------|----|---------|----|-------------|----|----------------|----|------------|----|
|           |      |       | Average     | N  | Average | N  | Average     | N  | Average        | N  | Average    | N  |
| Al        | 20   | 2     | 38          | 19 | 8       | 10 | 72          | 9  | 44             | 15 | 16         | 4  |
| As        | 0.3  | 0.03  | 0.59        | 49 | 0.58    | 28 | 0.61        | 21 | 0.47           | 38 | 1.03       | 11 |
| Au        | 0.02 | 0.002 | 0.016       | 6  | 0.004   | 3  | 0.027       | 3  | 0.021          | 4  | 0.004      | 2  |
| Ba        | 1    | 0.1   | 65.7        | 59 | 99.7    | 33 | 22.6        | 26 | 28.9           | 45 | 183.8      | 14 |
| Br        | 30   | 3     | 222         | 29 | 257     | 24 | 52          | 5  | 25             | 19 | 597        | 10 |
| Ca        | 7000 | 700   | 71806       | 60 | 66396   | 35 | 79378       | 25 | 71632          | 44 | 72284      | 16 |
| Cd        | 0.1  | 0.01  | 0.09        | 23 | 0.09    | 19 | 0.11        | 4  | 0.01           | 19 | 0.07       | 4  |
| Ce        | 0.01 | 0.001 | 0.135       | 38 | 0.010   | 20 | 0.275       | 18 | 0.161          | 31 | 0.023      | 7  |
| Co        | 0.05 | 0.005 | 0.38        | 19 | 0.68    | 8  | 0.16        | 11 | 0.15           | 12 | 0.77       | 7  |
| Cr        | 5    | 0.5   | 5.8         | 10 | 1.4     | 2  | 6.9         | 8  | 5.8            | 10 |            |    |
| Cs        | 0.01 | 0.001 | 2.87        | 29 | 3.76    | 22 | 0.08        | 7  | 0.22           | 17 | 6.62       | 12 |
| Cu        | 2    | 0.2   | 2.7         | 26 | 2.7     | 21 | 2.8         | 5  | 1.3            | 18 | 5.9        | 8  |
| Dy        | 0.01 | 0.001 | 0.074       | 11 | 0.024   | 2  | 0.085       | 9  | 0.085          | 9  | 0.024      | 2  |
| Er        | 0.01 | 0.001 | 0.041       | 13 | 0.005   | 6  | 0.071       | 7  | 0.046          | 11 | 0.014      | 2  |
| Eu        | 0.01 | 0.001 | 0.023       | 20 | 0.017   | 14 | 0.038       | 6  | 0.019          | 13 | 0.032      | 7  |
| Fe        | 100  | 10    | 100         | 23 | 62      | 18 | 240         | 5  | 95             | 17 | 118        | 6  |
| Ga        | 0.1  | 0.01  | 0.08        | 3  | 0.08    | 3  |             |    | 0.04           | 1  | 0.10       | 2  |
| Gd        | 0.01 | 0.001 | 0.051       | 23 | 0.018   | 6  | 0.064       | 17 | 0.061          | 18 | 0.019      | 5  |
| Ge        | 0.1  | 0.01  | 0.98        | 13 | 0.98    | 13 |             |    | 0.22           | 5  | 1.45       | 8  |
| Hf        | 0.01 | 0.001 | 0.023       | 19 | 0.023   | 8  | 0.024       | 11 | 0.020          | 13 | 0.030      | 6  |
| Ho        | 0.01 | 0.001 | 0.025       | 6  | 0.002   | 1  | 0.030       | 5  | 0.030          | 5  | 0.002      | 1  |
| I         | 10   | 1     | 58          | 52 | 82      | 31 | 23          | 21 | 16             | 38 | 172        | 14 |
| K         | 300  | 30    | 19801       | 60 | 13963   | 35 | 27975       | 25 | 16583          | 44 | 28652      | 16 |
| La        | 0.01 | 0.001 | 0.14        | 35 | 0.004   | 18 | 0.29        | 17 | 0.17           | 30 | 0.009      | 5  |
| Li        | 10   | 1     | 360         | 21 | 460     | 16 | 37          | 5  | 35             | 10 | 654        | 11 |
| Lu        | 0.01 | 0.001 | 0.011       | 4  | 0.001   | 1  | 0.015       | 3  | 0.015          | 3  | 0.001      | 1  |
| Mg        | 2    | 0.2   | 73052       | 63 | 102903  | 35 | 35739       | 28 | 31133          | 47 | 196190     | 16 |
| Mn        | 1    | 0.1   | 104.4       | 34 | 161.9   | 15 | 59.0        | 19 | 76.0           | 23 | 163.9      | 11 |
| Mo        | 1    | 0.1   | 1.3         | 16 | 1.0     | 12 | 2.0         | 4  | 1.3            | 13 | 1.1        | 3  |
| Na        | 50   | 5     | 130601      | 63 | 194151  | 35 | 51165       | 28 | 34701          | 47 | 412309     | 16 |
| Nb        | 0.05 | 0.005 | 0.05        | 4  | 0.02    | 1  | 0.06        | 3  | 0.06           | 3  | 0.02       | 1  |
| Nd        | 0.01 | 0.001 | 0.137       | 42 | 0.015   | 20 | 0.248       | 22 | 0.155          | 36 | 0.028      | 6  |

| Parameter                     | DL1  | DL2       | All samples |    | Waters  |    | Soft drinks |    | Non-carbonated |    | Carbonated |    |
|-------------------------------|------|-----------|-------------|----|---------|----|-------------|----|----------------|----|------------|----|
|                               |      |           | Average     | N  | Average | N  | Average     | N  | Average        | N  | Average    | N  |
| Ni                            | 3    | 0.3       | 7.4         | 19 | 7.9     | 14 | 5.8         | 5  | 2.9            | 11 | 13.5       | 8  |
| Pb                            | 1    | 0.1       | 0.18        | 24 | 0.15    | 20 | 0.38        | 4  | 0.15           | 18 | 0.29       | 6  |
| Pd                            | 0.1  | 0.01      | 0.2         | 5  | 0.2     | 2  | 0.2         | 3  | 0.2            | 3  | 0.2        | 2  |
| Pr                            | 0.01 | 0.001     | 0.075       | 12 | 0.001   | 1  | 0.082       | 11 | 0.082          | 11 | 0.001      | 1  |
| Rb                            | 0.05 | 0.005     | 30.0        | 63 | 48.2    | 35 | 7.3         | 28 | 6.0            | 47 | 100.5      | 16 |
| Re                            | 0.01 | 0.001     | 0.006       | 19 | 0.004   | 13 | 0.010       | 6  | 0.006          | 18 | 0.002      | 1  |
| Sb                            | 0.1  | 0.01      | 0.27        | 54 | 0.31    | 32 | 0.21        | 22 | 0.23           | 41 | 0.38       | 13 |
| Sc                            | 10   | 1         | 9           | 10 | 9       | 10 |             |    | 2              | 3  | 12         | 7  |
| Se                            | 2    | 0.2       | 1.3         | 9  | 0.7     | 7  | 3.4         | 2  | 1.4            | 6  | 1.0        | 3  |
| Si                            | 2000 | 200       | 12391       | 60 | 13621   | 33 | 10888       | 27 | 8975           | 45 | 22639      | 15 |
| Sm                            | 0.01 | 0.001     | 0.063       | 14 | 0.007   | 5  | 0.095       | 9  | 0.086          | 10 | 0.007      | 4  |
| Sn                            | 1    | 0.1       | 27          | 2  |         | 0  | 27          | 2  | 27             | 2  |            |    |
| Sr                            | 0.4  | 0.04      | 486         | 63 | 750     | 35 | 155         | 28 | 243            | 47 | 1199       | 16 |
| Ta                            | 0.01 | 0.001     | 0.043       | 30 | 0.004   | 3  | 0.048       | 27 | 0.046          | 28 | 0.006      | 2  |
| Tb                            | 0.01 | 0.001     | 0.026       | 5  |         | 0  | 0.026       | 5  | 0.026          | 5  |            |    |
| Th                            | 0.01 | 0.001     | 0.07        | 13 | 0.05    | 2  | 0.079       | 11 | 0.079          | 11 | 0.047      | 2  |
| Ti                            | 1    | 0.1       | 4.1         | 44 | 4.1     | 26 | 4.1         | 18 | 2.9            | 32 | 7.4        | 12 |
| Tl                            | 0.01 | 0.001     | 0.06        | 27 | 0.055   | 19 | 0.077       | 8  | 0.046          | 18 | 0.092      | 9  |
| Tm                            | 0.01 | 0.001     | 0.011       | 5  | 0.001   | 2  | 0.018       | 3  | 0.018          | 3  | 0.001      | 2  |
| U                             | 0.02 | 0.001     | 0.479       | 62 | 0.470   | 34 | 0.490       | 28 | 0.486          | 47 | 0.457      | 15 |
| V                             | 1    | 0.1       | 0.6         | 19 | 0.6     | 17 | 0.8         | 2  | 0.6            | 15 | 0.8        | 4  |
| W                             | 0.2  | 0.02      | 0.03        | 3  | 0.04    | 2  | 0.02        | 1  | 0.03           | 3  |            |    |
| Y                             | 0.03 | 0.003     | 0.31        | 29 | 0.04    | 17 | 0.69        | 12 | 0.36           | 23 | 0.11       | 6  |
| Yb                            | 0.01 | 0.001     | 0.034       | 13 | 0.007   | 5  | 0.051       | 8  | 0.037          | 11 | 0.018      | 2  |
| Zn                            | 5    | 0.5       | 13.9        | 38 | 13.9    | 25 | 13.8        | 13 | 9.6            | 29 | 27.7       | 9  |
| Zr                            | 0.1  | 0.01      | 1.1         | 32 | 1.3     | 19 | 0.8         | 13 | 0.5            | 21 | 2.2        | 11 |
| Cl <sup>-</sup>               |      | 0.2       | 35.2        | 63 | 35.0    | 35 | 35.0        | 28 | 23.6           | 47 | 69.1       | 16 |
| F                             |      | 0.03/0.05 | 186         | 37 | 187     | 33 | 185         | 4  | 124            | 22 | 279        | 15 |
| HCO <sub>3</sub> <sup>-</sup> |      | /         | 609000      | 63 | 1087000 | 35 | 12000       | 28 | 125000         | 47 | 2030000    | 16 |
| NH <sub>4</sub> <sup>+</sup>  |      | 0.02      | 180         | 4  | 180     | 4  |             |    | 180            | 4  |            |    |
| NO <sub>2</sub> <sup>-</sup>  |      | 0.5       | 46          | 5  | 1       | 4  | 228         | 1  | 47             | 5  |            |    |
| NO <sub>3</sub> <sup>-</sup>  |      | 0.001     | 1           | 15 | 1       | 11 | 1           | 4  | 1              | 15 |            |    |
| PO <sub>4</sub> <sup>3-</sup> |      | 0.05      | 890         | 27 | 240     | 10 | 1270        | 17 | 1020           | 22 | 330        | 5  |
| SO <sub>4</sub> <sup>2-</sup> |      | 2         | 126000      | 49 | 181000  | 31 | 32000       | 18 | 23000          | 36 | 412000     | 13 |

All units are in µg/l. DL1 – detection limit for the solution with TDS >500 mg/l, DL2 – detection limit for the solution with TDS <500 mg/l. Nitrogen species are given as nitrogen concentrations.

The concentration of  $\text{Cl}^-$  was determined at Joanneum Research, Institute of Water Resources Management, Graz, Austria. According to purpose of the study the accuracy and precision of anion analyses were determined as reasonable.

Isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) was determined on  $\text{CO}_2$  collected after reaction of sample with 100 %  $\text{H}_3\text{PO}_4$  on a continuous flow Europa 20-20 ANCA-TG stable isotope mass spectrometer at Jožef Stefan Institute. Results are expressed in relative ( $\delta$ ) notations as deviations in per mil (‰) from the V-PDB standard. Measurement reproducibility of duplicates was generally better than  $\pm 0.3$  ‰.

Isotopic composition of oxygen ( $\delta^{18}\text{O}$ ) was determined by equilibration of  $\text{CO}_2$  with water samples on a dual inlet Finnigan DELTA<sup>plus</sup> stable isotope mass spectrometer, and isotopic composition of hydrogen ( $\delta^2\text{H}$ ) was measured on  $\text{H}_2$  generated by reduction of water over hot chromium on a continuous flow Finnigan DELTA<sup>plus</sup> XP stable isotope mass spectrometer at the Joanneum Research, Institute of Water Resources Management, Graz, Austria. Results are reported as per mil deviations from the V-SMOW standard. Measurement reproducibility of duplicates was better than  $\pm 0.05$  ‰ for  $\delta^{18}\text{O}$  and  $\pm 1$  ‰ for  $\delta^2\text{H}$ .

## RESULTS

A large data set was obtained according to sampling and performed analyses. In this paper are presented only results as averages according to the type of water and soft drinks that are similar to water. Averages for different groups of waters are given in Table 1, together with detection limits that are reported in two groups. Average values were calculated for brands and their bottle replicates, therefore total number of all statistical units is 63. Sample replicates are not included in this number; sample and control sample were joined as two sample value before the average value calculations.

The first group of detection limits DL1 is valid for samples with total dissolved solids larger than 500 mg/l and the second group DL2 for samples with total dissolved solids smaller than 500 mg/l. Only one detection limit is given for anions, except for fluoride.

According to different measurement procedures and different physical meaning average values of conductivity, pH and isotopic composition of hydrogen, oxygen and DIC for different groups of waters are reported separately (Table 2).

**Table 2.** Averages and number of samples of different waters and soft drinks classifications – conductivity (20°C), pH and stable isotopes.

**Tabela 2.** Povprečja in število vzorcev glede na različne skupine vod in pijač podobnim vodam - elektroprevodnost (20°C), pH in stabilni izotopi.

| Parameter                            | All samples |    | Waters  |    | Soft drinks |    | Non-carbonated |    | Carbonated |    |
|--------------------------------------|-------------|----|---------|----|-------------|----|----------------|----|------------|----|
|                                      | Average     | N  | Average | N  | Average     | N  | Average        | N  | Average    | N  |
| Conduct. $\mu\text{Si}/\text{cm}$    | 1283        | 63 | 1646    | 35 | 831         | 28 | 687            | 47 | 3038       | 16 |
| pH                                   | 5.4         | 63 | 6.6     | 35 | 3.8         | 28 | 5.3            | 47 | 5.7        | 16 |
| $\delta^2\text{H}$ ‰                 | -66         | 63 | -66     | 35 | -66         | 28 | -65            | 47 | -70        | 16 |
| $\delta^{18}\text{O}$ ‰              | -9.6        | 63 | -9.7    | 35 | -9.6        | 28 | -9.4           | 47 | -10.2      | 16 |
| $\delta^{13}\text{C}_{\text{DIC}}$ ‰ | -11.9       | 63 | -12.6   | 35 | -11.1       | 28 | -10.8          | 47 | -15.3      | 16 |

**Table 3.** Classification of elements and anions according to the share of samples under the detection limit [%].**Tabela 3.** Klasifikacija elementov in anionov glede na delež vzorcev pod detekcijsko mejo [%].

| Share of samples under the detection limit [%] | Element                                                           | Number of elements |
|------------------------------------------------|-------------------------------------------------------------------|--------------------|
| 90 – 100                                       | Au, Ga, Ho, Lu, Nb, Pd, Sn, Tb, Tm, W,                            | 10                 |
| 80 – 90                                        | Cr, Dy, Er, Pr, Sc, Se, Sm, Yb, $\text{NH}_4^+$ , $\text{NO}_2^-$ | 8                  |
| 70 – 80                                        | Al, Co, Eu, Ge, Gd, Hf, Mo, Ni, Re, V, Th, $\text{NO}_3^-$        | 11                 |
| 60 – 70                                        | Cd, Fe, Li, Ti, $\text{PO}_4^{3-}$                                | 4                  |
| 50 – 60                                        | Br, Cu, Cs, Pb, Ta, Zr, Y                                         | 7                  |
| 40 – 50                                        | Ce, La, Mn, F <sup>-</sup>                                        | 3                  |
| 30 – 40                                        | Nd, Zn                                                            | 2                  |
| 20 – 30                                        | As, Ti,                                                           | 2                  |
| 10 – 20                                        | I, Sb, $\text{SO}_4^{2-}$                                         | 2                  |
| 0 – 10                                         | Ba, Ca, K, Si, U                                                  | 4                  |
| 0                                              | Na, Mg, Rb, Sr, $\text{Cl}^-$ , $\text{HCO}_3^-$                  | 4                  |

The statistics for water and soft drinks similar to water are divided into five main groups (Table 1 and 2). The first group represents results from all analyzed bottles; the second only of waters and the third are the results of all soft drinks similar to water. The last two groups represent samples divided according to the presence of gaseous  $\text{CO}_2$ . Samples with gaseous  $\text{CO}_2$  are defined as carbonated and without as non-carbonated. The two classifications of soft drinks and non-carbonated waters are partially covered over. All soft drinks are non-carbonated. This is the reason why they are included into the group of non-carbonated samples.

The average values were calculated only for values above detection limit; censured values below detection limit were simply omitted from the calculations. Concentrations of elements Ag, Be, Bi, Hg, In, Os, Pt, Ru, Te were in all samples under the detection limit. The classification of elements and anions according to the share of samples under the detection limit for other elements and anions are given in Table 3.

The averages calculated with this procedure are biased to the right of the determined

element or ion empirical distribution. This bias is larger for determinations with greater share of values below detection limit than for the determinations with lower share. In the geochemical literature the approach of MIESCH (1976) is usually adopted where only variables with more than 70 % of determinations are included in data reduction. In the present study this approach was used only in graphical presentation of the results (see Discussion).

## DISCUSSION

Results show that mainly all elements that are possible to detect with ICP-MS are present in analyzed drinks. But only few elements and ions are present in all samples. This fact leads us to the conclusions that such chemical composition is the consequence of various sources and geochemical processes. Different chemical composition of waters and soft drinks similar to water is also a consequence of various filling and pumping procedures, while in soft drinks it depends also on composition and combinations of flavours.

**Table 4.** Comparison of different groups of waters and soft drinks similar to water according to the overall average.**Tabela 4.** Primerjava različnih skupin vod in pijač podobnih vodam glede na celotno povprečje analiziranih vzorcev.

| Parameter                     | Waters | Soft drinks | Non - carbonated | Carbonated |
|-------------------------------|--------|-------------|------------------|------------|
| As                            | -      | +           | -                | +          |
| Ba                            | +      | -           | -                | +          |
| Ca                            | -      | +           | -                | +          |
| I                             | +      | -           | -                | +          |
| K                             | -      | +           | -                | +          |
| Mg                            | +      | -           | -                | +          |
| Na                            | +      | -           | -                | +          |
| Rb                            | +      | -           | -                | +          |
| Sb                            | +      | -           | -                | +          |
| Si                            | +      | -           | -                | +          |
| Ti                            | 0      | 0           | -                | +          |
| U                             | -      | +           | +                | -          |
| Cl <sup>-</sup>               | +      | -           | -                | +          |
| HCO <sub>3</sub> <sup>-</sup> | +      | -           | -                | +          |
| SO <sub>4</sub> <sup>2-</sup> | +      | -           | -                | +          |

+ average of the group is larger than overall average, - average of the group is smaller than overall average, 0 average of the group is the same as overall average

Calculated averages show big differences between various groups of waters. This can be seen from the general characteristics such as pH and electrical conductivity (Table 2). Soft drinks have relatively low average pH, much lower than other groups. This fact is the consequence of added organic acids, mainly citron acid that should act as refresher. Carbonated waters have much higher electrical conductivity than other waters.

To define the differences among groups of waters and soft drinks comparison between average value for all samples and averages for particular group was made. The comparison was made numerically without statistical testing and the results are presented in Table 4 and Figure 1. When the group average in the Table 4 is higher than overall

average (+) is given, otherwise (-) is presented. It can be clearly seen that in all cases the average value of element or anion is higher for carbonated waters then for non-carbonated waters. Only in the case of uranium the average is higher for non-carbonated waters. Nevertheless the differences for all elements and anions are small and the average values are very similar.

The comparison between soft drinks and waters is not so straightforward as it is in the case of gaseous CO<sub>2</sub>, however it shows that waters have in general higher averages than soft drinks. Sampled soft drinks are waters without gaseous CO<sub>2</sub>. Therefore, we can expect that the pattern in Table 4 should be similar as is in the case of the comparison between carbonated and non-carbonated

samples. But higher concentrations of some elements in soft drinks direct to the interpretation that some flavours change original chemistry of water that represent the base for soft drinks and therefore they have higher average concentrations.

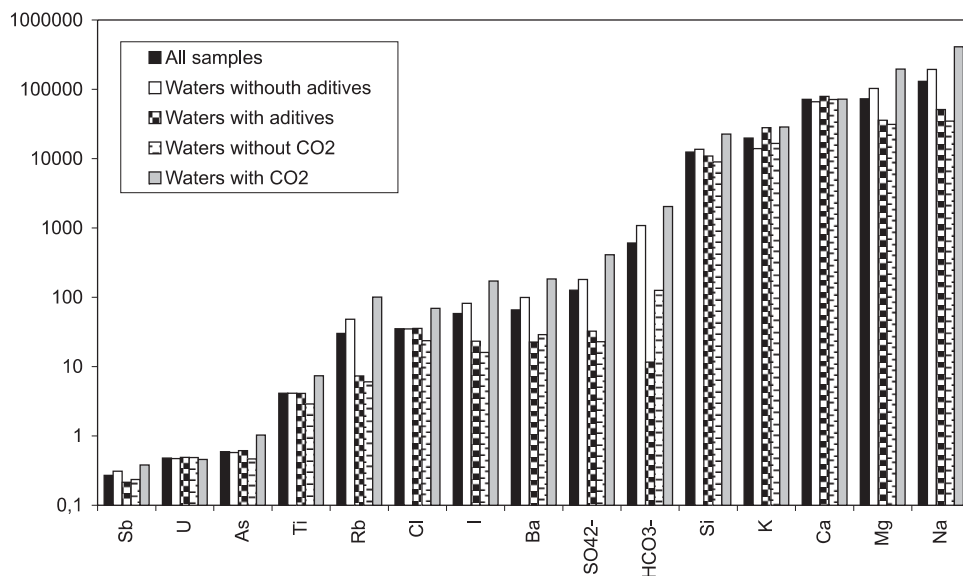
Differentiation between carbonated and non-carbonated samples is mainly a consequence of the presence of highly mineralized waters in samples that have their source from deep groundwater in east and northeast Slovenia. These waters are carbonated and have high mineral content. Those samples with high total dissolved solids are usually without flavours and they contribute to higher averages of waters.

It is not intention of the present study to deeply analyze the isotopic content of the sampled waters and soft drinks. Better interpretation of the results is possible with

the data reduction based on particular samples. However, according to the isotopic composition different groups of waters and soft drinks are very similar (Table 2). Differences in calculated averages are characteristic between particular groups for  $\delta^{13}\text{C}_{\text{DIC}}$ , while for  $\delta^{18}\text{O}$  only carbonated waters differ considerably. Carbonated waters have slightly lower  $\delta^{13}\text{C}_{\text{DIC}}$ . This result is not in agreement with belief that  $\text{CO}_2$  in these waters is geogenic.

## CONCLUSIONS

The present study shows that chemical composition of waters and soft drinks similar to water available on the Slovene market is very wide. Nearly all elements that are possible to detect with ICP-MS are present but only few elements and anions are detected in all samples. The general



**Figure 1.** Comparison of different groups averages of waters and soft drinks similar to water.

**Slika 1.** Primerjava povprečij različnih skupin vod in pijač podobnih vodam.

characteristics such as pH and conductivity show that the composition of samples differs according to the type of water and soft drinks. In general we can differentiate within samples with gaseous CO<sub>2</sub> or without it and between water with or flavours additives. The CO<sub>2</sub> differentiation is mainly a consequence of the presence of highly mineralized waters originating from east and northeast Slovenia. They are carbonated and those with high total dissolved solids are usually without flavours.

Average isotopic composition of hydrogen, oxygen and DIC for different groups of waters and soft drinks is very similar. From the calculated averages difference are seen mainly in  $\delta^{13}\text{C}_{\text{DIC}}$  and in waters with CO<sub>2</sub> in  $\delta^{18}\text{O}$ . However, more detailed analyses of obtained isotopic results will show big differentiation among various types of waters and soft drinks.

The aim of the present study was to give a geochemical overview of bottled waters and soft drinks similar to water available on the market in Slovenia. Adopted approach was used to establish the procedure for sampling and analyses, to expose open questions related to bottled waters and present exploration of groundwater for bottling of water. However, further work is needed on the statistical analyses and more rigorous statistical testing should be applied. Several multivariate statistics could be performed; among them analysis of variance, multivariate regression analysis, discriminant analysis, cluster analysis and factor analysis of R and Q type. Waters must be classified according to the hydrogeochemical classifications and more interpretation is needed in connection with the origin of

waters. Further research will be directed also in more differentiate classification of samples based on cross-tabulation.

### Acknowledgement

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### POVZETEK

#### Splošne kemijske karakteristike ustekleničenih vod na slovenskem tržišču

Potrošnja ustekleničenih vod in pijač, ki so podobne vodam, narašča iz dneva v dan. Že bežen pregled tržišča pokaže, da se te pijače med seboj zelo razlikujejo. Na tržišču bomo našli vode, ki so opredeljene kot mineralne vode, kot izvirske vode ali pa kot vode z dodatki. Takšne razmere na tržišču so posledica dejanskega slabšanja nekaterih vodnih virov, naraščujoče zavesti potrošnikov, še bolj kot to pa zakonitosti tržišča in proizvajalcev, ki skušajo čimbolj povečevati prodajo. Pri potrošnji teh pijač se pogosto zastavljajo številna vprašanja o kvaliteti, njihovem izvoru in kemizmu.

V članku so predstavljeni rezultati raziskav 58 ustekleničenih voda in pijač podobnih vodi, kupljenih na slovenskem tržišču septembra 2004. Vzorčenje je potekalo po shemi neuravnotežene analize variance.

Analiza vzorcev je zajemala določitev koncentracije 67 elementov z ICP-MS, anionov z ionsko kromatografijo in izotopske sestave vodika, kisika in raztopljenega anorganskega ogljika z masno spektrometrijo. Vzorce smo razdelili v štiri skupine (vode in pijače ter gazirane in negazirane vode).

Rezultati analiz kažejo, da so v analiziranih pijačah prisotni skoraj vsi elementi, ki jih lahko določimo z metodo ICP-MS (tabela 1). Toda le nekateri elementi so prisotni v vseh analiziranih vzorcih (tabela 3). Takšne razlike nas privedejo do sklepa, da je kemijska sestava analiziranih vzorcev posledica različnega izvora in geokemičnih procesov. Razlike v kemijski sestavi so tudi posledica različnih postopkov polnjenja in črpanja podzemne vode, ki predstavlja osnovo za izdelavo teh pijač. Pri pijačah, ki so podobne vodam, pa na kemizem vplivajo tudi različni dodatki.

Izračunana povprečja kažejo na zelo velike razlike med pijačami (tabela 1 in 2). Te razlike zlahka opazimo že, če med seboj primerjamo splošne karakteristike skupin, kot sta pH in elektroprevodnost (tabela 2). Vode z dodatki imajo relativno nizek pH, mnogo nižji kot ostale skupine. To je posledica različnih dodatkov, predvsem organskih kislin in še posebej citronske kisline, ki naj bi delovala kot osvežilo. Vode s prostim plinskim CO<sub>2</sub> pa imajo dosti višjo električno prevodnost kot pijače iz ostalih skupin.

Primerjava med povprečji posameznih skupin je bila izvedena le numerično, brez statističnih testiranj. Rezultati primerjave so predstavljeni v tabeli 4 in na sliki 1. Če je povprečje skupine višje kot povprečje

celotnega niza vzorcev je ta razlika predstavljena s +, če je nižja pa z -. Iz primerjave v tabeli 4 sledi, da je pri gaziranih pijačah v vseh primerih koncentracija elementov in anionov višja od koncentracije v negaziranih vodah. Le v primeru koncentracije urana je povprečna koncentracija višja pri negaziranih kot pri gaziranih pijačah. Razlika med gaziranimi in negaziranimi pijačami je posledica prisotnosti visoko mineraliziranih vod, ki imajo svoj izvor v globoki podzemni vodi severovzhodne in vzhodne Slovenije. Kljub temu pa so razlike majhne in izračunana povprečja zelo podobna.

Primerjava med skupinama vod in vod z dodatki pa ni tako premočrtna, kot je to v primeru gaziranih in negaziranih vod. Kljub temu primerjava pokaže, da imajo vode brez dodatkov pravilom višje koncentracije kot vode z dodatki. Analizirane vode z dodatki so negazirane, kar bi lahko pojasnilo razliko, saj imajo gazirane vode višjo mineralizacijo. Na podlagi tega bi lahko pričakovali, da bo primerjava med vodami in vodami z dodatki v tabeli 4 podobna primerjavi med gaziranimi in negaziranimi pijačami. Toda višje koncentracije nekaterih elementov v vodah z dodatki nas napeljujejo na interpretacijo, da nekateri dodatki spremenijo kemizem vode, ki predstavlja osnovo za izdelavo pijače.

Rezultati izotopskih analiz kažejo, da so si analizirane skupine med seboj dokaj podobne (tabela 2). Razlike v izračunanih povprečjih so med skupinami opazne predvsem pri  $\delta^{13}\text{C}_{\text{DIC}}$ , medtem ko pri  $\delta^{18}\text{O}$  znatno odstopajo le gazirane vode. Gazirane vode imajo nekoliko nižjo vrednost  $\delta^{13}\text{C}_{\text{DIC}}$ , kar nakazuje, da izvor CO<sub>2</sub> v nekaterih vodah ni geogenega izvora.

Namen članka je predstaviti osnovne geokemijske značilnosti ustekleničenih voda in vod z dodatki, ki jih je mogoče kupiti na slovenskem tržišču. V okviru opravljene raziskave smo poizkušali vzpostaviti postopek za vzorčenje in odpreti nekatera vprašanja, ki se navezujejo na polnjenje ustekleničenih voda ter na izkoriščanje podzemne vode za potrebe ustekleničenja. Predstavljeni rezultati so le prvi korak k iskanju odgovorov na ta vprašanja. V nadaljnjih koraki bo potrebno izvesti podrobnejšo statistično analizo z rigoroznejšimi statističnimi testi. Statistične analize bodo usmerjene v multivariatne statistike kot so multipla analiza variance, multivariatna regresijska analiza, diskriminantna naliza, clusterska analiza ter faktorska analiza tipa Q in R. Pri nadaljnji analizi bo potrebno izvesti tudi nekatere fizikalno kemijske izračune in hidrogeokemijske klasifikacije ter jih navezati na hidrogeološki izvor vode. Nadaljnje raziskave bodo usmerjene tudi v podrobnejšo klasifikacijo vzorcev.

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## Razširjenost onesnaženja s cinkom in kadmijem v Celjski kotlini

### Distribution of zinc and cadmium pollution in Celje basin

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**Izvleček:** V raziskavi smo proučevali upadanje vsebnosti cinka in kadmija v odvisnosti od razdalje od vira onesnaženja. Vir onesnaženja v Celju je Cinkarna celje, ki je v 100 letnem obdobju proizvedla približno 580.000 ton surovega rafiniranega cinka. Vzorci tal (0-5 cm) in podstrešnega prahu so bili odvzeti do oddaljenosti 12 km od obrata. Vzorčne točke smo postavili po dolinah Savinje, Voglajne in Hudinje in se na ta način izognili hribovitemu svetu, ki predstavlja naravno pregrado za širjenje onesnaženega zraka. Rezultati so pokazali, da se vsebnosti Zn in Cd nižajo po potenčni funkciji. Koeficienti determinacije s teoretično potenčno krivuljo so v obsegu od 0,75 do 0,98. Vplivno območje onesnaževalca smo ocenili med 15 in 60 km za podstrešni prah ter med 7 in 20 km za tla in je odvisno od tega, proti kateri strani neba se od topilnice oddaljujemo. Najbolj je obremenjena vzhodna dolina, najmanj pa severna.

**Abstract:** In this research we have examined the decreasing of the concentrations of pollutants in the attic dust and topsoil with increasing distance from the source of pollution, which is in this case zinc smelter plant Cinkarna in Celje town. In the 100-year period Cinkarna has produced around 580,000 tonnes of raw zinc. The samples of topsoil (0-5 cm) and attic dust have been taken up to 12 kilometers distance from the plant. The sampling plan based on the sampling in the river valleys: Savinja on the W and S, Voglajna at the E and Hudinja valley at the N side from the polluter. In that way we have avoided the uplands, which represents the natural barrier for the polluted air. The research has shown that lowering of zinc and cadmium concentrations can be described by power equation with high determination coefficients between hypothetical power curve and measured values, which varies between 0.75 and 0.98. The influence area is between 15 and 60 kilometers in attic dust and between 7 and 20 km for topsoil. It depends on the orientation of the valley. The most polluted is east valley and the least polluted the north valley.

**Ključne besede:** onesnaženje, težke kovine, podstrešni prah, tla, Celje, Slovenija.

**Key words:** pollution, heavy metals, attic dust, topsoil, Celje, Slovenia.

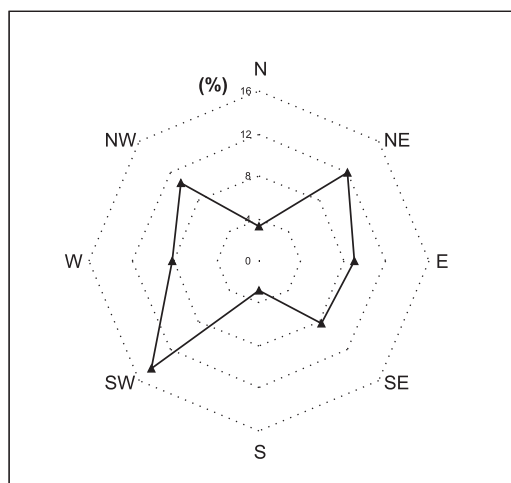
## Uvod

V številnih dosedanjih raziskavah je ugotovljeno, da je stopnja onesnaženosti mesta Celje zelo visoka (BATIČ, 1984; DOMITROVIČ-URANJEK, 1990; LOBNIK ET AL., 1989). Viri onesnaženja so predvsem celjska industrija, promet ter drobna kurišča. Vsak vir pa ima svoje značilne geokemične karakteristike. Tako Železarna Štore izpušča siderofilne prvine, kot so železo, krom, mangan, nikelj in kobalt, individualna kurišča so pomemben vir kalcija, magnezija ter stroncija, obrati Cinkarne Celje pa so bili močan vir cinka, kadmija, svinca in arzena ter v zadnjih 30 letih tudi titana (ŠAJN, 2001; ŠAJN, 2005; ŽIBRET, 2002a). Ker je Cinkarna Celje močan vir cinka in kadmija v okolici, je mogoče določiti, do kam sega vpliv onesnaževalca oziroma kako daleč je opazen vpliv nekdanje topilnice.

Celjska kotlina se razteza v smeri vzhod-zahod. Od zahoda priteče reka Savinja, ki prav v Celju naredi oster ovinek proti jugu v Posavske gube, ki predstavljajo ostro geografsko mejo. V Savinjo se od vzhoda izliva reka Voglajna, od severa pa priteče reka Hudinja. V neposredni bližini sotočja treh rek so se nahajale topilnice cinka. V 100 letnem obratovalnem obdobju je po ocenah, dobljenih iz statističnih letopisov SR Slovenije ter posameznih poročil (FELICIAN, 1993), bilo pridobljenih 580.000 ton surovega rafiniranega cinka. Postopek predelave je bil takšen, da je vsaj 3% celotne produkcije Zn bilo emitiranih v okolje v obliki prašnih delcev. Posledica je ta, da tla na vzorčni točki v bližini Cinkarne vsebujejo 0,86 % cinka in 60 mg/kg kadmija (ŽIBRET, 2002a). Še višje vsebnosti zasledimo v podstrešnem prahu, ki je po ekonomsko-

geoloških karakterizacijah kvalitetna cinkova ruda, saj vsebuje 5,6 % Zn in 456 mg/kg kadmija. Emisije v okolje ocenjujemo na približno 1700 ton cinka in 9 ton kadmija (ŽIBRET, 2002b).

Geokemično ozadje Slovenije za tla (0-5 cm) znaša 124 mg/kg Zn in 0,5 mg/kg Cd, za podstrešni prah pa 327 mg/kg Zn in 1,2 mg/kg Cd (ŠAJN, 2003). Približno 7 km severozahodno od Celja je hidrotermalno polimetalno svinčevo-cinkovo rudišče Zavrh (DROVENIK ET AL., 1981), ki na porazdelitev Zn in Cd v okolju verjetno nima večjega vpliva.



Slika 1. Roža vetrov za mesto Celje.

Figure 1. The wind rose for the town of Celje.

Na razširjanje onesnaženosti na celjskem območju najbolj vplivajo podnebni dejavniki, kot so veter, njegova smer in hitrost ter pojav temperaturne inverzije predvsem v zimskem obdobju. Ker leži Celje v kotlini, je zanj roža vetrov (slika 1) neznčilna in zelo lokalno pogojena. Na splošno pa prevladujeta severovzhodnik (12 %) in jugozahodnik (15 %) s povprečno hitrostjo vetra okoli 2 m/s. Brezvetrje traja v

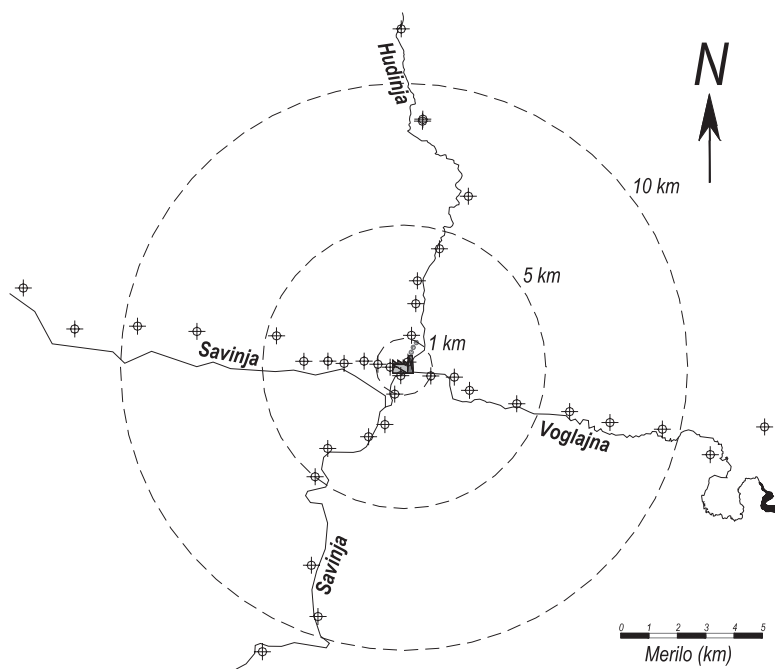
povprečju 32,1 % celotnega časa. Pojav temperaturne inverzije traja povprečno 95,2 dni v letu in je prisoten predvsem od septembra do februarja.

## MATERIALI IN METODE

Za določitev vplivnega območja topilnic cinkove rude v Celju smo vzorčili podstrešni prah in tla po rečnih dolinah v smereh vzhod, zahod, sever in jug. Vzorčni načrt je predvideval vzorčenje glede na oddaljenost od topilnic Cinkarne Celje, in sicer v bližini cinkarne na vsakih 500 m, potem pa na vsaka 2 km (slika 2). Največja oddaljenost odvzetega vzorca od Cinkarne je po zračni črti znašala 11,9 km proti severu, južno 11,2 km, zahodno 13,7 km in vzhodno 12,9 kilometrov.

Podstrešni prah smo vzorčili tako, da smo zbirali prah z lesene konstrukcije podstrešja, ki ni bila v neposrednem stiku s strešniki ali tlemi. Na ta način smo se izognili pobiranju delcev strešnikov, ostankov lesa in malte. Pri vzorčenju podstrešnega prahu smo izbirali starejše objekte, po možnosti z zapuščenim podstrešjem (ŠAJN, 1999). Tla so bila vzorčena do globine 5 cm. Izven naselij smo vzorčili travniška tla, v naseljih pa vrtna tla ali tla zelenic. Posamezni vzorec je sestavljen iz najmanj 7 podvzorcev, odvzetih v teoretično šesterokotnem načrtu na razdaljah 25 m od središčne točke. Celotni zbrani vzorec tal je tehtal približno 1 kg.

Vzorke smo pripravili po postopkih, ki so priporočeni v sklepih UNESCO-vega projekta IGCP 259 (DARNLEY ET AL., 1995). Zbrani vzorčni material smo sušili v ventilatorski omari pri 40° C. Vzorke tal smo potem



**Slika 2.** Položaj vzorčnih točk glede na vir onesnaženja.

**Figure 2.** Locations of sampling points with regard to source of pollution.

narahlo pretrli ter presejali skozi sito na zrnastost pod 2 mm. Presevky smo po četrтинjenju mleli v keramični terilnici ter sejali na analizno zrnastost pod 0,125 mm. Vzorce podstrešnega prahu smo presejali na posamezne razrede zrnastosti: od 1 do 0,5 mm, od 0,5 do 0,25 mm, od 0,25 do 0,125 mm in manjši od 0,125 mm. Presevek, manjši od 0,125 mm, je predstavljal material za kemijsko analizo po metodi plazemske emisijske spektrometrije (ICP) po štirikislinskem razklopu ( $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$  in  $\text{HF}$ ), ki je potekal pri temperaturi 200°C. Vzorce so analizirali na 42 prvin (Al, Ca, Fe, K, Mg, Na, P, S, Ti, Ag, As, Au, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Hf, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn in Zr) v laboratoriju družbe ACME v Kanadi. Vsebnosti Hg so bile po razklopu z zlatotopko določene z atomsko absorpcijsko spektrometrijo (AAS), po postopku hladnega izparevanja.

Zmanjševanje vsebnosti Zn in Cd v prahu in tleh z oddaljenostjo od vira onesnaženja v Celju lahko opišemo s potenčno krivuljo z asimptotičnim približevanjem ničli v neskončnosti. Enačba 1 opisuje potenčno krivuljo, tabela 1 pa njene posamezne koeficiente glede na prvino, material in smer vzorčenja.  $X$  v enačbi 1 pomeni oddaljenost opazovane točke od vira onesnaženja, izraženo v kilometrih,  $C$  pa vsebnost v mg/kg. Linearni faktor  $\alpha$  in eksponentni faktor  $\beta$  opisujeta hitrost padanja vsebnosti cinka in kadmija glede na oddaljenost od vira onesnaženja. Oba faktorja sta navedena v tabeli 1.  $D^2$  v tabeli 1 pomeni moč povezave med empirično in teoretično krivuljo zmanjševanja vsebnosti prvine.

$$C = \alpha \cdot X^{-\beta} \quad (1)$$

Slaba stran potenčne krivulje je ta, da zadovoljivo opisuje padanje vsebnosti polutantov le na določenem intervalu, izven tega intervala pa vrne nerealne vrednosti. Največje pomanjkljivosti so:

- potenčna krivulja predpostavlja neskončen doseg onesnaževalca;
- potenčna krivulja predpostavlja neskončne vsebnosti polutanta na mestu onesnaževalca (če za razdaljo vnesemo vrednost 0, dobimo vsebnost neskončno);
- vsebnosti se asimptotično približujejo ničli, namesto, da bi se približevale vrednosti geokemičnega ozadja.

$$C = \text{ozadje} + \alpha \cdot X^{-\beta} \quad (2)$$

Asimptotično približevanje geokemičnemu ozadju se da enostavno korigirati (enačba 2), vendar slednji model slabše opisuje obnašanje vsebnosti cinka in kadmija glede na oddaljenost od vira, saj so vrednosti determinacijskih koeficientov nižje (od 1 do 12 odstotnih točk). Zato je tudi bil uporabljen model po enačbi 1.

Vplivno območje topilniških obratov je razdalja, na kateri je vpliv topilnic že tako majhen, da naravna prisotnost cinka in kadmija preseže ocenjeni antropogeni vnos. Takrat ni več možna ločitev med naravno prisotnim cinkom in kadmijem ter med antropogenim vnosom teh dveh prvin. Ta podatek je izračunan po enačbi 3, ki predstavlja rešitev enačbe 1 po  $X$ -u v kilometrih. Za koncentracijo ( $C_{\text{ozadja}}$ ) je bila upoštevana vrednost geokemičnega ozadja za posamezno prvino in material v mg/kg. Linearni faktor  $\alpha$  in potenčni faktor  $\beta$  sta za posamezno prvino, smer in material enaka, kot pri enačbi 1.

$$X_{\text{ozadja}} = \left( \frac{\alpha}{C_{\text{ozadja}}} \right)^{1/\beta} \quad (3)$$

**Tabela 1.** Parametri potenčnih krivulj.**Table 1.** Parameters of power curves ("ne doseže" means "does not reach").

| <b>Cink (prah) / Zinc (dust)</b>        | $\alpha$ | $\beta$ | $D^2$ | <b>ozadje (km)/<br/>background<br/>teoretično /<br/>theoretical</b> | <b>ozadje (km)/<br/>background<br/>izmerjeno /<br/>measured</b> |
|-----------------------------------------|----------|---------|-------|---------------------------------------------------------------------|-----------------------------------------------------------------|
| sever (N)                               | 9193,9   | 1,2497  | 0,98  | 14,44                                                               | ne doseže                                                       |
| jug (S)                                 | 7741,8   | 1,0251  | 0,91  | 21,91                                                               | ne doseže                                                       |
| zahod (W)                               | 18907    | 1,1771  | 0,97  | 31,40                                                               | ne doseže                                                       |
| vzhod (E)                               | 25545    | 1,1020  | 0,88  | 52,19                                                               | ne doseže                                                       |
| vse točke / all points together         | 13026    | 1,0908  | 0,80  | 29,31                                                               |                                                                 |
| <b>Cink (tla) / Zinc (soil)</b>         |          |         |       |                                                                     |                                                                 |
| sever (N)                               | 1522,9   | 1,0596  | 0,88  | 10,67                                                               | 8                                                               |
| jug (S)                                 | 1082,1   | 0,9744  | 0,81  | 9,24                                                                | 10                                                              |
| zahod (W)                               | 3357,5   | 1,2448  | 0,87  | 14,15                                                               | ne doseže                                                       |
| vzhod (E)                               | 4567,5   | 1,3872  | 0,95  | 13,46                                                               | ne doseže                                                       |
| vse točke / all points together         | 2056,9   | 1,0828  | 0,79  | 13,38                                                               |                                                                 |
| <b>Kadmij (prah)<br/>Cadmium (dust)</b> |          |         |       |                                                                     |                                                                 |
| sever (N)                               | 52,207   | 1,1413  | 0,94  | 27,27                                                               | ne doseže                                                       |
| jug (S)                                 | 39,237   | 1,0410  | 0,85  | 28,50                                                               | ne doseže                                                       |
| zahod (W)                               | 114,68   | 1,0322  | 0,89  | 82,90                                                               | ne doseže                                                       |
| vzhod (E)                               | 124,25   | 1,0703  | 0,96  | 76,34                                                               | ne doseže                                                       |
| vse točke / all points together         | 71,135   | 1,0251  | 0,75  | 53,64                                                               |                                                                 |
| <b>Kadmij (tla)<br/>Cadmium (soil)</b>  |          |         |       |                                                                     |                                                                 |
| sever (N)                               | 4,6098   | 1,2238  | 0,90  | 5,95                                                                | 7                                                               |
| jug (S)                                 | 39,237   | 1,0410  | 0,85  | 63,64                                                               | 8                                                               |
| zahod (W)                               | 114,68   | 1,0322  | 0,89  | 186,37                                                              | ne doseže                                                       |
| vzhod (E)                               | 124,25   | 1,0703  | 0,96  | 166,76                                                              | ne doseže                                                       |
| vse točke / all points together         | 9,6470   | 1,0276  | 0,65  | 17,15                                                               |                                                                 |

## REZULTATI

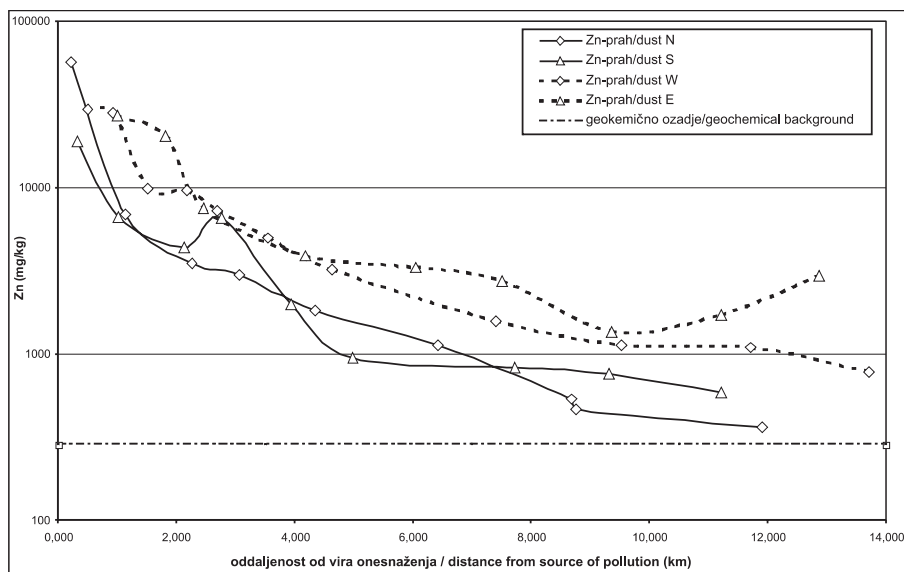
Analizne rezultate kažejo slike od 3 do 6. Slika 3 prikazuje upadanje vsebnosti cinka v podstrešnem prahu glede na oddaljenost od vira onesnaženja. Najmanjši koeficient  $\alpha$  je v dolini reke Savinje na jugu, kar pomeni manjšo splošno onesnaženost, kot v ostalih treh dolinah. Najvišji koeficient  $\beta$  pa je v dolini reke Hudinje na severu, kar pomeni, da vsebnosti cinka v podstrešnem prahu najhitreje upadajo v tej smeri. Vrednosti geokemičnega ozadja nismo ugotovili niti na oddaljenosti več kot 13 km od topilnic cinkove rude. Najbolj so se vsebnosti približale ozadju v dolini reke Hudinje proti severu in sicer v vzorcu, odvzetem v Socki.

Glede na izračun vplivnega območja ocenjujemo, da se vrednosti cinka v podstrešnem prahu spustijo na raven geokemičnega ozadja med 15 km (N dolina) in 60 km (E dolina) od vira. Če upoštevamo vse opazovane točke, znaša vplivno območje topilnic približno 30 km za cink v podstrešnem prahu.

Podobne karakteristike kaže tudi vedenje kadmija v podstrešnem prahu (slika 4). Spet se najvišje vrednosti linearnega faktorja  $\alpha$  pojavijo v vzhodni dolini, kar pomeni najvišjo stopnjo onesnaženja, najvišje vrednosti potenčnega koeficienta  $\beta$  pa v severni dolini, kar nakazuje na najhitrejšo padanje vsebnosti glede na oddaljenost od vira. Tudi v tem primeru nismo zaznali

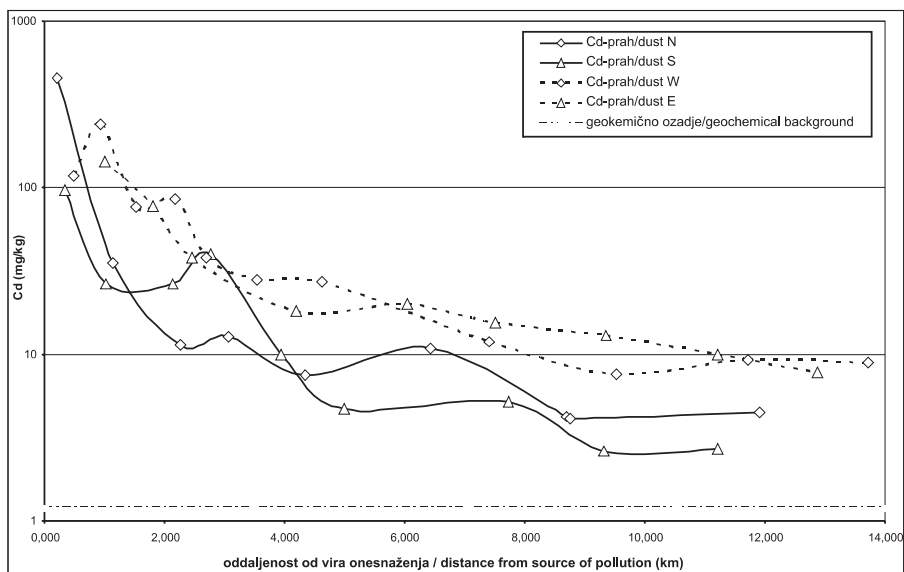
upadanja vsebnosti do geokemičnega ozadja. Najnižje vsebnosti kadmija smo zaznali v Laškem, torej v južni dolini. Izračunano vplivno območje znaša približno 30 km proti

severu in jugu ter približno 80 km proti vzhodu in zahodu. Ob upoštevanju vseh meritev skupaj znaša vplivno območje približno 50 km.



**Slika 3.** Porazdelitev Zn v podstrešnem prahu glede na oddaljenost.

**Figure 3.** Distribution of Zn in attic dust versus distance.

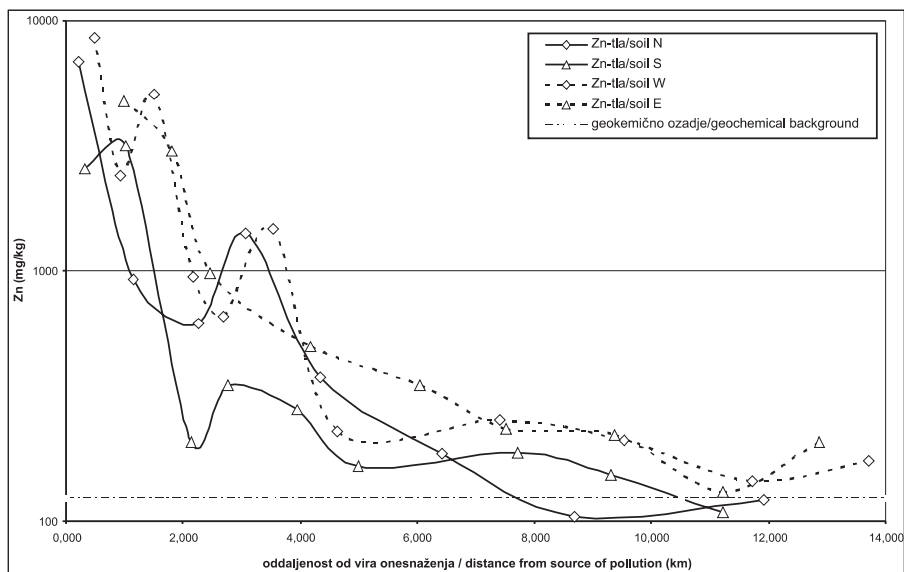


**Slika 4.** Porazdelitev Cd v podstrešnem prahu glede na oddaljenost.

**Figure 4.** Distribution of Cd in attic dust versus distance.

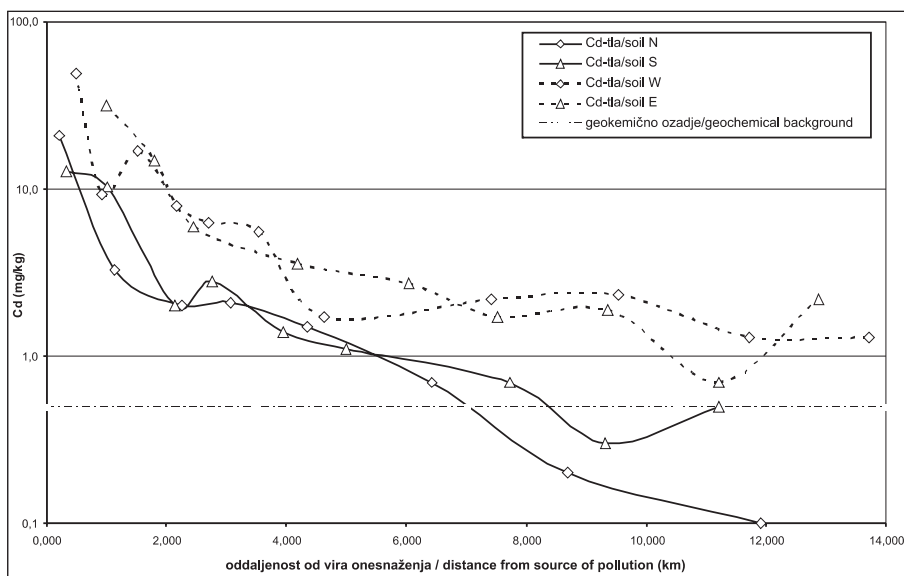
Sliki 5 in 6 prikazujeta upadanje vsebnosti cinka in kadmija v tleh. Ob tem lahko potegnemo analogijo s podstrešnim prahom. Najbolj obremenjeni sta vzhodna (najvišje

vrednosti linearnega koeficienta  $\alpha$ ) in zahodna dolina, najmanj pa severna in južna. Za razliko od podstrešnega prahu smo v tleh zaznali vsebnosti cinka in kadmija, ki so



**Slika 5.** Porazdelitev Zn v tleh (0-5 cm) glede na oddaljenost.

**Figure 5.** Distribution of Zn in topsoil versus distance.



**Slika 6.** Porazdelitev Cd v tleh (0-5 cm) glede na oddaljenost.

**Figure 6.** Distribution of Cd in topsoil versus distance.

upadle na raven geokemičnega naravnega ozadja na razdalji med 7 in 10 km v severni in južni dolini. Izračunano vplivno območje za cink v tleh znaša 10 km proti severu in jugu ter 14 km proti vzhodu in zahodu. Izračuni za vplivno območje pri kadmiju v tleh pa dajo nenavadne rezultate, kar lahko pripišemo visokim vsebnostim kadmija v tleh na velikih oddaljenostih od vira onesnaženja v vzhodni in zahodni dolini. Možno je, da je vrednost geokemičnega ozadja na tem območju podcenjena, ali pa je v okolici Celja prisoten regionalni onesnaževalec (TE Šoštanj ali TE Trbovlje npr.). Vseeno lahko ocenimo, da znaša vplivno območje v tleh med 10 in 20 km.

## DISKUSIJA

V raziskavi je ugotovljeno, da vsebnosti cinka in kadmija v prahu in tleh upadajo od vira onesnaženja po hipotetični potenčni krivulji. Iz korelacijskih koeficientov med resničnimi podatki in teoretičnimi krivuljami vidimo, da se podatki izredno dobro ujemajo s potenčnimi krivuljami (najmanjša vrednost  $D^2$  za posamezne smeri je 0,81), kar pomeni, da je s teoretično krivuljo pojasnjeno v najslabšem primeru 81 % celotne variance.

Vpliv lokalnih vetrov vidimo iz dejstva, da vsebnosti prvin najhitreje padajo v smeri severno od Cinkarne (največji koeficienti  $\beta$ ), najpočasneje pa proti vzhodu (najmanjši koeficienti  $\beta$ ). Na opazen vpliv vetrov lahko sklepamo tudi iz dejstva, da potenčne krivulje za posamezne smeri dosti bolje opišejo padanje vsebnosti kot pa potenčna krivulja za vse vzorce skupaj (tabela 1).

Geokemično ozadje za cink v tleh je v splošnem najbližje doseženo v smereh sever-jug od Cinkarne, in sicer v oddaljenosti približno 10 km. V smereh vzhod-zahod geokemično ozadje z raziskavo ni doseženo niti v oddaljenosti več kot 13 km, čeprav so se vrednosti zelo približale ozadju. To kaže bodisi na rahlo podcenjene naravne vrednosti na tem območju, bodisi na izredno velik vpliv Cinkarne ali pa na prisotnost regionalnega onesnaževalca. Skoraj identična situacija je pri kadmiju. Ob tem lahko ocenimo, da je vplivno območje topilnice za Cd in Zn od 7 do 20 km v tleh ter od 15 do 60 km v podstrešnem prahu. Višje vrednosti so v smereh vzhod-zahod, kar je tudi prevladujoča smer vetrov, ki so onesnaženje prenašali. Ne smemo pa tudi zanemariti vpliva 150-letnega železniškega transporta na relaciji Dunaj-Trst, ki poteka od vzhoda skozi Celje ter dalje proti jugu, poleg tega pa je blizu Žalca delovala tudi manjša topilnica, ki je vlivala zvonove. Vendar je njun vpliv glede na Cinkarno najbrž neznatn.

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## Kovinskih rudniki in okolje (nekateri slovenski primeri)

## Metal mines and environment (some Slovenian case studies)

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**Izvleček:** V prispevku obravnavamo vplive na okolje, ki so posledica pridobivanja kovinskih rud in njihove predelave. Na vplivnem območju opuščenih rudnikov in predelovalnih obratov rude so večkrat posledice rudarjenja zelo pereče. Vsebnosti težkih kovin v tleh, sedimentih in vodi so mnogokrat povišane, iz rudnikov lahko nenadzorovano odteka kisle rudniške in odcedne vode. Območje Slovenije je od nekdaj znano po številnih rudnikih in predelavi kovin. Od prazgodovinskih časov pa do danes poznamo v Sloveniji 49 rudnikov barvastih kovin, od katerih so bili štirje večji veliki (Idrija, Mežica-Topla, Litija in Žirovski vrh), in 25 predelovalnih obratov in topilnic, ki so delovale predvsem v okolici večjih rudnikov (Idrija, Žerjav). Ugotovili smo, da rudarstvo in predelava rude v Sloveniji predstavljata enega od glavnih načinov antropogenega vnosa težkih kovin v okolje.

**Abstract:** The impact of mining and processing of metal ores on the environment is described. In the surroundings of abandoned mining and smelting locations environmental problems such as elevated metal concentrations in soils/sediments, dispersion of toxic metals in soil and water and ecological damage are observed. Slovenia has long been known for its numerous mines and ore processing locations. From the prehistoric times to now, 49 mines and open pits were opened, four of them were large (Idrija, Mežica-Topla, Litija and Žirovski vrh). There were also 25 ore processing plants and smelters, which were operating mostly in the vicinity of larger mines (Idrija, Žerjav). It was established that, in Slovenia, mining and ore processing represents one of the major modes for anthropogenic input of heavy metals into the environment.

**Ključne besede:** vplivi rudarjenja, rudniški odpadki, težke kovine, Slovenija.

**Key words:** mining impacts, mining waste, heavy metals, Slovenia.

### Uvod

Rudarstvo je zelo stara človekova dejavnost. Prvi vidni sledovi pridobivanja soli in kresilnega kamna so iz časa okoli 5000 pr.n.š. Ob odkritju prvih kovin (bakra, svinca, železa) se je z rudarstvom zelo povežalo topilništvo. Že v starem Egiptu so poznali in

uporabljali železo in zlato, tudi stari Grki in Rimljani so rudarili. Takratne metode pridobivanja rude so zajemale tudi segrevanje in hitro ohlajevanje, kar je povzročilo razpokanost kamnine. Za razsvetljavo so uporabljali oljenke, vodo so iz jam odstranjevali z lesenimi vodnimi kolesi. Prazgodovinski človek je tudi na ozemlju Slovenije

že poznal in izkoriščal pohorska rudišča (TRŽAN, 1989). Za kopanje je uporabljal kamnita orodja (kladivo, klin, dleto, sekiro) pri pridobivanju rude si je pomagal tudi z ognjem, les je bil pri roki v pohorskih gozdovih. Rudo so ročno prebirali in jo talili v bližini rudišč. Dokaz za rudarjenje v prazgodovini na Pohorju je celoten spekter tam najdenega rudarskega kamnitega orodja, kakršnega poznajo tako bližnja kot oddaljena območja rudarjenja (TRŽAN, 1989). Domnevajo, da se je izkoriščanje sulfidnih rud na Pohorju začelo v začetku bronaste dobe. V pozni bronasti dobi je dosegla produkcija bakra v vzhodnih Alpah svoj višek, pridelovati so začeli tudi svinec in železo. S starejšo železno dobo, ko se je pojavila potreba po novi kovini, sta nastali ob pohorskih nahajališčih dve pomembnejši postojanki. Na lokaciji ene (Poštela) so našli vzhodnonoriški srebrnik, kar kaže na to, da je Pohorje predstavljalo ekonomsko zaledje vzhodnonoriškega območja.

Z razpadom rimskega cesarstva je rudarjenje zelo nazadovalo. V 16. stoletju je rudarska tehnika spet napredovala, predvsem pri odvodnjavanju in prezračevanju. Iz tega časa je delo *De re metallica* (AGRICOLA, 1556), ki podrobno opisuje tudi rudarjenje v idrijskem rudniku.

Da so nekatere kovine strupene, so vedeli že stari Rimljani, ki so opazili bolezenske znake pri sužnjih, ki so delali v rudnikih. Tudi iz obdobja srednjega veka imamo že veliko pisanih virov o zastrupitvah rudarjev delavcev v topilnicah.

## VPLIVI KOVINSKIH RUDNIKOV NA OKOLJE

Pridobivanje in predelava kovinskih rud imata več neželenih vplivov na okolje. Kovine so v rudnih telesih navadno prisotne v nizkih koncentracijah, zato nastaja ob njihovem pridobivanju velika količina odpadkov, ki lahko vsebujejo težke kovine in kemikalije iz predelovalnega postopka. Posledica topilniške in metalurške dejavnosti ob rudnikih so emisije plinov ( $\text{CO}_2$ ,  $\text{SO}_2$  in ostalih) in trdnih delcev, izcedne vode in rudniški odpadni material. Letno je posledica rudarjenja več milijard ton jalovine in ostalih rudniških odpadkov, ki so pod vplivom oksidacijskih pogojev na zemeljskem površju izpostavljeni preperevanju. To poteka v dveh zaporednih procesih, ki lahko negativno vplivata na okolje. Prvi je nastanek kislih izcednih vod, drugi proces pa je mobilizacija potencialno strupenih kovin na površje kot posledica preperevanja (SIEGEL, 2002).

Dejavnosti, ki so povezane z rudarjenjem lahko razdelimo v šest zaporednih procesov:

- **Iskanje in raziskovanje** nahajališč koristnih rudnin in rudninskih snovi, ki zajema razne geološke, geokemične in geofizikalne metode. Sledijo sledilna dela, ki omogočajo presojo o zalogah in vrednostih nahajališča.
- **Odpiranje nahajališča** z vrtinami, površinskim kopom ali s podzemeljskimi rudarskimi deli ter izdelava potrebne infrastrukture
- **Pridobivanje rude** (odkop materiala, drobljenje ter mletje)
- **Bogatenje mineralne surovine**, da bi ločili del nekoristne izkopenine - jalovine ali posamezne minerale različnih kovin

- **Metalurški procesi**, s katerimi pridobimo različne kovine
- **Sanacija rudarskih del**, ko poidejo zaloge rude

Pri vseh naštetih fazah rudarjenja prihaja do neželenih vplivov na okolje. Te lahko delimo na **vplive na prostor, onesnaževanje in vplive na zdravje delavcev** (HOSKIN ET AL., 2000).

Najpomembnejši prostorski vplivi so:

- Uničenje naravnih habitatov na območjih rudarjenja in odlagališč rudniških odpadkov ter kot posledica zračnih emisij in izpustov odpadnih voda
- Spremembe v rečnem režimu kot posledica nasipanja jalovine v rečne tokove
- Degradacija površja zaradi neustrezne sanacije rudarskega območja
- Geomehanska nestabilnost površja in deponij rudarskih odpadkov
- Opuščeni rudarski obrati in oprema

Vplivi na onesnaževanje so:

- Odvajanje odpadnih voda in (onesnaženih) sedimentov v okolje
- Onesnaževanje tal
- Izluževanje onesnažil iz rudarskih in metalurških odpadnih deponij ter onesnaženih tal
- Zračne emisije iz predelovalnih obratov in prezračevalnih jaškov
- Emisije prašnih delcev

Pri rudarjenju je še posebej pereče ravnanje z jalovino. Pri pridobivanju mineralnih surovin, še posebno kovin, nastajajo velike količine jalovine, ki vsebujejo težke kovine in kemikalije iz predelovalnega postopka in zato lahko negativno vplivajo na okolje.

Velike ekološke nesreče, ki so se zgodile v svetu v zadnjih 10-ih letih in še posebno dve, ki sta se pripetili v Evropi (Aznacollar, Španija, leta 1998 in Baia Mare, Romunija, leta 2000), so opozorile svet na veliko nevarnost ekoloških nesreč zaradi posledic rudarjenja.

#### **EVROPSKA DIREKTIVA O RAVNANJU Z ODPADKI, KI NASTAJAJO V RUDARSTVU**

Da bi v bodoče varno rudarili in imeli nadzor tudi nad opuščenimi rudarskimi jalovišči, sta Evropski parlament in Svet Evropske unije pripravila osnutek direktive o ravnanju z odpadki, ki nastajajo v rudarstvu (<http://europa.eu.int/comm/environment/waste/mining/index.htm>). Direktiva določa minimalne zahteve, da se v največji možni meri prepreči ali zmanjša škodljive vplive na okolje ali zdravje ljudi, ki jih povzroča ravnanje z odpadki iz rudarskih dejavnosti. O omenjeni direktivi je možno več prebrati v prispevku KORTNIKA IN SOD. (2005).

Predlog evropske direktive o odpadkih rudarske industrije obravnava odpadke, ki nastanejo pri izkoriščanju mineralnih surovin, tako pri njihovem pridobivanju, predelavi in skladiščenju. Direktiva med drugim predvideva, da upravljavci rudarskih dejavnosti pripravijo ustrezne načrte ravnanja z odpadki za obdelavo, predelavo in odlaganje odpadkov. Odpadke, ki nastajajo pri rudarskih dejavnostih, bo potrebno razvrščati glede na njihovo sestavo iz vidika možnih vplivov na okolje. Tistim, ki vsebujejo velike količine nevarnih snovi (težke kovine, radioaktivne snovi, itd.), pa

je potrebno posvetiti posebno pozornost. Še posebej to velja za jalovino nastalo pri fizikalno-kemijskih procesih bogatenja kovinskih mineralnih surovin, ki se hrani na odprtih deponijah ali v bazenih, katerih poškodbe ali porušitve lahko predstavljajo veliko nevarnost za okolje.

Ker v Sloveniji ni več aktivnih kovinskih rudnikov, je za nas še posebno zanimiv tisti člen bodoče direktive, ki določa, da bodo morale države članice zagotoviti pripravo in redno posodabljanje inventarja zaprtih in opuščenih objektov z rudarskimi odpadki, ki so nameščeni na njihovem ozemlju in povzročajo resne negativne vplive na okolje ali utegnejo srednjeročno ali kratkoročno postati resna grožnja za zdravje ljudi ali okolje. Inventar bo moral vsebovati osnovne podatke o površini in prostornini odloženih rudarskih odpadkov, fizikalno-kemijsko karakterizacijo odloženih snovi in oceno tveganosti. Takšen inventar, ki bo moral biti dosegljiv javnosti, bo potrebno pripraviti v štirih letih od sprejetja direktive. Direktiva predvideva tudi izmenjavo znanstvenih in tehničnih informacij o načinu izvajanja tega inventarja in opredelitev potrebnih raziskav na njihovem območju ter o razvoju metodologij morebitnih potrebnih sanacij zaprtih jalovišč (<http://europa.eu.int/comm/environment/waste/mining/index.htm>).

## KOVINSKI RUDNIKI V SLOVENIJI

Slovenija je območje zgodovinske rudarske in metalurške dejavnosti, ki sta trajali več stoletij. Rudo so začeli v večjem obsegu topiti že v srednjem veku. Največ je bilo železarstva, čeprav so rudo zbirali na površini ali kopali v manjših rudnikih.

Izkoriščali so tudi velika kovinska rudišča, kot so Idrija, Mežica in Litija. V sredini 19. stoletja sta rudarstvo in topilništvo v Sloveniji doživela razcvet. Poleg že prej omenjenih velikih rudnikov je delovalo tudi veliko manjših. Razen železa so začeli v večjih količinah pridobivati barvne kovine - predvsem svinec, cink, živo srebro, baker in antimon. Na prehodu v 20. stoletje so se obdržali le največji rudniki (ČEŠMIGA, 1959; BUDKOVIČ ET AL., 2003). Ti so večinoma z manjšimi prekinitvami delovali do začetka osemdesetih let prejšnjega stoletja, ko je bila sprejeta odločitev o postopnem zapiranju vseh kovinskih rudnikov in večine premogovnikov v Sloveniji. Sprejeti so bili programi zapiralnih del za vsak rudnik (BAJŽELJ, 2001). Tako so v preteklem desetletju vsi kovinski rudniki v Sloveniji prenehali s pridobivanjem kovin, zapiralna dela v nekaterih rudnikih pa še potekajo. Glede na naravo predelovalnih postopkov so za njimi ostale številne anomalije težkih kovin, katerih razsežnosti raziskujemo. V preteklih letih smo na podlagi raznih virov locirali rudarske in topilniške obrate, ugotovili obdobje njihovega delovanja in ocenili količine pridobljenih kovin (BUDKOVIČ ET AL., 2003). Poleg tega smo naredili nekaj raziskav o vsebnostih težkih kovin v tleh in sedimentih v okolici nekaterih največjih kovinskih rudnikov, katerih povzetek bo predstavljen v nadaljevanju. Na nekaterih drugih lokacijah pa so raziskave še v teku.

## IDRIJSKO OZEMLJE

Petstoletna proizvodnja živega srebra v Idriji se odraža v povečanih vsebnostih živega srebra v okolju. V celotni zgodovini rudnika

se je okoli 37.500 t živega srebra med procesom pridobivanja izgubilo v okolju (DIZDAREVIĆ, 2001).

V času delovanja topilnice so bile najpomembnejši dejavnik širjenja živega srebra v okolje atmosferske emisije, ki so povzročile povišane vsebnosti živega srebra v tleh na širšem območju Idrije. Na podlagi podatkov raziskave porazdelitve živega srebra v tleh (GOSAR & ŠAJN, 2001; 2003), smo določili ozemlja, kjer vsebnosti živega srebra presegajo zakonsko določene normative (Uradni list, 1996, tabela 1) (slika 1). Z odvzemom 118 vzorcev tal smo zajeli 160 km<sup>2</sup> ozemlja Idrije in njene okolice ter ugotovili, da na ozemlju, velikem 112 km<sup>2</sup>, vsebnosti težkih kovin v tleh presegajo mejne oz. opozorilne vrednosti za tla (Uradni list, 1996). 21 km<sup>2</sup> ozemlja je kritično onesnaženega (ŠAJN & GOSAR, 2004).

Za obremenitev okolja z živim srebrom na idrijskem so pomembni tudi odvali siromašne rude in predvsem odvali žgalniških ostankov, ki vsebujejo še precej živega srebra. Osnovni vzrok za veliko razširjenost in zapleteno prostorsko razporeditev žgalniških ostankov v Idriji in njeni okolici je v načinu žganja rude v preteklosti in uporabi žgalniških ostankov v gradbene namene v povojnem obdobju (ČAR, 1998). Do srede 17. stoletja so žgali rudo v glinastih posodah na bližnjih gričih Pront, Pringl, pa tudi na bolj oddaljenih krajih v Čekovniku in Kanomlji, o čemer pričajo številni ostanki razbite lončevine. Več lokacij starih žgalnic je našel I. Mlakar pri geološkem kartiranju idrijske okolice, nekaj pa so jih našli tudi kasneje (ČAR, 1998). Prva trajneje locirana žgalnica v mestu je bila na Lenštat. Leta 1652 so začeli graditi žgalnico na Prejnuti, ki je delovala vse do 19. stoletja.

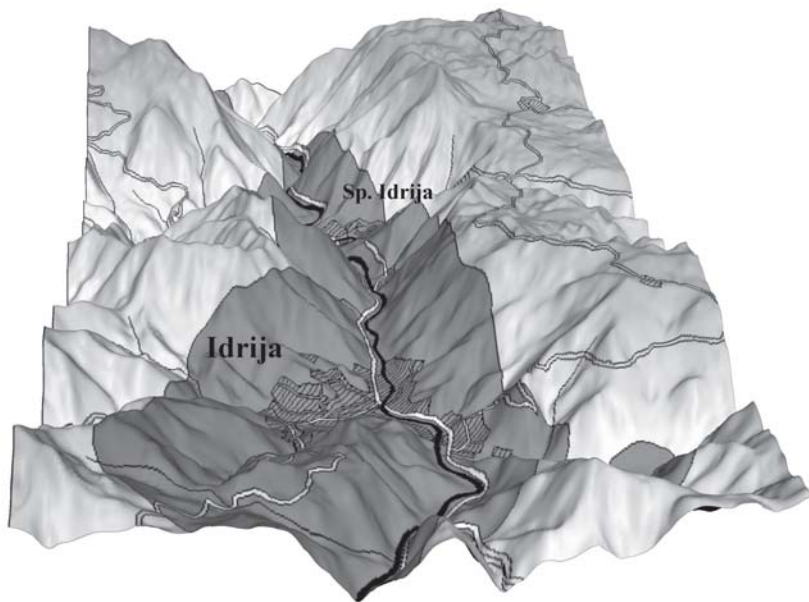
**Tabela 1.** Mejne, opozorilne in kritične vrednosti težkih kovin v tleh (Ur. list RS 68/96).

**Table 1.** Limit, warning and critical emission values of the contents of elements in soils (Ur. list RS 68/96).

| kovina<br>metal | mejna<br>vrednost<br>limit<br>value<br>(mg/kg) | opozorilna<br>vrednost<br>warning<br>value<br>(mg/kg) | kritična<br>vrednost<br>critical<br>value<br>(mg/kg) |
|-----------------|------------------------------------------------|-------------------------------------------------------|------------------------------------------------------|
| As              | 20                                             | 30                                                    | 55                                                   |
| Cd              | 1                                              | 2                                                     | 12                                                   |
| Co              | 20                                             | 50                                                    | 240                                                  |
| Cr              | 100                                            | 150                                                   | 380                                                  |
| Cu              | 60                                             | 100                                                   | 300                                                  |
| Hg              | 0.8                                            | 2                                                     | 10                                                   |
| Mo              | 10                                             | 40                                                    | 200                                                  |
| Ni              | 50                                             | 70                                                    | 210                                                  |
| Pb              | 85                                             | 100                                                   | 530                                                  |
| Zn              | 200                                            | 300                                                   | 720                                                  |

Po letu 1868 so postopoma zgradili novo žgalnico na Brusovšu, na Prejnuti pa so žganje opustili. Od takrat pa vse do leta 1977 so večino žgalniških ostankov neposredno vsipavali v Idrijco, ki je material ob visokih vodah odnašala v Sočo in ta naprej v Jadransko morje. Tako so v spodnjem toku Idrijce nastali obsežni rečni nanosi z visokimi vsebnostmi živega srebra (GOSAR ET AL., 1997; BIESTER ET AL., 2000), ki so in bodo vir z živim srebrom obremenjenega sedimenta tudi v prihodnosti. Zato vsebnosti živega srebra v aktivnih rečnih sedimentih Idrijce in Soče v zadnjih nekaj letih ne vpadajo. Določali smo jih julija leta 1991, 1995 in

2001 (GOSAR, 2003). V zgornjem toku Idrijce vsebuje sediment okoli 2 mg/kg živega srebra. V območju med Idrijo in Spodnjo Idrijo koncentracije zelo nihajo in so ekstremno visoke (od 171 do 4.121, povprečno 735 mg/kg). Od Spodnje Idrije nizvodno vsebuje sediment nekoliko manj živega srebra (od 3,2 do 878, povprečno 218 mg/kg). V soških sedimenti vsebnosti živega srebra nekoliko manj nihajo in so zelo razredčene (od 18 do 183, povprečno 67 mg/kg). Še vedno pa so to visoke vsebnosti. Tako Soča letno prinese velike količine živega srebra v Tržaški zaliv, po oceni ŠIRCE IN SOD. (1999) kar okoli 1.500 kg na leto.



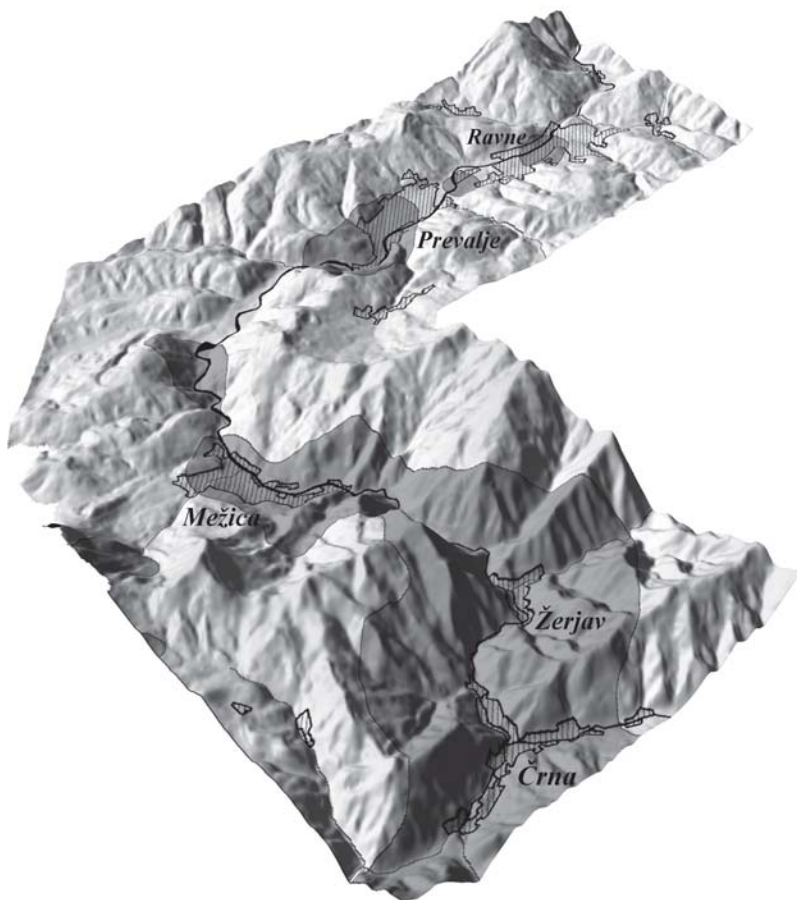
**Slika 1.** Območje kritično onesnaženih tal na idrijskem ozemlju s težkimi kovinami, pretežno s živim srebrom (Ur. list RS 68/96).

**Figure 1.** Spatial distribution of critically polluted soil in Idrija area with heavy elements, mainly with mercury (Ur. list RS 68/96).

## MEŽIŠKO OZEMLJE

Prvi pisni viri o izkoriščanju svinčeve rude na območju Mežice so iz leta 1665. V naslednjih stoletjih so rudarili v predgorju in na pobočjih Pece. Rudnik se je začel močno razvijati v 20. stoletju in še posebno po drugi svetovni vojni. V celotnem obdobju rudarjenja so pridobili okoli 19 milijonov ton svinčeve in cinkove rude. V drugi polovici 20. stoletja so pridobivali tudi majhne količine molibdena.

V Mežiški dolini smo preučevali porazdelitev vsebnosti težkih kovin v tleh, ki so posledica 300 letnega rudarjenja in predelave rude. V letu 2000 smo na območju 101 km<sup>2</sup> ozemlja, ki se vleče od Črne pa do Raven na Koroškem in zajema skoraj celotno dolino reke Meže v pasu širokem 6 km, odvzeli 115 vzorcev tal (ŠAJN, 2002). Na raziskanem ozemlju živi okrog 23.000 prebivalcev, kar predstavlja skoraj 90% celotnega prebivalstva štirih koroških občin, ki jih je raziskava zajela.



**Slika 2.** Območje kritično onesnaženih tal v dolini reke Meže s težkimi kovinami, pretežno s svincem (Ur. list RS 68/96).

**Figure 2.** Spatial distribution of critically polluted soil in Meža valley with heavy elements, mainly with lead (Ur. list RS 68/96).

Ugotovili smo, da je večina raziskanega ozemlja obremenjena s težkimi kovinami. Na 74 km<sup>2</sup> površine vsebnosti težkih kovin presežejo zakonsko določeno mejno oz. opozorilno vrednost (Uradni list, 1996). Kritično je onesnaženih 24,4 km<sup>2</sup> ozemlja (ŠAJN & GOSAR, 2004). To zajema celoten zgornji del Mežiške doline, predvsem okolico Črne na Koroškem in Žerjav. Pas kritično onesnaženih tal se nadalje s prekinitvami vleče vzdolž reke Meže vse do Raven na Koroškem (slika 2). Na kritično onesnaženem območju Mežiške doline izstopajo zlasti visoke vsebnosti svinca (Pb) in kadmija (Cd), povišane pa so tudi vsebnosti cinka, molibdena in arzena. Povprečna vsebnost Pb znaša 878 mg/kg (216 - 27.122 mg/kg) in preseže slovensko povprečje (ŠAJN, 2003) za več kot 20-krat. Povprečje Cd je 6,2 mg/kg (1,4 - 71 mg/kg) ter preseže slovensko povprečje za skoraj 12-krat. Glavni vzrok onesnaženosti tal sta

rudarjenje na območju Mežice in predelava svinčeve rude na Poleni in kasneje v Žerjavu, ki je potekala skoraj 300 let. Ne smemo pa zanemariti vpliva železarske industrije, ki se je prvotno razvila na območju Prevalj in kasneje na Ravnah na Koroškem. Vplivi prometa in drobnih kurišč so na območju Mežiške doline drugotnega pomena.

## ZAKLJUČEK

Lahko zaključimo, da predstavljajo posledice rudarjenja veliko obremenitev okolja. Na območju Slovenije so dosedanje študije pokazale, da je rudarjenje in z njim povezana predelava rude pustila velike posledice predvsem na območju Idrije in Mežice. Problematiki, vezani na tovrstne vplive, bomo v prihodnosti posvetili posebno pozornost.

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## Litofaciesna in konodontna conacija spodnjetriasnih plasti severozahodnega dela Zunanjih Dinaridov (Gorski Kotar, Hrvaška)

## Lithofacies and Conodont Zonation of Lower Triassic in Northwestern External Dinarides (Gorski Kotar, Croatia)

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**Izvleček:** Raziskani spodnjetriasni sedimentni kompleks Gorskega Kotarja predstavlja del Zunanjih Dinaridov. Raziskano je pet profilov, v katerih je bilo mogoče razlikovati več litofaciesov. Prevladujoče karbonatne litofaciese, ki karakterizirajo začetek spodnjetriasne sedimentacije, zaradi vse večjega vpliva terigenega materiala v mlajših delih triasa postopno zamenjajo pretežno klastični sedimenti. Različni faciesi so interpretirani kot sedimenti ooidnih sipin omejenega robnega šelfa, ki se vsled transgresije transformira v prostrano epikontinentalno morje. Natančni podatki kronostratigrafskega položaja raziskanih sedimentov znotraj spodnjetriasnega sedimentnega kompleksa doslej niso bili znani. Zato so bile izvedene obširne dodatne paleontološke raziskave s ciljem definiranja konodontnih con, s katerimi bi lahko podrobneje opredelili starost faciesov raziskanih profilov. Ugotovljene so bile cone *parvus-isarcicella* in *obliqua* ter podcona *Platyvillosus*. Konodontna conacija in litofaciesna definicija prispevata k boljšemu definiranju širšega spodnjetriasnega sedimentacijskega prostora in omogočata korelacijo z drugimi deli zahodne Tetide.

**Abstract:** The investigated area of the Gorski Kotar region (Croatia) is located in the External Dinarides. In the Lower Triassic sedimentary complex several facies were differentiated and interpreted as deposits of a restricted ooid rimmed shelf that transforms to a wide epicontinental sea due to continuous transgression. Predominantly carbonate sedimentation that characterized the beginning of deposition had changed and the increased terrigenous influx was noticed in the later deposited sediments. Five sections have been sedimentologically and palaeontologically investigated. The paper aims to present the chronostratigraphic position of the investigated sections based on conodont fauna. The biostratigraphical data allow recognition of the *parvus-isarcicella* zones, *obliqua* Zone and *Platyvillosus* Subzone. The conodont zonation and lithofacial definition contribute to the definition of the Lower Triassic depositional realm of the External Dinarides and prove the correlative elements for comparison with some other parts of the Western Tethys.

**Ključne besede:** spodnji trias, plitvovodni morski litofacies, konodonti, Zunanji Dinaridi, Hrvaška.

**Key words:** Lower Triassic, Shallow marine lithofacies, Conodonts, External Dinarides, Croatia.

## Uvod

Spodnjetriasne plasti Gorskega Kotarja v severozahodnem delu Zunanjih Dinaridov (Hrvaška) so bile dolgo časa predmet različnih nasprotujočih razlag. Na Osnovni geološki karti SFRJ 1:100.000, list Delnice niso izdvojene, temveč so uvrščene v podoben litološki kompleks zgornjetriasnih sedimentov (SAVIĆ & DOZET, 1984, 1985). ŠČAVNIČAR IN ŠUŠNJARA (1966, 1967), ĐURĐANOVIĆ (1967) in BABIĆ (1968) so poleg litoloških značilnosti pri izdvajanju in definiranju spodnjetriasnih plasti upoštevali tudi najdbe foraminifere *Meandrospira iulia* in značilne makrofavne v osrednjem delu Gorskega Kotarja. BABIĆ (1968) iz plitvomorskih sedimentov vzhodnega dela Gorskega Kotarja navaja vrste *Pseudomonotis (Claraia) cf. orbicularis* (Richtofen), *Myacites (Anodontophora) fassaensis* (Wissmann), *Myacites (Anodontophora) cf. canalensis* (Catullo), *Pseudomonotis (Claraia) cf. inaequicostata* (Benecke). Natančnejše litološke raziskave (ŠČAVNIČAR, 1973) so dale dodatne osnove za razlikovanje spodnje- in zgornjetriasnih plasti, ki temelje na bistvenih razlikah v sestavi težke mineralne frakcije (prisotnost ali odsotnost filosilikatov). Najdbe mikro- in makrofosilov so bili doslej edini kronostratigrafski podatki, na osnovi katerih pa ni bilo mogoče natančneje razčleniti plasti spodnjega triasa. Čepprav sta PALINKAŠ IN SREMAC (1987) pisala o kontinuirani sedimentaciji iz perma v spodnji trias, do danes P-T meja ni palontološko dokazana. Na področju Gorskega Kotarja je prav tako težko privzeti razčlenitev na starejše "seiske" in mlajše "campilske" plasti kot je mogoče ponekod v drugih delih Zunanjih Dinaridov, n.pr. na

območju Knina in Muća v Dalmaciji (ŠČAVNIČAR IN ŠUŠNJARA, 1983; ALJINOVIĆ, 1995; JELASKA ET AL., 2003), zato je raziskavam spodnjetriasnega kompleksa v Gorskem Kotarju definitivno manjkala kronostratigrafska komponenta.

Spodnjetriasni konodonti Hrvaške so bili doslej poznani le iz dveh profilov Dalmacije. V profilu Muć, ki je bil predlagan za tipičen zgornjeskitijski profil v Evropi, so bile opravljene številne geološke raziskave (HERAK ET AL., 1983, ŠČAVNIČAR IN ŠUŠNJARA, 1983; ŠČAVNIČAR ET AL., 1983; JELASKA ET AL., 2003). Litostratigrafski profil Muća so HERAK ET AL., (1983) v grobem razdelili v več neformalnih enot (od spodaj navzgor): bazalni karbonatni kompleks ter člene A, B in C. Apneno-laporni kompleks člena B vsebuje pogoste fosile, med drugimi tudi konodont *Ellisonia triassica* Müller, *Hadrodontina anceps* Staesche, *Neospathodus triangularis* (Bender) in *Pachycladina tricuspidata* Staesche. Na osnovi fosilne vsebine so avtorji ta člen primerjali s členom Val Badia v Dolomitih, vendar dodajajo, da ima verjetno ta enota na Muću (člen B) večji stratigrafski razpon. Dolomitni kompleks člena C je na osnovi litostratigrafskih značilnosti anizijske starosti. Tudi vzhodnejše od Muća v profilu ob cesti na Zelovo (planina Svilaja) izdanja velik del spodnjetriasnega zaporedja, vendar sedimenti P-T intervala niso razkriti (JELASKA ET AL., 2003). Iz najnižjega oolitnega dela profila je bila izdvojena konodontna združba, ki pripada coni *obliqua*. V njej prevladuje element *Pachycladina obliqua* Staesche v združbi z redkejšimi predstavniki *Hadrodontina* sp. (tip *biserialis*) in *Parachirognathus ethingtoni* Clark.

Novejše sedimentološke raziskave v Gorskem Kotarju (ALJINOVIĆ, 1997; ALJINOVIĆ & TIŠLJAR, 2000) so dale rezultate za detajlno interpretacijo litofaciesov, medtem ko podatki o starosti plasti manjkajo, zato je bila korelacija litofaciesov različnih lokalitet negotova, prav tako pa tudi definiranje sedimentacijskega prostora. Sledile so kompleksne raziskave, katerih cilj je kronostratigrafsko definiranje izdvojenih litofaciesov na osnovi konodontnih analiz. Ti ponujajo natančne kronostratigrafske podatke o sedimentih, v katerih drugih fosilov ni ali pa njihova slaba ohranjenost ne omogoča natančne določitve. Vsi raziskani spodnjetriasni profili so dopolnjeni z rezultati mikropaleontoloških analiz.

Konodontni elementi *Hindeodus parvus*, *Platylavosus costatus* in *Pl. hamadai* so tokrat prvič najdeni v Zunanjih Dinaridih. Sestav konodontnih združb, kakor tudi natančna litofacialna razčlenitev spodnjetriasnih plasti predstavljajo prispevek k definiranju sedimentacijskega prostora Zunanjih Dinaridov. Na osnovi litologije in konodontne conacije je omogočena primerjava z drugimi prostori Zunanjih Dinaridov, kakor tudi sosednjih prostorov zahodne Tetide (Notranji Dinaridi: Jadarska cona in Južne Alpe: Dolomiti, Karnijske Alpe).

## GEOLOŠKE RAZMERE

Hribovito območje Gorskega Kotarja se nahaja v severozahodnem delu Zunanjih Dinaridov. Raziskani profili ležijo na prostoru globokih prelomov (PRELOGOVIĆ ET AL., 2004), širše območje pa tektonsko označujejo narivne strukture (HERAK, 1980). Zaradi intenzivne tektonike so izdanki

spodnjetriasnih sedimentov redki in prostorsko omejeni (slika 1A), korelacija med posameznimi profili pa razmeroma težka in negotova. Ker so dobri kronostratigrafski markerji redki, interpretacija sedimentacijskega okolja sloni v glavnem le na interpretaciji pogojev nastanka prisotnih litofaciesov in na predpostavljene generalnem vertikalnem zaporedju plasti. Na osnovi podatkov dosedanjih raziskav in glavnih značilnosti sedimentov je spodnjetriasni sedimentacijski prostor v generalnem smislu interpretiran kot področje stabilnega kontinentalnega šelfa. Na permskih sedimentih transgresivno ležijo karbonatni in mešani karbonatno-siliciklastični sedimenti spodnjega triasa, ki so raziskani v petih lokalitetah.

### Raziskani profili: litofacies in konodontna favna

Spodnjetriasni sedimenti so raziskani v petih lokalitetah: H-Homer, ŠB-Školski Brijeg, ZC-Zelin Crnoluški, KP-Kramarčin Potok in D-Dobra (slika 1B,D,F). Opazne so litofacialne razlike osrednjega dela Gorskega Kotarja (okolica Lokev in Mrzle Vodice) in robnih delov območja - mejno območje s Slovenijo v okolici Čabra in Vrbovsko. Pričetek sedimentacije spodnjega triasa označuje dominantna karbonatna sedimentacija z močnejšim terigenim vplivom in povečano vsebnostjo siliciklastične komponente v mlajših nivojih. Litofacialna analiza je dopolnjena z raziskavo konodontov v vseh petih profilih.

Od skupno petindvajset preiskanih vzorcev jih je trinajst vsebovalo konodontne elemente, vendar je njihova vsebnost večinoma nizka ali zelo nizka. Izjemo



predstavljajo elementi konodontnega aparata *Pachycladina obliqua*, ki so večinoma nepopolno ohranjeni. Barvni indeks kondotov (CAI – Color Alteration Index) je višji od 5, kar kaže na temperature po sedimentaciji v območju od 300–480 °C in 490–720 °C (EPSTEIN ET AL., 1977; REJEBIAN ET AL., 1987).

### Profila Homer in Školski Brijeg

Dominantno karbonatni razvoj spodnjega triasa je najbolje viden v osrednjem delu Gorskega Kotarja v starih kopih barita, v lokalitetah Homer, zahodno od Lokev in v lokaliteti Školski Brijeg blizu Mrzle Vodice (slika 1B). V obeh lokalitetah na permskih

**Slika 1. A)** Lokacija profilov in geološka karta raziskanega območja (prirejeno po SAVIĆ IN DOZET, 1984 in BUKOVAC ET. AL., (1983)); **B)** Zaporedje sedimentov v profilu Školski Brijeg; **C)** sedimentacijski model spodnjetriasnih plasti profila Školski Brijeg: Facies ooidnih sipin (F-1) predstavlja bariero odprto proti morju oziroma z laguno v zaledju (F-2). **D)** Zaporedje sedimentov v profilu Zelin Crnoluški; **E)** Sedimentacijski model profila Zelin Crnoluški: Hitra transgresija je povzročila potopitev ooidne bariere in nastanek nove obale z vplivom odprtega morja, ki se manifestira v nizu značilnih nevihtnih sekvenc “shoreface-offshore” faciesa (F-3); CZ – položaj profila Zelin Crnoluški, ŠB – položaj profila Školski Brijeg; **F)** Zaporedje sedimentov v profilu Kramarčin Potok; **G)** Sedimentacijski model profila Kramarčin Potok: Napredovanje transgresije je povzročilo nastanek prostranega epikontinentalnega morja, ki se odraža v robnem severo-zahodnem in vzhodnem delu Gorskega Kotarja. Vpliv kopna v prostranih plitvinah je viden v povečani količini peščenega (siliciklastičnega) materiala. Sedimenti so interpretirani kot ooidno-peščeni facies F-4, facies zatišnega zaliva F-5 in facies intraformacijskih konglomeratov F-6. DO položaj profila Dobra, KP položaj profila Kramarčin Potok.

**Legenda:** 1-dolomitizirani ooidni grainstone, 2-dolomit, 3-peščeni dolomit in karbonatni peščenjak, 4-navzkrižna slojevitost, 5-horizontalna laminacija, 6-valovne sipinice, 7-tokovna laminacija, 8-intraklastični detritus, 9-muljni klasti, 10-žlebaste erozijske teksture, 11-bioturbacija, 12-kopasta navzkrižna laminacija (“hummocky-cross lamination”), 13-vzorčevani interval z oznako vzorcev, 14-baritne žile, 15-sekvence z zmanjševanjem zrn, 16-predpostavljene sekvence z zmanjševanjem zrn, 17-delno pokrit interval, 18-ooidni grainstone, 19-dolomit, 20-peščenjak, 21-laminiran dolomikrit in siltit, 22-rdeč siltit in glinovce, 23-intraformacijski konglomerat, 24- nepravilni vložki glinovca. Velikost zrn: a-glina, b-silt, c-zelo drobnorznat pesek, d-drobnorznat pesek, e-srednjeznat pesek, f-debeloznat pesek, g-psefit.

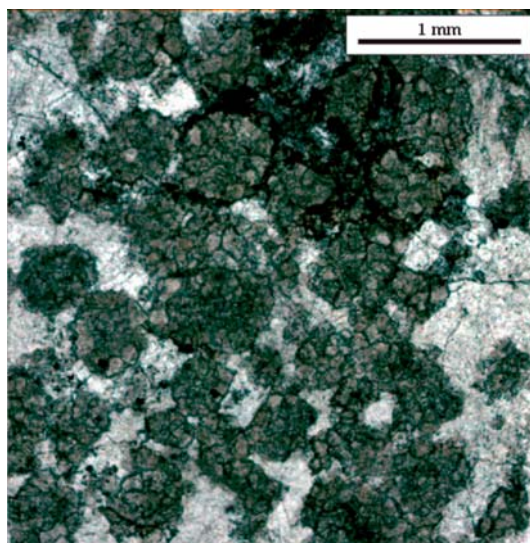
**Figure 1. A)** Location of sections and geologic map of the investigated area (modified after SAVIĆ & DOZET, 1984); **B)** Školski Brijeg section located in the central part of Gorski Kotar; **C)** The model of sedimentation proposed for Školski Brijeg section: Shallow shelf with the subtidal ooid bars as a barrier (F-1) and the land laying lagoon (F-2); **D)** Zelin Crnoluški section located between central and marginal part of the Gorski Kotar region; **E)** The model of sedimentation proposed for Zelin Crnoluški section: due to rapid transgression the bars drowned and a new coast formed opened to the influences of waves and storms which can be seen in vertical succeeded storm sequences – forming shoreface-offshore facies F-3; proposed position of the sections ŠB - Školski Brijeg and ZC - Zelin Crnoluški; **F)** Kramarčin Potok section located in the marginal part of Gorski Kotar; **G)** The model of sedimentation proposed for Kramarčin Potok section: due to the advanced transgression the wide epicontinental sea is established with the deposition in ooid-sandy shoals (F-4) and restricted muddy bays (F-5); proposed position of the sections KP – Kramarčin Potok and DO – Dobra;

**Legend:** 1-dolomitised oolitic grainstone, 2-dolomite, 3-sandy dolomites and calcarenaceous sandstones, 4-cross bedding, 5-horizontal lamination, 6-wave ripples, 7-current ripple cross-lamination, 8-intraclastic detritus, 9-mud clasts, 10-gutter cast structure, 11-bioturbation, 12-hummocky cross-lamination, 13-sampled interval, 14-barite veins, 15-fining upward sequences, 16-uncertain fining upward sequences, 17-partly covered interval, 18-ooid grainstone, 19-dolomite, 20-sandstone, 21-laminated dolomicrite and siltite, 22-red siltite and shale, 23-flat-pebble conglomerate, 24-shale partings. Grain size: a-shale, b-silt, c-very fine sand, d-fine sand, e-medium sand, f-coarse sand, g-pebbles.



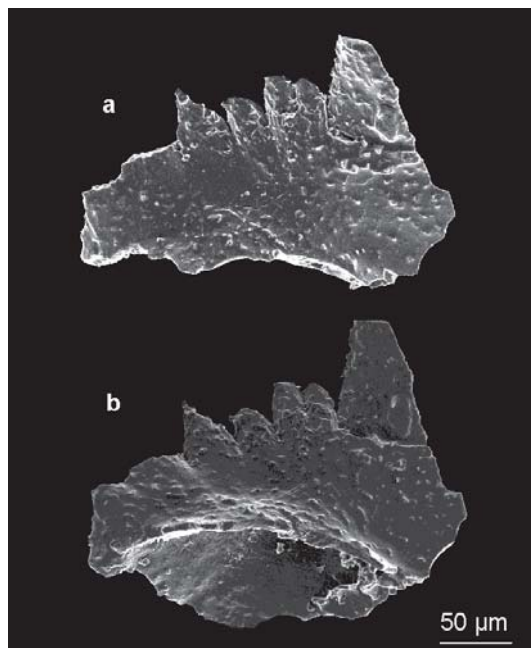
**Slika 2.** Zaporedje sedimentov v profilu Školski Brijeg; *Hindeodus parvus* v spodnjem delu profila (facies F-1) dokazuje najnižji del spodnjega triasa.

**Figure 2.** Školski Brijeg section where in facies F-1 *Hindeodus parvus* has been found (lower part of the section).



**Slika 3.** Mikrofotografija dolomitiziranega ooidnega grainstona z epigenetsko baritno mineralizacijo v medzrnskem prostoru.

**Figure 3.** Photomicrograph of dolomitised oolitic grainstone with relict of ooid detritus and epigenetic barite mineralization in intergranular space (white).



**Slika 4.** *Hindeodus parvus* (Kozur & Pjatakova, 1976), conid *parvus*–*isarcica*, Školski Brijeg, vzorec ŠB-1 (GeoZS 3636).

**Figure 4.** *Hindeodus parvus* (Kozur & Pjatakova, 1976), *parvus*–*isarcica* zones, Školski Brijeg, sample ŠB-1 (GeoZS 3636).

sedimentih transgresijsko ležijo ooidni apnenci, ki so izdvojeni kot **facies ooidnih sipin (F-1)** (slika 2). Prevladujoča značilnost tega faciesa je navzkrižna slojevitost apnenca in baritno-piritna mineralizacija (slika 3). Ooidne sipine faciesa F-1 so ustvarjale tipično morfologijo “bariernih sipin”, nameščenih med odprtim morjem in obalo (slika 1C). Za njimi, v smeri proti obali se je v lagunah sedimentiral karbonatni mulj, z občasnim dotokom terigenega siliciklastičnega detritusa. Ti sedimenti so izdvojeni kot **lagunski facies (F-2)**, ki ga označujejo tankoplastovit dolomikrit, peščen dolomikrit in karbonatni peščenjak.

Za konodontne raziskave smo analizirali pet vzorcev iz profila Homer, vendar sta le dva pozitivna (H-1, H-2). Najdeni konodontni

elementi so slabo ohranjeni in ne omogočajo določitve.

Iz profila Školski Brijeg smo preiskali štiri vzorce, od katerih dva (ŠB-1, ŠB-2) vsebujeta po en element rodu *Hindeodus*. V vzorcu ŠB-1 je določena vrsta *Hindeodus parvus* (KOZUR & PJATAKOVA) (slika 4).

### Profil Zelin Crnoluški

Razvoj spodnjetriasnih karbonatnih kamnin tega profila se razlikuje od razvojev v profilih Homer in Školski Brijeg. V krovlini faciesa ooidnih sipin F-1 ni lagunskega faciesa F-2, marveč so sedimenti “**shoreface-offshore**” **faciesa F-3** (slika 1D). Zanj so značilni mikro- do makrokristalasti dolomiti in peščeni dolomiti z redkimi vložki silita in

so organizirani v “fining- upward” sekvencah (slika 1D) z značilnostmi nevihtne sedimentacije. Sedimentacija “shoreface– offshore” faciesa je potekala v močno razburkani coni blizu obale odprtega šelfa (slika 1E).

Iz profila Zelin Crnoluški smo pregledali le vzorec iz njegovega spodnjega dela (ZC-1). Ta vsebuje maloštevilne konodontne elemente *Hadrodontina* sp., *Pachycladina obliqua* Staesche in *Parachirognathus* sp.

**Tabela 1.** Shematski prikaz primerjave spodnjetriasnih standardnih konodontnih con po Sweet et al., 1971 s konodontno conacijo Južnih Alp (po PERRI, 1991 in PERRI & FARABEGOLI, 2003).

**Table 1.** Schematic presentation of standard conodont biozones for the Lower Triassic (after Sweet et al., 1971) correlated with conodont zonation of the Southern Alps, Italy (after PERRI, 1991 AND PERRI & FARABEGOLI, 2003).

| SWEET et al. 1971  |                                | PERRI 1991<br>PERRI & FARABEGOLI<br>2003 |        |
|--------------------|--------------------------------|------------------------------------------|--------|
| SPATHIAN STAGE     | Timorensis                     | Triangularis                             |        |
|                    | Jubata                         |                                          |        |
|                    | Neosp. n. sp. G.               |                                          |        |
|                    | Platyvillosus                  |                                          |        |
| SMITHIAN STAGE     | Milleri                        | Obliqua                                  |        |
|                    | Conservativus                  |                                          |        |
|                    | Parachirognathus<br>Furnishius |                                          |        |
|                    | Pakistanensis                  | Anceps                                   |        |
| DIENERIAN STAGE    | Cristagalli                    | Aequabilis                               |        |
|                    | Dieneri                        |                                          |        |
|                    | Kummeli                        |                                          |        |
|                    | Carinata                       |                                          |        |
| GRIES -<br>BACHIAN |                                | Isarcica                                 | T      |
|                    |                                | Staeschei                                |        |
|                    |                                | Lobata                                   |        |
|                    |                                | Parvus                                   |        |
| PER -<br>MIAN      | Typicalis                      | Praeparvus                               | P      |
|                    |                                |                                          | U<br>L |

### Profil Kramarčin Potok in profil Dobra

V severozahodnem (Čabar) in vzhodnem delu Gorskega Kotarja (Vrbovsko) niso najdeni karbonatni faciesi F-1, F-2 in F-3, kar lahko razložimo s paleogeomorfološkimi razmerami tega področja, to je s postopnim širjenjem morskega sedimentacijskega prostora in napredovanjem transgresije. Bližina in vpliv kopna se izraža v povečanem donosu siliciklastičnega, pretežno peščenega materiala in v visoki vsebnosti rdečega železovega pigmenta. V vertikalnem zaporedju se izmenjujejo **ooidno-peščeni facies F-4** (dolomitizirani ooidni grainstone ali peščenjaki), **facies plitvin z muljastimi sedimenti (facies zatišnega zaliva) F-5** in **facies intraformacijskih konglomeratov F-6**. Menjavanje teh faciesov je značilno za "seiske" plasti.

### Profil Kramarčin potok

V profilu se izmenjujejo sedimenti faciesa F-4 in F-5, ki so organizirani v sekvencah s zmanjševanjem zrn (slika 1F). Od teh sekvenc vsaka prične z ooidnim apnencem in/ali rdečim peščenjakom (F-4) in konča z laminiranimi dolomiti in muljastimi sedimenti zatišnih zalivov (F-5) (slika 1F). Za sedimentacijski prostor sta značilna obilica terigenega materiala in njegovo mešanje z intrabazenskim (ooidnim) detritusom. Prisotnost rdečega železovega pigmenta kaže na dobro prezračeno plitvomorsko okolje (slika 1G).

Facies F-5 označuje menjavanje zelo tankih plasti in lamin dolomikrita in silta. Usedanje delcev različne zrnivosti kaže na različno energijo tokov ali nakazuje na obstoj permskih plimskih tokov.

Iz profila Kramarčin Potok smo mikropaleontološko analizirali skupno devet vzorcev. Določeni so naslednji elementi: *Pachycladina obliqua* Staesche, *Platyvillosus costatus* Staesche, *P. hamadai* Koike, ? *Parachirognathus* sp., *Hadrodontina* sp. (tip *biserialis*), ? *Ellisonia* sp. in *Foliella gardenae* (Staesche).

### Profil Dobra

Značilnosti profila Dobra je prisotnost plasti konglomerata s muljnimi klasti ki so izdvojeni kot facies intraformacijskih konglomeratov (F-6). Facies F-6 se nepravilno izmenjuje s faciesoma F-4 in F-5, podobno kot v profilu Kramarčin Potok. Pojavi nezaobljenih fragmentov (razlomljenih muljnih lamin ali plasti) in izsušitvenih razpok kažejo na razmeroma plitvo okolje ter na akumulacijo razlomljenih fragmentov in situ.

Vsi vzorci (skupno pet) za konodontne analize so bili vzeti iz faciesa F-4. Združbo sestavljajo odlomki konodontnih elementov *Hadrodontina* sp., ? *Ellisonia* sp. in *Pachycladina obliqua* Staesche.

### Komentar k spodnjetriasnim konodontom

Stratigrafsko pomembne spodnjetriasne vrste pripadajo skupini *Hindeodus-Isarcicella*. Prvi pojav (FAD-first appearance datum) vrste *Hindeodus parvus* je bil izbran za definiranje spodnje meje triasnega sistema, kar je potrdila tudi Mednarodna komisija za stratigrafijo in stratotip za permsko-triasno mejo odobrila profil D v Meishanu, Kitajska (YIN, 1993; YIN ET AL., 1996; 2001). *Hindeodus parvus* je lahko določljiva vrsta z veliko geografsko razširjenostjo in ima

veliko facialno toleranco in je hkrati prva globalno razširjena vrsta, ki se pojavi tik nad minimumom favnistične diverzitete, ki jo nakazuje minimum  $\delta^{13}\text{C}$  (KOZUR, 1996).

Različne spodnjetriasne konodontne biofaciese v odvisnosti od litofaciesa, so najprej prepoznali v Severni Ameriki (SOLIEN, 1979; CLARK & CARR, 1984; PAULL, 1982; PAULL & PAULL, 1994). Konodontne conacije spodnjega triasa so slonele na vrstah iz različnih biofaciesov. Šele v letu 1998 sta Orchard in Krystyn uvedla dvojne konodontne cone za najnižji del triasa Spitija (Himalaja), v kateri je vpeljana conacija na osnovi rodu *Neogondolella* in interkalibrirana z vzporedno conacijo na osnovi skupine *Hindeodus-Isarcicella*. Ločeni conaciji je omogočilo prepoznavanje dveh konodontnih biofaciesov: prevladujoči pelagični biofacies z *Neogondolella* in manj zastopan biofacies s skupino *Hindeodus-Isarcicella*. Vpliv faciesa na sestav P-T konodontnih združb so temeljito proučevali ORCHARD (1996), KOZUR (1996) in ORCHARD & KRISTYN (1998). Ugotovljena je različna pogostnost rodov *Hindeodus* in *Neogondolella*: gondolellide so bolj pogoste v globljih in /ali hladnejših morskih okoljih, medtem ko je *Hindeodus* uspeval bližje obali, v plitvejših in /ali toplejših območjih. KOZUR (1996) navaja izjemno visoko ekološko toleranco skupine *Hindeodus typicalis*, ki presega toleranco ostalih konodontov, saj se pojavljajo v številnih plitvovodnih sedimentih in so zato najbolj primerni za korelacijo.

Prvo popolnejšo konodontno conacijo za spodnji trias je uvedel SWEET (1970), ki je bila razdeljena na 9 konodontnih biocon. Na Simpoziju za konodontno biostratigrafijo so

predlagali razdelitev celotnega triasnega sistema v 22 biocon, od tega je bilo 13 biocon v spodnjem triasu in so slonele na podatkih iz Pakistana in zahodnega dela ZDA (SWEET ET AL. 1971). Zgornjo mejo vsake cone označuje prvi pojav vodilne konodontne vrste za naslednjo biocono.

Zaradi povečanega poznavanja biostratigrafije v različnih delih sveta in uvedbo številnih novih vrst ter hkratno dopolnjeno ali popravljeno stratigrafsko in geografsko pojavljanje starejših vrst je botrovalo bolj natančnim biostratigrafskim shemam. Pri primerjavah je potrebno upoštevati razlike v taksonomiji (npr.: *H. minutus* so številni avtorji vsaj deloma vključili v sinonimiko vrste *H. praeparvus*), kakor tudi na ostale razlike, na katere je opozoril že MATSUDA (1985), predvsem prvi pojav posamezne vrste in sestav združb v različnih območjih/provincah. Tabela 1 je shematski prikaz primerjave standardnih konodontnih biocon spodnjega triasa po SWEETU ET AL. (1971) s konodontno conacijo Južnih Alp (PERRI, 1991; PERRI & FARABEGOLI, 2003). Natančna razdelitev najnižjega dela spodnjega triasa Južnih Alp je mogoča zaradi srednje do hitre sedimentacije (medium – high sedimentation rate) P-T intervala (PERRI & FARABEGOLI, 2003).

## ZAKLJUČKI

Na prostoru Gorskega Kotarja smo raziskali pet profilov: Homer, Školski Brijeg, Zelin Crnoluški, Kramarčin Potok in Dobra. Spodnjetriasni sedimentni kompleks Gorskega Kotarja se razlikuje v lateralni in vertikalni porazdelitvi faciesa. V centralnem delu prevladuje sedimentacija stabilnega

robnege šelfa ("stable rimmed shelf") in zanj značilni plitvovodni karbonatni faciesi. Bazalni interval ooidnega apnenca z navzkrižno plastovitostjo in debelino ca 10 m (Homer, Školski Brijeg) je interpretiran kot ooidna sipina, medtem ko na njem ležijo predvsem tankoploščasti ali laminirani, sivi dolomikriti, peščeni dolomiti ali karbonatni peščenjaki, ki so verjetno bili odloženi v laguni, (slika 1C). Ooidni apnenec verjetno predstavlja bariero odprto proti morju oziroma v laguno v zaledju. Zaradi posledic plime in oseke so nastajale ooidne sipine. Ooidni grainstone je bil kasneje dolomitiziran, medtem ko lagunski facies odraža zgodnjediagenetske procese. V profilu Školski Brijeg je določena konodontna vrsta *Hindeodus parvus*. Ta vrsta je pomembna za določitev P-T intervala in njen prvi pojav (FAD – first appearance datum) dokazuje spodnjo mejo triasnega sistema (YIN ET AL., 2001).

Hitra transgresija je povzročila potopitev ooidne bariere in nastanek nove obale, ki jo predstavljajo dolomiti in peščeni dolomiti v tipičnem "shoreface-offshore" faciesu (Zelin Crnoluški) (slika 1E).

Nadaljnje napredovanje transgresije je povzročilo nastanek prostranega epikontinentalnega morja. To je razvidno v sedimentih profilov Kramarčin Potok in Dobra (zahodni in vzhodni del Gorskega Kotarja). Vpliv kopna v prostranih plitvinah je viden v povečani količini peščenega (siliciklastičnega) materiala z bistveno večjim deležem rdečega železovega pigmenta, ki kaže na dobro prezračeno okolje nastanka. Rdeči siliciklastični sedimenti teh dveh profilov odgovarjajo tipičnim "seiskim plastem".

Konodontna favna treh profilov, Zelin Crnoluški, Kramarčin Potok in Dobra, označuje prisotnost vrste *Pachycladina obliqua* v združbi z nekaterimi značilnimi spodnjetriasnimi rodovi (*Ellisonia*, *Hadrodontina*, ? *Parachirognathus* in *Platyvillosus*). *P. obliqua* je pomemben biostratigrafski element za lokalno konodontno conacijo, podobno kot drugod v zahodni Tetidi.

Konodontne združbe iz petih raziskanih lokalitet Gorskega Kotarja označuje prisotnost rodu *Hindeodus* v najstarejših plasteh, v mlajših plasteh pa se večinoma pojavlja združba *Pachycladina* - *Hadrodontina* ter ponekod tudi *Ellisonia*. Redki predstavniki rodov *Foliella* in *Platyvillosus* se pojavljajo v dveh nivojih. Za vse najdene konodontne rodove menimo, da kažejo na plitvovodno okolje, le *Hindeodus parvus* je ubikvitarna vrsta, saj je navzoča v plitvih in bazenskih okoljih.

Na osnovi konodontne združbe je bilo mogoče izdvojiti naslednje cone in podcono (od najstarejše k najmlajši):

- **coni *parvus-isarcica*.** Združbo predstavlja le rod *Hindeodus*. Določena vrsta *H. parvus* je ekološko zelo tolerantna, saj se pojavlja v plitvejših in globljih okoljih. *H. parvus* je stratigrafsko pomembna spodnjetriasna vrsta in je globalno prepoznaven marker permsko-triasne meje. Njegov stratigrafski razpon poleg cone *parvus* sega še v naslednjo cono *isarcica* (sensu KOZUR 1996, 2003);

- **cona *obliqua*.** To cono označuje prevladujoči element *Pachycladina obliqua* Staesche. Ponekod se ta pojavlja kot monospecifična favna (profil Dobra), drugod (Kramarčin Potok, Zelin Crnoluški) pa jo spremljajo še predstavniki rodov *Hadrodontina* in ? *Parachirognathus*, redkeje tudi *Ellisonia* in *Foliella*. Vsi omenjeni rodovi so značilni za plitvovodna okolja spodnjega triasa. *P. obliqua* je geografsko razširjena vrsta, njen razpon sega od smithija do spathija (PERRI & ANDRAGHETTI, 1987). V Severni Ameriki združbo *Pachycladina-Hadrodontina* primerjajo s cono 7 (cona *Parachirognathus-Furnishius*) sensu SWEET ET AL. (1971) in jo tako uvrščajo v smithijsko stopnjo (Solien, 1979). Ta vrsta ima velik biostratigrafski pomen v zahodni Tetidi in jo zato upoštevamo tudi pri konodontni conaciji Slovenije (KOLAR-JURKOVŠEK & JURKOVŠEK, 1996);
- **podcona *Platyvillosus*.** V profilu Kramarčin Potok smo ugotovili nivo s *Platyvillosus*. To je redko zastopan spodnjetriasni rod, ki je v združbi predstavljen z dvema vrstama: *P. costatus* (Staesche) in *P. hamadai* Koike. V biozonaciji SWEET IN SOD. (1971) je cona 10 (cona *Platyvillosus*) izdvojena v najnižjem delu spathija na osnovi pojava tega rodu. Vrsta *P. costatus* je bila prvič opisana iz campilskih plasti Južnih Alp (STAESCHE, 1964). Kasneje so bile opisane še nekatere maloštevilne vrste tega rodu. Najstarejši pojavi rodu iz dienerijskih plasti so zabeleženi samo v nekaterih lokalitetah Azije (GOEL, 1977; KOIKE, 1988), zato je povsem verjetno,

da je pojavljanje rodu zaradi ekoloških faktorjev geografsko in stratigrafsko omejeno.

Izdvojitev nivoja s *Platyvillosus* (podcona *Platyvillosus* znotraj cone *obliqua*) temelji tudi na podatkih o njegovem pojavljanju drugod v zahodni Tetidi in je poznana iz campilskih plasti Južnih Alp in zahodne Srbije. Vrsti *Foliella gardenae* in *Platyvillosus costatus*, se pojavljata v campilskih plasteh, vendar nikoli hkrati (STAESCHE, 1964) in glede na njuno različno vertikalno pojavljanje sta bili izdvojeni cona *costatus* v spodnjem delu, in cona *gardenae* v njenem zgornjem delu (BUDUROV & PANTIĆ, 1974).

## SUMMARY

### Lithofacies and Conodont Zonation of Lower Triassic in Northwestern External Dinarides (Gorski Kotar, Croatia)

The investigated area of the Lower Triassic sedimentary complex in the Gorski Kotar region – Croatia, is located in the External Dinarides between the Alps and the Velebit Mt. The Lower Triassic depositional environment is envisaged as shallow marine realm of a passive continental margin (JELASKA ET AL., 2003). Sedimentary complex differentiates in predominantly carbonate sedimentation that characterise the beginning of deposition with upward increasing trend of terrigenous influx. Five Lower Triassic sections (Homer, Školski Brijeg, Zelin Crnoluški, Kramarčin Potok and Dobra) have been investigated (ALJINOVIĆ, 1997) (Fig. 1A), but their chronostratigraphical position was uncertain due to lack of fossils or their inadequate preservation.

A facial assemblage investigated in central part of Gorski Kotar region (Homer, Školski Brijeg and Zelin Crnoluški sections) differs from those appeared in marginal parts (Kramarčin Potok and Dobra sections). In central part the shallow water carbonate facies predominate. Basal cca. 10 m thick cross-bedded interval of ooid grainstones (Homer and Školski Brijeg sections) was interpreted as dolomitised **ooid bar facies (F-1)** (Fig. 1B, Fig. 2) that possibly formed subaqueous oolitic barrier with the landward laying lagoon. The overlaying thin or medium-bedded grey dolomicrites, sandy dolomites and calcarenaceous sandstones were interpreted as **lagoonal facies (F-2)**. Storms and post-storm tidal reworked processes influenced the deposition of ooid bars. Ooid grainstones were late diagenetically dolomitised (Fig. 3), while the **lagoonal facies (F-2)** reflects the early diagenetic processes. The widening of the lagoon has been conceived through overall transgressive trend (Fig. 1C). The rapid transgression caused in-place drowning of the ooid bars and formation of a new seaward oriented coast that is represented by sediments organized in typical storm sequences of Crnoluški Zelin section and defined as **shoreface-offshore facies (F-3)** (Fig. 1D,E). Deposition occurred near fair weather wave base of unrestricted shelf. The intense influx of a dominantly red siliciclastic terrigenous material has been recorded in the Lower Triassic sediments of the marginal, north-western and eastern parts of Gorski Kotar region (Kramarčin Potok and Dobra sections). The thick-bedded ooid bar facies as well as overlaying lagoonal facies are missing in those sections. Vertical successions are characterised by the interbedded **ooid-sandy shoal facies (F-4)** (oolitic limestone/dolostone and sandstone

beds) and carbonate siliciclastic mudstone or red siltite of **restricted bay facies (F-5)** (Fig. 1F). Flat pebble conglomerates appear occasionally and are defined as **F-6**. Beds vary in thickness from few decimetres up to 1 m and are organised in fining upward sequences that represent shifting of a laterally existed ooid/sandy shoals and restricted muddy bays (Fig. 1F,G). The lithofacies present in Kramarčin Potok and Dobra sections resemble red clastic sediments i. e. Siusi Beds of the Southern Alps that make them compatible to the wide area of the External Dinarides. The different lateral facies distribution was interpreted as the result of transgression that transformed narrow rimmed shelf with ooid bars and lagoon facies to unrestricted shelf and finally to the wide epicontinental sea (Fig. 1C,E,G).

This interpretation has never been proved while the precise chronostratigraphic dating of the investigated sections were missing in previous investigations. Therefore the lithofacial investigations were supplemented by conodont studies at each of five localities. The oldest investigated strata are marked by the presence of *Hindeodus parvus* in the Školski Brijeg section (Fig. 4). The first appearance datum (FAD) of this taxon has been approved to define the base of the Triassic system (Yin et al., 2001). The biostratigraphical data obtained from the five studied sections in Gorski Kotar allow recognition of the *parvus-isarcicella* zones, *obliqua* Zone and *Platylavosus* Subzone (Table 1). The conodont zonation and lithofacial definition contribute to the definition of the Lower Triassic depositional realm of the External Dinarides and prove the correlative elements for comparison with some other parts of the Western Tethys.

## Zahvala

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# Numulitine iz Lokavca v Vipavski dolini

## Nummulitins from Lokavec in Vipava valley (Vipavska dolina, SW Slovenia)

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**Izvleček:** Opisane so numulitine iz flišnih olistostrom v Lokavcu pri Ajdovščini. Starost je srednji cuisij.

**Abstract:** Described are nummulitins from flysch olistostroms in Lokavec near Ajdovščina. The age is Middle Cuisian.

**Ključne besede:** numulitine, spodnji eocen, fliš, Slovenija.

**Key words:** nummulitins, Lower Eocene, flysch, Slovenia.

### UVOD

V flišnih plasteh Vipavske doline je veliko nahajališč numulitin. Marsikatero še ni podrobneje obdelano, mnoga pa brez dvoma še niso odkrita. Numulitine so predvsem v olistostromnih plasteh, čeprav tako bogatih njihovih nahajališč, kot so recimo v Istri (cf. HAGN ET AL., 1979; PAVLOVEC, 2003b), doslej v Vipavski dolini ne poznamo. Numulitine v olistostromah so na sekundarnem nahajališču in so bile zanešene v flišno morje iz karbonatnih platform. Na ta način lahko sklepamo na favno, ki je takrat živela v plitvejših delih morja (PAVLOVEC, 1988). V olistostromah so tudi olistoliti, ki izhajajo iz različno starih plasti od krede do paleogena, morda tudi jure.

Lokavec je vas severno od Ajdovščine v Vipavski dolini. Tam je v olistostromnih

plasteh iskal fosile neumorni zbiralec Stanislav Bačar iz Ajdovščine. V njegovi zbirki so tudi opisani primerki. Poleg numulitin so korale, mehkužci, morski ježki in alge. Zanimivo je, da je v Vipavski dolini in Brkinih v flišu precej numulitov z gostimi septami in ne posebno visokimi zavoji. To so med drugim *Nummulites ustjensis* De Zanche & Pavlovec, *N. vipavensis* De Zanche & Pavlovec, *N. brkiniensis* Khan & Pavlovec, iz Lokavca doslej še nedoločena vrsta *Nummulites* sp., številni primerki, označeni kot *N. aff. aquitanicus* sensu SCHAUB (1981), in najbrž še nekateri. Takšni numuliti so bili očitvidno na spodnjeeocenski karbonatni platformi dosti pogosti in morda kažejo celo na določeno specifično okolje. Ponovno se odpira vprašanje, zakaj najdemo nekatere numulitinske vrste dokaj pogosto v flišu, v apnencih pa mnogo redkeje ali sploh ne.

Numulitine pri Lokavcu so iz manjše olistostrome ali morda iz roba večjega podmorskega plazu. So dobro ohranjene. Nahajališče je bilo odkrito ob zidavi in bilo kasneje uničeno ali vsaj povsem spremenjeno, plasti pa so bile uničene med gradnjo. Na žalost nimamo nobenih podatkov o plasteh nad in pod sedimenti s preiskanimi numulitinami, tako da nahajališče pri Lokavcu nima drugega pomena, kot da je droben prispevek k poznavanju numulitin iz fliša pri nas. Numulitinske hišice niso vedno najbolj preparirane, tako da je pri nekaterih težko videti podrobno površinsko strukturo, kar ovira lažjo in zanesljivo determinacijo. Nabrani so samo primerki mikrosferičnih oblik. Najbrž je vzrok za to zbiralec negeolog, ki nabira le vidnejše večje primerke.

## NUMULITINE IZ VIPAVSKE DOLINE

Doslej je bilo opisanih nekaj nahajališč numulitin v Vipavski dolini. Prve numulitine iz tega prostora, poznane od novjših raziskav (PAVLOVEC, 1963), so srednjecuisijska podvrsta *Nummulites burdigalensis cantabricus* Schaub, najdena južno od Lozic in pri Vipavskem Križu.

Najbolj znano nahajališče je pri Ustjah nedaleč od Ajdovščine (DE ZANCHE ET AL., 1967). Ugotovljeni sta bili novi vrsti *Nummulites vipavensis* De Zanche & Pavlovec, *N. ustjensis* De Zanche & Pavlovec, nadalje *N. rotularius* Deshayes, *N. cf. inkermanensis* Schaub, *N. partschi* De la Harpe, *N. praelucasi* Douvillé, *N. ornatus* Schaub in *N. jacquoti* De la Harpe. Flišne plasti z numulitinami pri Ustjah so iz prehoda med spodnjim in srednjim cuisijem, kar je potrjeno tudi z nanoplanktonom.

Pri Dolnjem mlinu ob Vipavi južno od Ajdovščine so bile v olistolitu ugotovljene vrste (PAVLOVEC & BAČAR, 2004) *Nummulites ornatus* Schaub, *N. bombitus* Hottinger, *N. haymanensis* Schaub in *N. subdistans* De la Harpe. Kos v flišnih olistostromah je spodnjecuisijske starosti, medtem ko so flišne plasti mlajše.

## OPISI VRST

### *Assilina escheri* (HOTTINGER, 1977)

(tabla 1, sl. 1, 2)

1977. *Operculina escheri* n.sp. – Hottinger, 76-78, sl. 27 A-E, tab. 33, sl. 1, 2, tab. 34, 35,

Material: Najdena sta bila dva dobro ohranjena primerka z oznako LO 6.

Mikrosferična generacija. Primerka sta v drobnozrnatem peščenjaku, torej v olistolitu iz olistostrome. Hišica je tanka. Zavoji se hitro višajo. Septa so močno upognjena, velikokrat srpasto. Zlasti vrhnji del sept je odebeljen in na njih so nežne granule. Premera hišic iz Lokavca sta 12,6 in 16,5 mm. HOTTINGER (1977) navaja med besedilom velikost mikrosferične generacije 25 mm, na slikah pa so tudi manjši primerki z velikostmi med 10 in 20 mm. Vrsto *escheri* so prvotno uvrščali v rod *Operculina*, danes je to *Assilina escheri* (SERRA-KIEL ET AL., 1998)

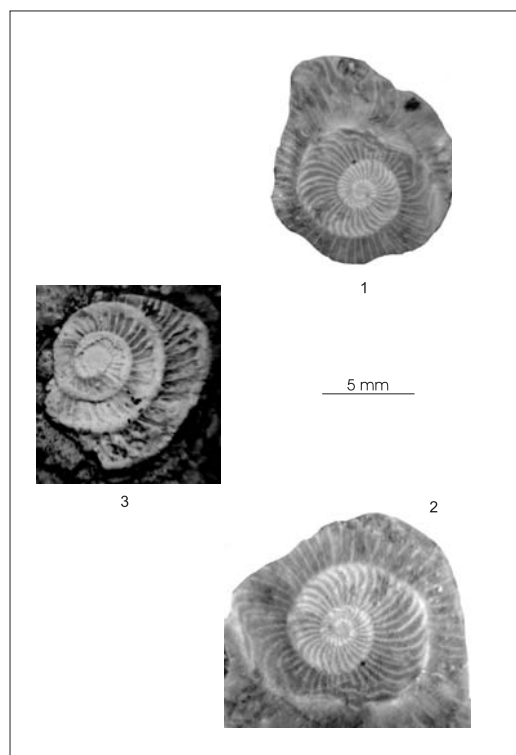
Ta vrsta je živela v spodnjem in srednjem cuisiju. Znana je iz Švice, avstrijske Koroške (Sonnenberg, Guttaring = Kotarče) in Furlanije (Buttrio). V Vipavski dolini je ugotovljena prvič.

**Assilina marinellii marinellii****(DAINELLI, 1915)**

(tabla 1, sl. 3)

1915. *Operculina Marinellii* n.sp. – Dainelli, 170-171, tab. 18, sl. 27-281977. *Operculina marinellii* Dainelli, 1915 – Hottinger, 68-69, tab. 27-292003-a. *Assilina marinellii marinellii* (Dainelli) – Pavlovec, 234, tab. 1, sl. 2

Material: Najdenih je bilo več večinoma dobro ohranjenih primerkov, ki imajo oznake LO 1,2,3,4,5,7,9.

**Tabla 1 – Plate 1:**

**Sliki 1 in 2 – Figures 1 and 2.** *Assilina escheri* (Hottinger), ekvatorialni prerez – equatorial section.

**Slika 3 – Figure 3.** *Assilina marinellii marinellii* (Dainelli), površina hišice – surface of the shell.

Mikrosferična generacija. Zavojni rob je močan. Zavoji se precej enakomerno in hitro višajo. Septa so ponekod skoraj ravna in upognjena samo v vrhnjem delu, drugod so nekoliko bolj usločena. Na površini hišice so v srednjem delu nežne granule, medtem ko jih v ostalih delih ni videti. Premeri hišic so 10,1 mm, 10,9 mm, 11,1 mm, 11,6 mm, 11,8 mm in 12,8 mm. Po velikosti ustrezajo omenjeni podvrsti. Nekateri primerki imajo nekoliko gostejša septa, vendar ta oblika precej variira. Podvrsta *Assilina marinellii similis* (KHAN & PAVLOVEC, 1975) je nekoliko manjša, vendar je vprašljivo, če je ne bi bilo treba uvrstiti v variacijsko širino podvrste *Ass. marinellii marinellii* (PAVLOVEC, 2003a).

*Assilina marinellii marinellii* je živel v spodnjem in srednjem cuisiju.

**Nummulites tauricus**

(tab. 2, sl. 1 in 2)

non 1963. *Nummulites partschi tauricus* (de la Harpe) – Pavlovec, 452-453, sl. 11

1973. *Nummulites partschi tauricus* De la Harpe – Kapellos, 86, tab. 43, sl. 1, tab. 46, sl. 2, tab. 49, sl. 2-3

1981. *Nummulites tauricus* De la Harpe, 1926 – Schaub, 109-110, tab. 29, sl. 15-33, tab. 31, sl. 1-9, 16, 18, 19, 22, 23, 25, 27

Material: Najdena sta bila dva primerka z oznakama L 11 in 30.

Mikrosferična generacija. Premera hišic sta 18,5 mm s 15 zavoji in 14,7 mm s 13 zavoji, medtem ko SCHAUB (1981) navaja velikosti 10 do 19 mm in pri polmeru 9 mm 15,5 zavojev. Zavoji se zlasti v srednjem delu precej hitro dvigajo, proti zunanjemu robu so nižji in tanjši. Septa so močno nagnjena

in upognjena zlasti v zgornji polovici. Zavojni rob je močan in obsega okrog  $1/3$  zavoja. Hišica je tanka in ima na površini nežne septalne podaljške. Drobni trni so na primerkih iz Lokavca slabo vidni, deloma pa je zgornja plast hišice odstranjena. Podobna vrsta *Nummulites praelorioli* Herb & Schaub ima nižje zavoje in gostejša septa. *Nummulites tauricus* je bil omenjen iz Goriških brd (PAVLOVEC, 1963), vendar je bilo pozneje ugotovljeno, da determinacija ni bila pravilna (CIMERMAN ET AL., 1974).

*Nummulites tauricus* je živel v srednjem in zgornjem cuisiju.

### ***Nummulites* sp.**

Material: Trije primerki z dobrim ekvatorialnim presekom in žal slabo preparirano površino. Oznake so L 3, 5, 10.

Mikrosferična generacija. Za omenjene tri primerke nismo mogli ugotoviti, kateri vrsti pripadajo. Hišice so precej tanke. Zavoji se počasi višajo, zavojni rob je precej enakomerno debel in obsega okrog  $1/4$  zavoja. Septa so gosta, rahlo ukrivljena in nagnjena. Velikosti hišic so 11,2, 12,1 in 12,4 mm s številom zavojev od 13 do 15. Na površini hišic so radialni, nekoliko ukrivljeni septalni podaljški.

Numulitom iz Lokavca je podobna srednje in zgornjecuisijska vrsta *Nummulites gracilis* Schaub, ki pa je manjša in tanjša. Po SCHAUBU (1981) so velikosti hišic te oblike med 5 in 9,5 mm. Tudi zavoje imajo nekoliko višje, septa pa v zgornjem delu bolj ukrivljena. Nekoliko podobna je tudi vrsta *Nummulites discorbinus* (Schlotheim), ki je živela v srednjem in zgornjem luteciju, torej je mlajša od nahajališča pri Lokavcu. Kamrice in septa

so precej podobna našim primerkom. Vendar je *Nummulites discorbinus* bistveno manjši, po SCHAUBU (1981) med 4 in 8,4 mm. Vsekakor so numuliti iz Lokavca zanimiva vrsta, ki jo bo ob boljšem in številčnejšem materialu tudi megalosferične generacije potrebno morda opisati kot novo vrsto.

### ***Nummulites pavloveci***

(tab. 2, sl. 3)

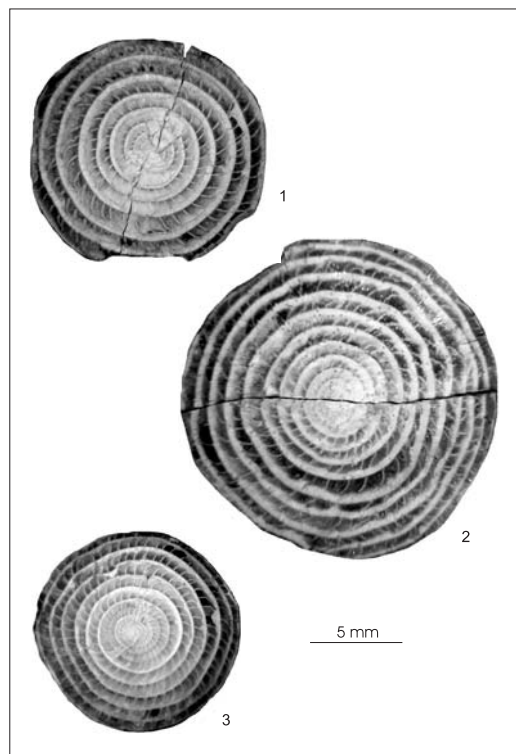
1981. *Nummulites pavloveci* nov.sp. - Schaub, 120-121, tab. 27, sl. 26-52, tab. 5, sl.m,n

Material: Primerki iz Lokavca ima oznako L 58.

Mikrosferična generacija. Hišica se proti sredini počasi debeli. Na površini ima tanke radialne septalne linije. Velikost hišice je 11,2 mm, debelina 4,8 mm. Schaub (1981) navaja velikosti med 8 in 15 mm, debeline pa med 3,2 in 5,8 mm. Zavoji se v notranjem delu hitro višajo, zunanja dva se znižata. Zavojni rob je močan in obsega tretjino do polovice višine zavoja. Septa so nagnjena, upognjena, pogosto srpasta. Kamrice so večinoma izometrične, le v zunanjih zavojih se podaljšajo, tako da pri nekaterih dolžina presega višino.

*Nummulites pavloveci* je živel od spodnjega do zgornjega cuisija.

Tabla 2 – Plate 2:



Sliki 1 in 2 – Figures 1 and 2. *Nummulites tauricus* De la Harpe, ekvatorialni prerez – equatorial section.

Slika 3 – Figure 3. *Nummulites pavloveci* Schaub, ekvatorialni prerez – equatorial section.

### *Nummulites* aff. *rotularius*

(tab. 3, sl. 1)

Material: Najdeni so primerki z oznakami L 25, C, D.

Mikrosferična generacija. Hišica je ploščata, na površini ima rahlo ukrivljene in ne posebno goste septalne linije. Pri najbolje ohranjenem primerku z oznako L 25 je velikost hišice 12 mm, debelina okrog 6,3 mm. Zavoji se hitro in enakomerno višajo, v zunanji polovici hišice nekoliko

hitreje. Zunanja dva zavoja se malo znižata. Zavojni rob je močan in obsega približno tretjino zavoja. Septa so nagnjena in precej upognjena, najmočnejše v zgornjem delu. Kamrice imajo v notranjih zavojih večjo višino od dolžine, v zunanjih se podaljšujejo in so včasih izometrične, včasih pa celo z večjo dolžino od višine.

Ta oblika iz Lokavca je zelo podobna vrsti *Nummulites rotularius* Deshayes, vendar je večja od nje. SCHAUB (1981) navaja velikosti hišic med 6 in 10 mm, najpogostejše med 5,7 in 7 mm. Pri polmeru 5,3 mm omenja 14 zavojev, medtem ko je pri našem primerku pri polmeru 6 mm 15 zavojev. Res pa je, da so tudi primerki iz Ustij v Vipavski dolini (DE ZANCHE ET AL., 1967) veliki med 9 in 11 mm, vendar so v ekvatorialnem prerezu zelo podobni tipičnim predstavnikom te vrste.

Morda je numulit iz Lokavca eden od naslednikov vrste *Nummulites rotularius*, katerih v smeri proti *N. perplexus* Schaub in *N. praediscorbis* Schaub avtor obeh vrst ni ugotovil (glej SCHAUB, 1981, slika 25). Žal po naših primerkih tega problema ni mogoče rešiti. Poleg tega še ni zadovoljivo rešena variacijska širina posameznih elementov te vrste, ki je glede na višino zavojev, debelino zavojnega roba in oblike kamric zelo različna (primerjaj SCHAUB, 1981, tabla 26). Zaradi vsega tega označujemo primerek 25 iz Lokavca kot *Nummulites* aff. *rotularius*.

Iz Lokavca sta primerka z oznakama L C in L D s premeroma hišic 8,8 in 7 mm in sta po tem bližja tipičnim primerkom. Imata pa zelo debel in nekoliko nepravilno potekajoč zavojni rob zlasti v srednjem delu hišice.

Kamrice imajo ponekod precej večjo dolžino od višine in to bolj od primerka L 25 ali numulitov na tablah pri SCHAUBU (1981).

Vrsta *Nummulites rotularius* je znana iz spodnjega in srednjega, morda še iz zgornjega cuisija.

### **Nummulites aff. aquitanicus sensu**

SCHAUB

(tab. 3, sl. 2 in 3)

1981. *Nummulites* aff. *aquitanicus* – Schaub, 161, tab. 7, sl. i

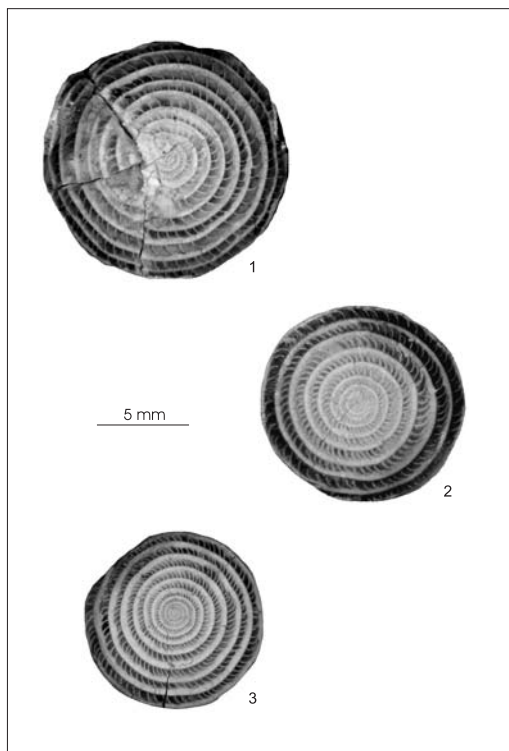
Material: Ta oblika numulitov je najpogostejša v Lokavcu. Oznake primerkov so L 15-18, 20, 21-24, 26-29, 31-45, 47-50.

Mikrosferična generacija. Hišice se proti sredini enakomerno debelijo, njihove velikosti so med 9,7 in 13,1 mm, po SCHAUBU (1981) med 5,5 in 15 mm. Na površini so tanke, goste in zavite septalne linije. Izrazite granulacije ni, le ponekod so redke nežne granule. Zavoji se počasi in enakomerno višajo. Zavojni rob je precej močan. Septa so nagnjena, rahlo upognjena, v zgornjem delu so močnejše nagnjena nazaj. Kamrice imajo večjo višino kot dolžino.

Ta oblika se loči od tipičnega *Nummulites aquitanicus* po površini, ker nima izrazitih granul. Zavoji so pri večini primerkov nižji kot pri tipičnih primerkih te vrste. Podobnega numulita označuje SCHAUB (1981) kot *Nummulites* aff. *aquitanicus* iz srednjecuisijskih plasti v nahajališču Colombres (Oviedo) v Španiji. Med sorodnimi vrstami je še nekaj prehodnih oblik. Tudi iz Campa v Španiji opisuje

SCHAUB (1966) *Nummulites* aff. *aquitanicus*, ki ima višje zavoje od naših primerkov. Tega numulita postavlja med vrsti *Nummulites aquitanicus* in *N. manfredi*, najden pa je bil v srednjecuisijskih plasteh. Te in druge podobne numulite bo potrebno revidirati in najbrž opisati kako novo vrsto ali podvrsto ali celo več nekoliko različnih oblik. Vsekakor pri teh numulitih zelo variirajo višine zavojev in debeline zavojnega roba. Nekateri primerki iz Lokavca so po velikosti hišic, obliki sept in kamric podobni vrsti *Nummulites praecursor* De la Harpe, ki pa je starejša, ilerdijska.

**Tabla 3 – Plate 3:**



**Slika 1 – Figure 1.** *Nummulites* aff. *rotularius* Deshayes, ekvatorialni prerez – equatorial section.

**Sliki 2 in 3 - Figures 2 and 3.** *Nummulites* aff. *aquitanicus* sensu Schaub, 1981, ekvatorialni prerez – equatorial section.

*Nummulites aquitanicus* je živel v spodnjem in srednjem cuisiju, *N. aff. aquitanicus* sensu Schaub 1981 je znan iz srednjega cuisija.

*Nummulites brkiniensis*

(tabla 4, sl. 1 in 2)

1975. *Nummulites brkiniensis* n.sp. – Khan et al., 35-37, tab. 6, sl. 4-6, tab. 7, sl. 1-2

1981. *Nummulites brkiniensis* Khan et Pavlovec – Pavlovec, 295-298, tab. 1, sl. 6

Material: Najdenih je bilo šest dobro ohranjenih primerkov. Imajo oznake L 6,7,8,9,12,14 in številne druge. Za nekatere primerke ni zanesljivo, ali sodijo v variacijsko širino te vrste.

Mikrosferična generacija. Zavoji se precej enakomerno višajo. Zavojni rob je močan. Septa so rahlo usločena, najbolj pri vrhu. Kamrice imajo večjo višino kot dolžino, le redke so izometrične. Pri premeru 12 mm je 15 zavojev, pri 14 mm 14 in pri 13 mm 13 zavojev. Velikosti hišic so v variacijski širini te vrste, ki je med 11,4 in 17 mm (KHAN ET AL., 1975). *Nummulites brkiniensis* je v južnozahodni Sloveniji dokaj pogost. Poleg uničene tipokalitete pri Podgradu na južnem robu Brkinov smo ga ugotovili še v nekaj nahajališčih, ki niso dokončno preučena. Pogosta je ta vrsta ali njej zelo podobne oblike tudi pri Lokavcu. Čeprav je bilo pri tej vrsti že doslej znano precejšnje variiranje, je vendar vprašljivo, če ne bi bilo potrebno ločiti kako novo vrsto ali podvrsto. Razlike so v višini zavojev in ponekod v nepravilnem poteku zavojev. Nekateri primerki so precej podobni obliki, označeni kot *Nummulites aff. aquitanicus* sensu SCHAU (1981).

*Nummulites brkiniensis* je znan iz srednjega cuisija.

*Nummulites praelaevigatus*

(tab. 4, sl. 3)

1951. *Nummulites praelaevigatus* nov.sp. – Schaub, 188, sl. 257, 273-275, tab. 8, sl. 1,2

1981. *Nummulites praelaevigatus* Schaub, 1951 – Schaub, 170-171, sl. 104, tab. 60, sl. 1-3,5, tab. 7, sl. u

Material: Primerek iz Lokavca ima oznako L 19.

Mikrosferična generacija. Tanka hišica ima na površini nežne, nekoliko vijugaste septalne linije. Velikost je 13,8 mm, in debelina okrog 4,4 mm. Po SCHAU (1981) so hišice velike med 4,7 in 11 mm, vendar precej variirajo in nekateri navajajo hišice celo 4,1 mm (cf. KAPPELLO, 1973). Zavoji se hitro višajo, le zunanja dva sta nižja. Pri polmeru hišice 6,5 mm je 15 zavojev. Zavojni rob je zlasti v notranjih zavojih močan. Septa so nagnjena in rahlo ukrivljena, najbolj zgoraj. Kamrice imajo v večini zavojev večjo višino od dolžine, le v zunanjih zavojih se podaljšajo in so nekatere izometrične ali celo bolj dolge kot visoke.

Po ekvatorialnem prerezu se numulit iz Lokavca ujema s tipičnimi primerki te vrste (cf. SCHAU, 1966, sl. 6 h), vendar je nekoliko večji. Numulita z oznako *Nummulites aff. praelaevigatus* iz fliša v Postojni (PAVLOVEC, 1981) in iz apnenca pri Ivartniku v severni Sloveniji (Drobne et al., 1977) imata nekoliko višje zavoje in sta manjša od numulita iz Lokavca.

*Nummulites praelaevigatus* je živel v zgornjem delu spodnjega in v srednjem cuisiju.

### ***Nummulites vipavensis***

(tab. 4, sl. 4)

1967. *Nummulites vipavensis* n.sp. oblika B – De Zanche et al., 228-230, tab. 6, sl. 1-2, tab.8, sl. 1

1981. *Nummulites vipavensis* De Zanche et Pavlovec – Pavlovec, 295, tab. 1, sl. 5

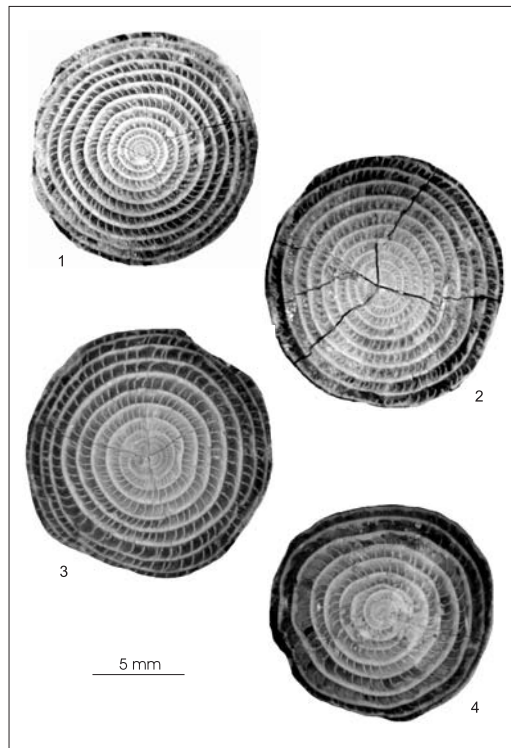
Material. Ta vrsta v Lokavcu ni pogosta, saj je bil doslej najden en sam primerek z oznako L 51.

Mikrosferična generacija. Vrsta *Nummulites vipavensis* je bila prvič opisana iz Ustij v Vipavski dolini, torej ne daleč od Lokavca. Hišica je tanka in ima na površini goste, nekoliko zavijajoče septalne linije z manj izrazitimi »trabécules transverses«. Velikost hišice je 11,6 mm, debelina okrog 5 mm. Pri dosedanjih opisih so omenjene velikosti med 11 in 12 mm, debeline pa med 5,5 in 6,5 mm (De Zanche et al., 1967; Pavlovec, 1981). Najhitreje se višajo zavoji v srednjem delu hišice, medtem ko so zunanji zavoji malo nižji. Potekajo nekoliko nepravilno. Zavojni rob je močan. Septa so nagnjena, usločena in najbolj upognjena v zgornjem delu. Kamrice imajo v notranjih zavojih večjo višino od dolžine. Proti zunanjim zavojem se daljšajo, tako da so nekatere skoraj izometrične. Na splošno oblike kamric in sept precej variirajo.

Vrsta *Nummulites vipavensis* je znana iz srednjega cuisija. Megalosferične oblike še vedno ne poznamo. V nahajališču holotipa

pri Ustjah smo pregledovali celoten material in lahko sklepamo, da so v flišu oblike A zelo redke.

**Tabla 4 – Plate 4:**



**Sliki 1 in 2 – Figures 1 and 2.** *Nummulites brkiniensis* Khan & Pavlovec, ekvatorialni prerez – equatorial section.

**Slika 3 – Figure 3.** *Nummulites praelaevigatus* Schaub, ekvatorialni prerez – equatorial section.

**Slika 4 – Figure 4.** *Nummulites vipavensis* De Zanche & Pavlovec, ekvatorialni prerez – equatorial section.

## **ZAKLJUČEK**

Lokavec je novo nahajališče numulitin v Vipavski dolini. Vrsta *Assilina escheri* je nova za to področje, najbližje doslej znana nahajališča so v Furlaniji. Dokaj pogosta je v flišnih plasteh pri nas *Assilina marinellii* in vse bolj se kaže tudi *Nummulites*

*brkiniensis*. Zanimivo je, da marsikatero v flišu ugotovljene pogoste vrste ne najdemo tako številčne v apnencih iz istočasne karbonatne platforme.

*Assilina escheri* in *Ass. marinellii marinellii* sta znani iz spodnjega in srednjega cuisija, vendar je prva v olistolitu, ki je najbrž starejši od flišnih plasti pri Lokavcu. *Nummulites pavloveci* je živel od spodnjega do zgornjega cuisija, enako vrsta *N. rotularius*, ki pa pri Lokavcu ni zanesljivo določena. *Nummulites aquitanicus* sensu SCHAUB (1981) je doslej znan v srednjem cuisiju. *Nummulites praelaevigatus* je živel od zgornjega dela spodnjega in v srednjem cuisiju, *N. vipavensis* in *N. brkiniensis* sta znana iz srednjega cuisija, *N. tauricus* pa iz srednjega in zgornjega cuisija. Po tem lahko sklepamo na srednjecuisijsko favno iz olistostrom v Lokavcu. Možno pa je, da je favna iz Lokavca nekoliko mlajša od one pri Ustjah, ki jo postavljajo na prehod med spodnji in srednji cuisij (DE ZANCHE ET AL., 1967).

Glede na klasifikacijo numulitinskih nahajališč (PAVLOVEC, 2003-b) uvrščamo favno pri Lokavcu med pretransportirano s karbonatne platforme. Večina oblik je sinhronih s flišnimi plastmi, tiste v olistolitu pa so lahko starejše.

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## SUMMARY

### Nummulitins from Lokavec in Vipava valley (Vipavska dolina, SW Slovenia)

In the flysch beds from Vipava valley (SW Slovenia) are more localities with nummulitins. Partly they are not researched, in future we expect to find new localities. The new finding place is in the olistostrom flysch sediments in Lokavec near Ajdovščina. Nummulitins, anthozoans, molluscs, echinoids and algae are discovered there. Determined species and subspecies are *Assilina escheri* (Hottinger), *Assilina marinellii marinellii* (Dainelli), *Nummulites tauricus* De la Harpe, *N. pavloveci* Schaub, *N. aff. rotularius*, *N. aff. aquitanicus* sensu Schaub 1981, *N. praelaevigatus* Schaub, *N. vipavensis* De Zanche & Pavlovec, *N. brkiniensis* Khan & Pavlovec, and *Nummulites* sp., that could be the new species, but we do not have enough good preserved samples. The flysch sediments in Lokavec are from Middle Cuisian.

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## Minerals Planning Policies in Europe

### Razvojne usmeritve planiranja mineralnih surovin v Evropi

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**Abstract:** This paper summarizes the main results of a study of minerals planning policies in Europe which objective was to provide information on different approaches to mineral planning policies, to evaluate them and to highlight best practices in the frame of sustainable development.

**Izvleček:** V članku povzemamo temeljne rezultate študije o razvojnih usmeritvah na področju planiranja mineralnih surovin v Evropi. Namen študije je bil predvsem zbrati informacije o različnih pristopih k planiranju mineralnih surovin, te pristope ovrednotiti ter izpostaviti primere dobre prakse, ki temelje na načelih trajnostnega razvoja.

**Key words:** mineral resources, policy, planning, European Union.

**Ključne besede:** mineralne surovine, razvojne usmeritve, planiranje, Evropska Unija.

## INTRODUCTION

This paper summarizes the main results of a study of minerals planning policies in Europe. The objective of the study was to provide information on different approaches to mineral planning policies and practices in the Member States. In the course of the study it was found that there are some general issues, which have a major impact on the non-energy extractive industries in Europe.

The study has shown that contrary to the public opinion the production of industrial minerals and construction minerals is significant, the former accounting for about 20 percent of global production, the latter

amounting to about 3 billion tonnes per annum. In contrast the importance of metal ores has diminished although metal production in some European countries can still be significant. The study revealed that very few Member States have clearly defined mineral policies. Common to most mineral policies is the emphasis on reducing minerals consumption and recycling, whereas the important aspect protecting access to minerals resources is not adequately addressed by most policies. Access to mineral deposits is regulated in most Member States by land use legislation and administration. Information on mineral deposits in land use planning databases tends to be scarce. This together with the absence

of formal mineral policies places minerals at a disadvantage in land use decision-making. The emergence in the recent past of environmental legislation and in particular environmental impact assessments has had a crucial effect on the duration of the authorization process for new mineral projects. Examples are given how minerals planning is handled in some of the Member States.

This paper concentrates on the general issues rather than discussing specific mineral planning policies and practices of the individual Member States. Only where appropriate will examples be given of specific mineral planning policies and practices. All details have been presented in a very comprehensive report, which has been submitted to the European Enterprise Directorate at the end of November 2004.

## **THE NON-ENERGY EXTRACTIVE INDUSTRY IN THE EU**

The non-energy extractive industry is often considered to be made up of three broad sub-sectors<sup>[1]</sup>:

- Metalliferous minerals,
- Industrial (non-construction) minerals,
- Construction minerals.

### **Metalliferous minerals**

During the past 50 years the structure of the European minerals industry has undergone fundamental changes. The production of metal ores has decreased steadily resulting in a situation where the requirements of the industry have to be met, with a few

exceptions, through imports of metal ores. Important metal ores mined in Europe are zinc, lead and copper. Production of all other metal ores is less than 2 % of global production. For most metal ores import dependency is in excess of 50 % and for some even in excess of 80 %. This makes the European metals industry very vulnerable to external developments.

### **Industrial minerals**

The production of industrial minerals has been growing steadily over the years and this sector of the non-energy extractive industries has increased in importance. In the field of industrial minerals, European producers play a major role and account for about 20 % of total world production. Europe is a major producer of kaolin, bentonite and salt.

### **Construction minerals**

The third and most important area is that of construction minerals. More than 3 billion tonnes of sand, gravel and crushed stone are produced annually to meet the demands of the European building and construction industries. While most of the construction minerals are produced close to the major development centres, the establishment of mega-quarries next to the sea in Norway and in Great Britain is a new development that could have important consequences for parts of Europe, which can be reached by bulk carriers. Assessment of the actual quantities of construction minerals produced in Europe is difficult because official statistics do not cover small and very small enterprises, which produce significant quantities of construction minerals.

**Table 1.** EU 25: European minerals Production as a Proportion of Total World Production  
(Source: World Mining Data, 2002).

| Ores                  | Production t (Metal)            | % Proportion World |
|-----------------------|---------------------------------|--------------------|
| Bauxite (Aluminum)    | 2,467,255                       | 1.8                |
| Copper                | 715,689                         | 5.2                |
| Lead                  | 271,190                         | 8.8                |
| Zinc                  | 843,810                         | 9.5                |
| Chrome                | 288,343                         | 5.6                |
| Nickel                | 22,201                          | 1.9                |
| Iron Ore              | 11,878,949                      | 1.6                |
| Industrial Minerals   | Production (t Minerals)         | % Proportion World |
| Baryte                | 398,936                         | 5.8                |
| Bentonite             | 2,586,585                       | 24.7               |
| Diatomite             | 128,387                         | 12.0               |
| Feldspar              | 4,684,413                       | 52.1               |
| Fluorspar             | 314,381                         | 7.1                |
| Graphite              | 21,479                          | 3.6                |
| Magnesite             | 2,649,830                       | 19.0               |
| Perlite               | 1,014,165                       | 46.1               |
| Salt                  | 44,878,991                      | 21.9               |
| Talk                  | 1,274,770                       | 17.2               |
| Agricultural Minerals | Production (t K <sub>2</sub> O) | % Proportion World |
| Potash                | 4,936,875                       | 19.9               |

### Annual per capita minerals consumption in Europe

Annual per capita consumption of minerals in the European Member States varies considerably, with consumption figures ranging from less than 3 tons per capita and year in some of the new Member States to more than 15 tons per capita and year in some of the other states.

## SUSTAINABLE DEVELOPMENT AND NATIONAL MINERALS POLICY

### Sustainable Development

The European Community has adopted the sustainable development concept as detailed in the Brundtland Report. The Brundtland

definition has been incorporated in the EU Strategy for sustainable development, adopted at the Gothenburg Council in 2001. This strategy requires that all policies should be judged by how they contribute to sustainable development<sup>[2]</sup>. The 5<sup>th</sup> and 6<sup>th</sup> Community Policy and Action Programmes make direct reference to the concept of sustainable development. As far as the extractive industries are concerned the most relevant document is the Communication on “Promoting sustainable development in the EU non-energy extractive industry” (COM (2000) 265). This was the first document to discuss the problem of sustainable mining. It made important statements such as:

- Mining is increasingly influenced by other competing land uses, such as urban development, agriculture, nature conservation;

- A balanced consideration of economic, environmental and social aspects to ensure the sustainable development of the industry is needed;
- A coherent Community policy is necessary.

The Communication raises two kinds of concern from the point of view of sustainable development. These are the use of non-renewable resources themselves, which may mean that these “resources will not be available for future generations”<sup>[3]</sup> and the quality of the environment, pointing to general and specific risks since mining may affect the quality of the environment.

Recent major environmental accidents involving tailing ponds on metal mines have switched the attention at EU level from sustainable development in the minerals industry to the safety and environmental hazards of mineral extraction. An example was the Communication from the Commission on “Safe operation of mining activities: A follow-up of recent mining accidents”, COM (2000) 664. From this followed three key follow-up actions, namely the amendment of the Seveso II Directive, an initiative on the management of mining waste, and a best available technology (BAT) reference document under the IPPC Directive. As a consequence of these accidents some of the important points raised in COM (2000) 265 have not been addressed.

Most Member States have taken measures to implement the principles of sustainable development. The emphasis has been on environmental protection, promoting reduced use of minerals, and recycling of materials. Examples of this are the policies adopted by the Netherlands and Sweden.

The important issue of safeguarding mineral deposits for future generations by protecting them from other land uses has been addressed by only but a few of the Member States. The Swedish landbank system developed by declaring various types of mineral deposits to be of national interest in accordance with the Environmental Code, and protecting the resources from being sterilised by other land use development, must be considered to be successful with regard to the future sustainability of minerals supply in Sweden. Austria is working on a raw materials plan, which as one of its main objectives has the protection of access to mineral deposits.

### Minerals Policy

Closely linked to the issue of sustainability of minerals supply is the question of minerals policies. The survey of EU-policies and Member States has shown that very few have comprehensive and published mineral policies. This is a marked change from the situation some years ago when minerals played a focal role in Europe as reflected by the European Coal and Steel Community, the original predecessor of the European Community. Member States, which have such policies, are amongst others the Czech Republic, the Netherlands and some of the German Federal States. Minerals policies are particularly important in connection with land use planning which is the main instrument for securing access to mineral deposits. As land use planning is about choices between different options minerals tend to be disadvantaged in the absence of clearly defined minerals policies. The need for minerals policies has been stressed by REGUEIRO from Spain in a recently published paper<sup>[4]</sup>.

### General Legal and Policy Framework

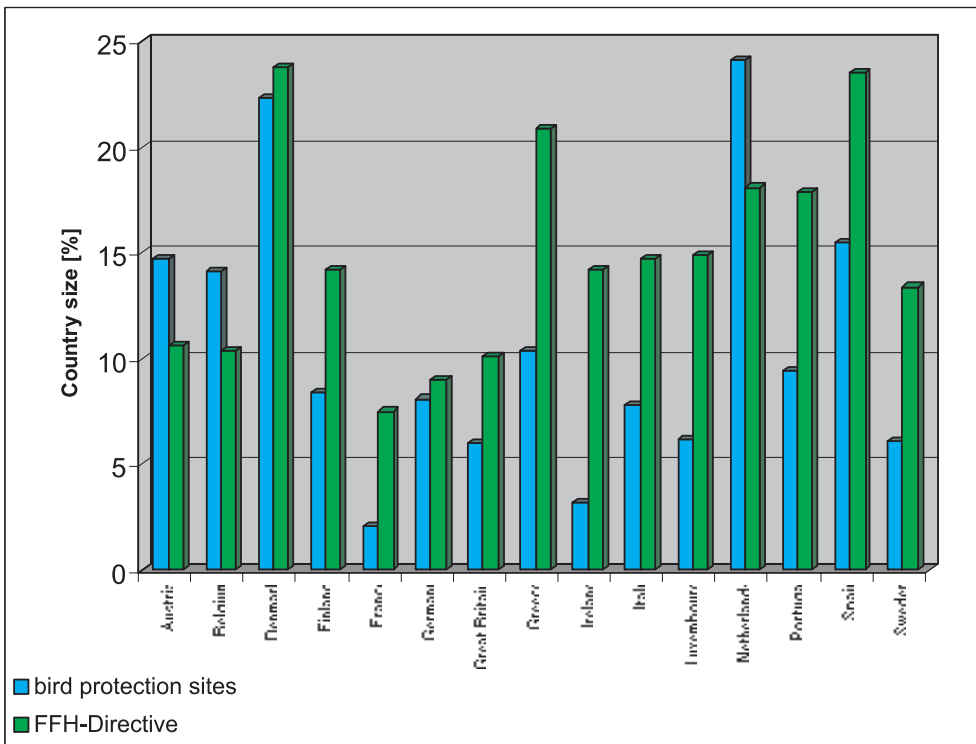
All Member States have some form of hierarchical government structure, with the national government at the apex and legal and administrative structures following the “cascade” principle, i.e. regional, county and local law and practices, which are *consistent* with national law and practice and, especially European law and practice.

#### *Impact of EU-legislation on non-energy extractive industries*

The emergence of environmental protection legislation/policy at the EU-level has added a number of additional factors that impact the authorisation process for mineral extraction. The influence of EU-legislation and policy on national legislation and

practice has grown markedly in recent years, especially regarding environmental matters. Table 1 at the end of the paper provides an overview of recent EU-legislation impacting on the non-energy extractive industries.

Many national laws were/are amended to implement EU-legislation (especially in the new Member States). While this is having a harmonising effect with regard to environmental matters, it has had an impact on the extractive industry due to increasing the number of restrictions on mineral extraction and increasing the time and costs required for approval. Both aspects have adverse effects on available mineral reserves. Reports from various countries show that the impact is more strongly felt by small extraction companies. Considering that the



**Figure 1.** Summary of land areas designated as Natura 2000 and bird protection areas.

largest sector of the European non-energy extractive industries, namely the construction minerals sector, consists of predominately small to very small enterprises, this trend could ultimately lead to a change in the structure of the industry with possible consequences for the local supply of construction minerals and increased minerals transport.

Extractive activities depend on geology and the particular location of mineral deposits. Access to the deposits is, therefore, of crucial importance for the competitiveness of the extractive industry. This, however, is made difficult by some of the directives. The most important impact results from the so-called Natura 2000 areas, a FFH – Directive. Mineral deposits that can be used for extraction are often found in undeveloped, mostly natural areas, thus the Natura 2000 protection areas can have a serious impact on the raw material industry in the field of land utilization. Areas set aside for nature protection vary considerably throughout Europe (Fig. 1).

#### *Principal Legislation Controlling Mineral Extraction*

The principal legislation governing mineral extraction in the Member States tends to be strongly influenced by the mineral rights issue. Historically mineral rights belong either to the state or to the owner of the land. State owned minerals in most countries are metal ores, rare industrial minerals and minerals of high purity. Landowner minerals are the bulk of the industrial minerals and the construction minerals.

In most Member States the extraction of state-owned minerals is covered by a specific

mining law. In many Member States the extraction of construction and most industrial minerals is covered by some other law, i.e. “Abgrabungsgesetz” in some German Federal States, land use planning laws or environmental laws. There is a trend to regulate minerals extraction through environmental laws, i.e. in Sweden.

The mineral rights no longer reflect the changing importance of industrial minerals and construction minerals (aggregates) which together account for more than 95 % of all non-energy minerals mined in Europe. Construction minerals in many parts of Europe are becoming of strategic importance and interstate trade of construction minerals is increasing.

In the light of the increased strategic importance of construction minerals in most European states and the difficulties encountered by the construction minerals industries in connection with the issuing of new extraction permits the question has been raised on several occasions whether it is still appropriate to consider landowner minerals as being minerals of low national importance<sup>[4]</sup>.

#### **Land Use Planning**

Short, medium and long-term access to mineral deposits is crucial for the sustainable development of the minerals industry. Two factors play a key role in this regard, namely whether a national minerals policy exists and the legislation and practice of land use planning.

Land use planning is an integrative process, in which different claims of utilization are subjected to an evaluation process. For land

use planning to be an effective tool it is essential that it is based on a solid and well substantiated database and that it includes all necessary information, including information on mineral deposits. The study has shown that in many Member States information on mineral deposits is not either not available at all or incomplete in land use planning data bases. From a minerals development point of view, it is crucial that the information concerning mineral deposits is entered into the land use databases to ensure that minerals are considered in all land use planning decisions. Geological surveys have to make the data on mineral deposits available. The need for closer involvement of national geological surveys in land use planning has been identified as one of the most important issues by the coordinating committee of the geological surveys of the Federal States in Germany. Similar views have been expressed by REGUEIRO of Spain<sup>[4]</sup>.

Key factors influencing land use planning are:

- Policy and legislation taken at EU-level
- Structure of government
- Role of national government in the planning process for minerals
- Planning framework

Policy and legislation taken at EU-level have shown to have a major impact on national land use planning (e.g., European Spatial Development Perspective (ESDP), NATURA 2000, etc.).

The structure of government in the Member States is another critical factor in the planning process for mineral extraction (hierarchical planning). The survey of Member States has shown that in most of them land use planning is done at two levels, namely at regional and

at district or municipal level. Since mineral deposits are not uniformly spread throughout a country land use planning for minerals at a low tier of government has been found to be not without problems and does not promote sustainable solutions. The view has been expressed by a number of industry representatives that land use planning for minerals should be done at high level - national or regional level - and should consider long time periods, which depending on the mineral could be 20 to more than 50 years.

A principal distinction between Member States is the degree to which land use plans provide detailed prescriptive information on where mineral extraction might be acceptable and where it is not acceptable. Some Member States have identified areas for minerals extraction, areas where minerals extraction may be possible subject to certain criteria and areas where minerals extraction is not allowed. Examples are the Scandinavian countries, Denmark, Belgium, certain Federal States of Germany and some provinces in Austria as well some regions in France. Experiences in some of these states have shown that the time required for the authorization process tends to be significantly shorter for projects situated in declared extraction areas.

Some Member States provide rather policy guidance and contrast the above-mentioned approach; for example the procedure adopted in England and Wales is that at ministerial level regional demand forecasts for aggregates are made for periods of 7 to 10 years. It is then up to the local authorities to ensure that sufficient extraction sites are available at local level to meet the demand.

## **Authorization of mineral development**

The issue of permits and authorisation depends to some extent on the mineral rights. For minerals permits to conduct mineral exploration work and to exploit minerals are required in all Member States for minerals that are important to the state or belong to the state. In the case of landowner minerals the situation differs. The permits fall into the following areas: mining rights, mining licences (exploration, mining), permits according land use plan, other permits, especially health and safety, environmental permits.

The procedures for granting mining licences have been updated in most Member States in recent years to incorporate more fully environmental impacts of minerals extraction in the approval procedures.

### *Applications*

The authorisation process for mineral extraction defines the details required by the applicant and the public bodies involved in the process. To assist the applicant with the preparation of application some of the Member States (Belgium, Denmark, England and Wales) have standard application forms.

An important aspect of the authorisation process is which public body is the lead authority and the relationship between the various public bodies involved in the process. In some Member States, five or six public bodies take part in the process, i.e. the mining authority, the environmental agency, the nature conservation agency, the water authority, and the health and safety agency. This tends to prolong the authorisation process. Critical for the time required to complete the authorisation process is whether

the various investigations that are requested by public bodies participating in the process can be carried out in parallel or have to be performed in sequence. Significant time-savings can be expected if the processes run in parallel as for example in the Netherlands.

### *Environmental impact assessments*

A key element of the authorisation process is whether or not a project application requires an environmental assessment (EA). The survey of Member States has shown that there exists no common pattern as far as environmental assessments are concerned. The span of threshold values ranges from 5 hectares in Ireland and Portugal up to 500 hectares in the case of state owned minerals in the Netherlands. With regard to marine aggregates, Ireland and the Netherlands make an EA compulsory for all project applications. Irrespective of defined threshold values it has become practice in some Member States to subject all applications for extraction licences to an EA. Examples are Greece, Norway, Portugal and all quarrying operations in France.

### *Right to appeal*

The study has shown that appeals are one of the major causes for delays in the authorisation process. Most Member States have the right of appeal by the applicant and by third parties as part of their authorisation process. As far as the applicant is concerned this right is confined in Denmark and Finland to strictly legal matters and not to the outcome of the application. All Member States except Great Britain have the right for appeal by third parties in their authorisation process. In Finland, Greece and Sweden this right is however confined to local residents. In Denmark appeals by third parties are

uncommon. This can be attributed to dealing with contentious issues at the planning stage.

#### *Funding of restoration work*

An issue, which is of concern to most Member States, is the funding of restoration work. For this reason, most of the Member States provide in their minerals legislation for mechanisms to secure the funding of restoration work. This is being done through provisions for the establishment of closure funds, bank guaranties or other forms of security. These arrangements are part of the extraction permissions. At this stage there is insufficient information to assess which arrangements are best.

#### *Monitoring*

Monitoring is a central element of the authorisation process. Its objective is to ensure adherence to regulations and good mining and environmental practices. In most Member States the staff of the mining authorities is qualified mining personnel having been trained on mines and/or at appropriate universities. The situation is different when the supervising and monitoring authority comes from lower tiers of government, as is the case with most landowner minerals. In these cases the inspection personnel tends to have a much broader background in the fields of works inspection and health and safety, but is often lacking in specific mining skills.

## **EVALUATION OF THE IMPACT OF MINERAL POLICIES/SYSTEMS**

### **Minerals Policy**

Minerals Policy in many Member States is a low-key issue and few Member States have

specific and clearly defined and published mineral policies.

A number of Member States have a minerals legislation which dates back to a time when minerals were considered as one of the pillars of economic development and for this reason minerals were given a high legal status as reflected by the category of “free minerals”, i.e. Austria, Germany, Finland, Norway, and Sweden.

Some of the Member States have a principal minerals legislation that is based on the concept of sustainable development. Most Member States delegate implementation of minerals policy issues to lower tiers of government. At this level the instrument to implement the policy is land use planning. Access to and protection of mineral deposits is an important aspect of mineral planning policies, particularly as far as construction minerals are concerned which constitute the bulk of non-energy minerals extracted in Europe. However, in countries, which do not have clearly defined mineral policies, minerals issues are often allocated lower priority in land use planning compared to other issues such as environment protection, nature conservation and water protection. In very few Member States reference is made to minerals being an important consideration in land use planning, e.g. identifying areas which have been set aside for minerals extraction. One of the critical issues is that in most Member States construction minerals are not considered to be of national or high importance. This is despite the fact that the European society is strongly dependent on a sustainable supply of construction minerals, which as far as the interior of Europe is concerned should, for environmental reasons, involve short transport distances<sup>[5]</sup>.

## Legislation

All Member States have legislation governing mineral rights, licensing of minerals exploration and exploitation, monitoring and supervising of mining activities and mine closure. In most Member States several categories of minerals are defined. Usually a distinction is made between more common minerals with an intrinsically lower value (construction minerals and some of the industrial minerals) with the mineral right belonging to the landowner and minerals of higher intrinsic value or of national importance (e.g. metallic ores) with the mineral right belonging to the state. With regard to the principal legislation controlling mineral extraction there, exists – in addition to the specific minerals legislation (i.e. mining act) other legislation, such as an excavation act, planning act or other laws that impact mineral extraction.

In some Member States the specific minerals legislation no longer applies (e.g. Belgium) or only applies to minerals that do not belong to the landowner. As a result minerals of low value (mostly construction minerals) are legislated by other laws, which are either a general land use planning law or an environmental law (e.g. Belgium, France, Germany). In addition to the specific minerals or raw materials legislation, there are a number of other laws, which are of direct or indirect relevance to minerals extraction in the Member States (e.g. environmental aspects). There is an increasing tendency in Europe to regulate minerals extraction through provisions in other legislations, i.e. environmental protection, forestry and water legislation. As most of these provisions are of a prohibitive nature, minerals extraction is adversely affected.

## Administration

The study has shown that a number of different laws, such as for mining law, nature conservation law, water law, waste law apply to mineral exploitation and that these laws are administered by different government, provincial and local authorities. This raises the issue of the effectiveness and efficiency of the administrative processes governing mineral extraction. The various country reports have shown that different approaches have been adopted by Member States and that the situation can be quite complex with the potential for inefficiencies, time delays and increased cost.

The analysis of the various procedures adopted in the different Member States shows that in all instances the authorisation process is such that it is unavoidable for local and regional authorities to become involved in the final decision making step. The main difference between the Member States is the role of the national level in the process. In some Member States and for some categories of minerals, the national authority becomes involved in the authorisation process in an operational manner.

An example is the applications for the exploitation of state owned minerals and free minerals in Austria. The other extreme are states where the role of national authorities is to define policies and to provide guidance but not to become operationally involved in the process. Examples of this approach are England and Wales. In addition, in these countries the lower level authority is charged with the responsibility to ensure that adequate mineral reserves are available for extraction (landbanks). In all other Member

States the issue of mineral reserves is controlled by private interests and initiatives. The authorities in these cases act as permitting agencies. Between those extremes falls France where the national authority has delegated the responsibility for the administration of minerals applications to its regional directorates, but in the case of state owned minerals has reserved the final decision to the national level. The difference between France and Austria is that in France the role of provincial and local authorities in the authorisation process is restricted.

The role of central government in the issue of permits for landowner minerals tends to be limited. In the majority of Member States, decisions concerning this category of minerals are taken at the regional and sometimes even local level. Finally, it should be noted that in a number of Member States minerals are not very well covered and considered in the land use planning process.

*The time required for extraction permission varies considerably.* It ranges from a few months to several years and usually exceeds the time specified. Reports from Member States indicate that the time required for an extraction permission is significantly shorter if the application concerns a mineral deposit that is situated in a designated mineral extraction area. The main reasons for time delays are the involvement of many different authorities in the licensing procedure and the involvement of the public in certain elements of the approval process. Experience shows that especially the preparation of Environmental Impact Assessments (EIA's) is a complex issue and tends to take up much of the time.

## **Minerals planning**

The level at which planning for minerals is done is crucial. At the national level regional demands for minerals can be considered and included in overall mineral development plans taking into consideration the distribution of mineral resources in the country. However, at this level it is impossible to include all detailed site-specific considerations. This is the responsibility of lower level planning. Lower level planning on the other hand lacks the broader background and the long-term vision. It appears therefore that minerals planning has to be done at two levels, namely long-term strategic planning at the national or at least regional level and detailed planning at the lower level. Models for such an approach are for instance England and France.

## **Social Benefit**

Societal benefits can be measured in the most direct way by the number of persons directly and indirectly involved in the non-energy extractive industries. Directly involved are persons working on the extraction and processing of minerals and the production of mineral based products such as cement, bricks, tiles and other mineral based building materials and ready made concrete. Indirectly involved are persons manufacturing goods and materials used by the non-energy extractive industry, those that provide services to it, and also the municipalities involved. One of the fundamental problems encountered in assessing the importance of the non-energy extractive industries is the incomplete statistical information. As far as the traditional mineral commodities such as metal ores and the more

important industrial minerals are concerned there exist relatively reliable statistical data. The same cannot be said for the bulk of minerals produced in Europe, namely construction minerals. For example in Germany and Austria the production of construction minerals is underestimated by the official statistics by as much as 50%. This is seen as a serious shortcoming as it does not reflect the true importance of the sector. In the case of construction minerals another difficulty is that many of the companies are also involved in downstream activities, which add value.

Typical examples are ready-mixed concrete or manufacturing of bricks or cement production. In the case of many industrial minerals producers the mineral extraction is only a minor aspect of the business. The difficult question is where to draw the line. According to figures published by UEPG (Union Europeenne des Producteurs des Granulats), which represents 17,000 companies employing 250,000 persons producing 2.6 billion construction minerals, the annual turnover of the construction minerals industry amounts to 18.5 billion Euros. To this have to be added the production values of companies not belonging to UEPG and the production from the New Member States.

Comparing the employment figures quoted by UEPG, which do not include companies from the New Member States, with the EU-15 figures and considering that the EU-15 figures are not confined to construction minerals but include all non-energy extractive industries, it is apparent that the official EU figures on the non-energy

extractive industries are a serious underestimation of the economic importance of the sector. A socio-economic study of the finish mineral industries indicate that job creation in downstream industries using mineral raw materials is 35-40 times the number of people working directly in the mineral sector.

### **Environmental Performance**

Environmental considerations are an important aspect of the planning and operation of minerals extraction sites in all Member States. In most member States the larger producing companies have established environmental quality management systems and report on their environmental performance. Many of the smaller mineral producers in Europe do not have the resources to implement such systems. One of the recommendations for overcoming this was that small enterprises should be supported with the implementation of new regulations<sup>[6]</sup>. No standardised approach to environmental performance reporting exists in the Member States. Most of the large mineral producing companies in Europe do however report on environmental performance in their Annual Reports. In some Member States the polarisation between environmental groupings and mineral producers no longer exists and meaningful ways of collaboration have been found to mutually benefit both sides<sup>[7]</sup>. A matter of concern to the European minerals producers is the continuing shifting of goalposts as far as environmental standards are concerned. This has adverse effects on investments in mineral development, which is long term in nature. Another concern is

that environmental standards increase continuously. This trend has to be seen against the life span of mineral production projects, which ranges from 20 to 100 years.

## CONCLUSIONS

Minerals and in particular construction minerals are crucial for the long-term development of Europe. In the case of construction minerals the consumption patterns and logistics are such that most European states will have to rely on local supply of such minerals.

The absence of clearly defined minerals policies, incomplete official statistical data on minerals production and consumption as well as the contribution of minerals to the European and national economies, and the lack of information on mineral resources in land use data banks indicate that minerals are a low priority issue in Europe.

In many Member States construction minerals and in particular aggregates are still considered as minerals that occur in abundance and require little protection. This can have long-term consequences for the sustainable supply with construction minerals.

As part of the concept of sustainability mineral resources should be considered as an integral part of the land use planning system and process.

Environmental legislation at the EU-level has a major influence on minerals extraction in Europe, both in terms of access to mineral deposits as well as in terms of cost of production. Environmental legislation has not been balanced by initiatives, which recognise the importance of minerals for the long-term development of Europe.

Minerals planning has to be done at two levels, namely long-term strategic planning at the national or at least regional level and detailed planning at the lower level.

Experiences from the different Member States show that there is potential for improving administrative procedures for the minerals industries.

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# Thermodynamic Analysis of AlSi10Mg Alloy

## Termodinamična analiza zlitine AlSi10Mg

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**Abstract:** The AlSi10Mg alloy is one of the most frequently used alloys for different purposes because of its suitable mechanical properties. The alloy was examined with chemical analyses, with the triple simple thermal analysis (TSTA), the simultaneous thermal analysis (STA), the computer simulation using Thermo-Calc program and with the metallographic analyses.

The triple simple thermal analysis has been performed in three measuring cells simultaneously, with different cooling rates. High cooling rates simulated the actual cooling rate in the die casting process. Chemical analyses were used to verify whether the concentration of alloying elements is in suitable limits. Metallographic analyses enabled us to define phases in the microstructure at different cooling rates and they were verified with the Thermo-Calc computer simulation method. Research showed that the alloy should contain the amount of silicon near to the highest limit and a suitable concentration of manganese, which prevents the formation of needle  $\beta$ -Al<sub>3</sub>FeSi phase and enables formation less harmful  $\alpha$ -Al<sub>15</sub>(MnFe)<sub>3</sub>Si<sub>2</sub> phase. The triple simple thermal analysis showed that higher cooling rate has beneficial influence on the development of microstructure.

**Key words:** Al-alloy, thermodynamics, solidification, triple simple thermal analysis.

## INTRODUCTION

The AlSi10Mg alloy is used for making complicated, heavy-duty castings with thick walls for aircraft, vehicle, chemical and food industry. It is suitable for sand casting, mould casting, and die casting. At casting of Al alloys often defects appear which cause that the casting is unsuitable. Reasons for casting defects and defects in the structure of the material can be found in the melt preparation technology and in the casting procedure itself.

Technically significant aluminium casting alloys are developed from the Al-Si binary system being extended with some other alloying elements to improve mechanical and other properties where it becomes important the process of precipitation. Excellent castability of aluminium casting alloys enables to produce castings of complicated shapes. Alloying the magnesium to the binary Al-Si alloys enables precipitation of alloy and attainment of prescribed mechanical properties.

For a reliable production of castings with prescribed properties we have to get insight into the course of solidification, development of microstructure and the structure of the alloy, which in practice represents bigger or smaller difficulties. To accomplish this purpose we have laboratorically examined AlSi10Mg alloys of three different manufacturers (Z1, Z2 and Z3). Foundries usually use chemical analyses for control of the melt, and optical and electron microscopy for control of the final castings. We have examined our alloys with chemical analyses, with the TSTA, the STA, with the computer simulation using the Thermo-Calc program, and with the metallographic analyses. The minimum and maximum liquidus temperatures –  $T_{L/min}$  and  $T_{L/max}$ , minimum and maximum eutectic temperatures –  $T_{E/min}$  and  $T_{E/max}$ , temperatures of completed solidification –  $T_K$ , and the temperatures of precipitation of the  $Mg_2Si$  phase were determined.

### Crystallography of AlSi10Mg alloy

Aluminium and silicon are showing limited mutual melting and they form a eutectic system with the eutectic point at 12.6 mass % Si and at temperature 577 °C.

Silicon as an alloying element causes small contractions during the cooling and solidification<sup>[1]</sup>. Concentration of silicon in aluminium alloys is 5 to 25 %<sup>[1]</sup>. With alloying magnesium to the binary alloys Al-Si the heat precipitation of the alloy is enabled.

It is necessary to prepare the melt before the casting process, because of its influence on the quality of final castings. Preparation of the melt before the alloying mainly consists of cleaning the melt to remove impurities, to degas and modify the melt in order to obtain the required shape, size and distribution of microstructure components and phases<sup>[1,2]</sup>.

The chemical composition of the casting alloy is presented in Table 1<sup>[1]</sup>. The alloy

**Table 1.** Chemical composition of alloy AlSi10Mg ISO (3522 AlSi10Mg (R164))<sup>[1]</sup>.

**Tabela 1.** Kemijska sestava zlitine AlSi10Mg po ISO 3522 AlSi10Mg (R164).

| Si       | Fe  | Cu  | Mn   | Mg       | Zn   | Other elements | Difference |
|----------|-----|-----|------|----------|------|----------------|------------|
| 9.0-10.0 | 0.6 | 0.1 | 0.05 | 0.45-0.6 | 0.05 | 0.15           | Al         |

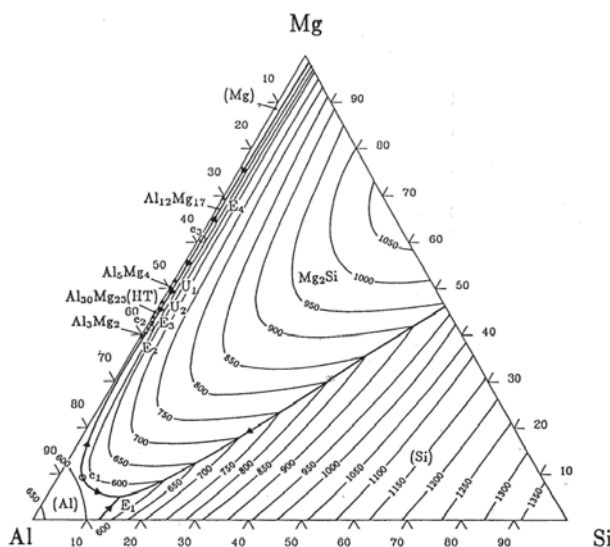
**Table 2.** Possible reactions during solidification of Al-Si-Mg alloy<sup>[1]</sup>.

**Tabela 2.** Reakcije, ki lahko potekajo med strjevanjem zlitine Al-Si-Mg.

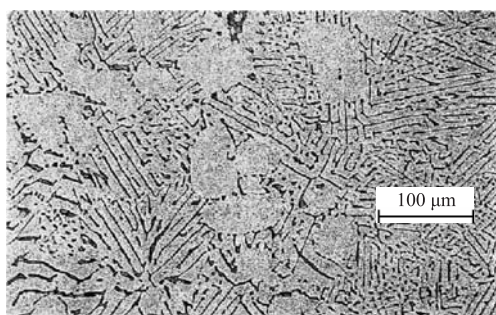
| Reaction                                                                  | Temp. [°C] |
|---------------------------------------------------------------------------|------------|
| e <sub>1</sub> $l \Leftrightarrow (Al) + Mg_2Si$                          | 593        |
| e <sub>2</sub> $l \Leftrightarrow Al_3Mg_2 + Mg_2Si$                      |            |
| e <sub>3</sub> $l \Leftrightarrow Al_{12}Mg_{17} + Mg_2Si$                |            |
| E <sub>1</sub> $L \Leftrightarrow (Al) + Mg_2Si + (Si)$                   | 550        |
| E <sub>2</sub> $L \Leftrightarrow (Al) + Al_3Mg_2 + Mg_2Si$               | 444        |
| E <sub>3</sub> $L \Leftrightarrow Al_3Mg_2 + Al_{30}Mg_{23}(HT) + Mg_2Si$ | 445        |
| E <sub>4</sub> $L \Leftrightarrow Al_{12}Mg_{17} + (Mg) + Mg_2Si$         | 434        |
| U <sub>1</sub> $L + Al_{12}Mg_{17} \Leftrightarrow Al_5Mg_4 + Mg_2Si$     | 452        |
| U <sub>2</sub> $L + Al_5Mg_4 \Leftrightarrow Al_{30}Mg_{23}(HT) + Mg_2Si$ | 448        |

belongs to the Al corner of the ternary system Al-Si-Mg, where the following equilibria occur:  $L > \alpha_{Al}$ ,  $L > \alpha_{Al} + \beta_{Si}$ , and ternary eutectic  $L > \alpha_{Al} + Mg_2Si + \beta_{Si}$  (Figure 1) [2]. In alloys of Al-Si-Mg system the process of solidification can be performed over the reactions that are shown in Table 2.

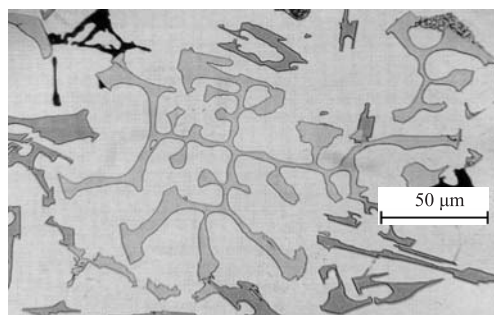
Depending on the cooling rate, especially for in practice typical larger cooling rates, dendritic shape primary crystals multi-component solid solution  $\alpha_{Al}$  can be obtained in the microstructure in the first stage of solidification (Figure 2a) [1], because of alloying elements like iron and manganese, we can trace in the microstructure labyrinthine phase  $\alpha_{Al}-Al_{15}(MnFe)_3Si_2$  (Figure 2b) [1,2].



**Figure 1.** Liquid surface of the ternary system Al-Si-Mg<sup>[7]</sup>.  
**Slika 1.** Likvidus ploskev ternarnega sistema Al-Si-Mg.



a)



b)

**Figure 2.** Microstructure of AlSi10Mg alloy: a) Primary crystal of solid solution  $a_{Al}$  dendritic shape and eutectic ( $a_{Al} + b_{Si}$ ), b) Dendritic phase of  $a_{Al}$  and  $a-Al_{15}(MnFe)_3Si_2$  phase (labyrinthine) and  $Mg_2Si$  (black)<sup>[7]</sup>.

**Slika 2.** Mikrostruktura zlitine AlSi10Mg: a) Primarni kristali trdne raztopine  $a_{Al}$  v obliki dendritov ter evtetik ( $a_{Al} + b_{Si}$ ), b) Dendriti faze  $a_{Al}$  ter faza  $a-Al_{15}(MnFe)_3Si_2$  (labirintasto) in  $Mg_2Si$  (črno).

## EXPERIMENTAL

In the present research we used standard blocks of AlSi10Mg alloy of three different manufacturers with composition, shown in Table 3.

TSTA measurements were carried out in three different cells simultaneously. Each measurement was performed three times. Figure 3 shows the measuring cells used in TSTA. We used two measuring cells made of gray cast iron with lamellar graphite, while the third cell was made by the Croning process. The first measuring cell, made of gray cast iron with lamellar graphite, had a diameter of 30 mm and volume of 33.807 mm<sup>3</sup>, the second one, made of the same materials, had a diameter of 15 mm and volume of 8.062 mm<sup>3</sup>, while the third cell, made of sand, had the same dimensions as the first one. We have put the K-type thermocouples in the center and at the same height of each measuring cell, as shown in Figure 3. The prepared alloys were melted in graphite crucibles in an induction furnace. As the temperature 750 °C was reached, the melt was poured from the graphite crucible into the three measuring cells. The thermocouples were connected to the National Instruments DAQPad-MI0-16XE-50 measuring card, and this to the personal computer, where the measured values were collected with the LabVIEW 5.0 program. Cooling curves were plotted using the Origin 6.0 program. Different geometries and

materials of the measuring cells caused various heat transfers, and, consequentially, different cooling rates.

Simultaneous thermal analysis of specimens of starting materials was performed on the STA 449 NETZSCH machine. We put together two equal cups made of corundum to the platinum sensor. In one cup there was the examined material, in the other one the reference material. The measurements were carried out in a protective atmosphere of inert gas 99.999 % pure nitrogen. The specimens were heated up to 720 °C with heating rate of 10 K/min and cooled with the same cooling rate to the room temperature.

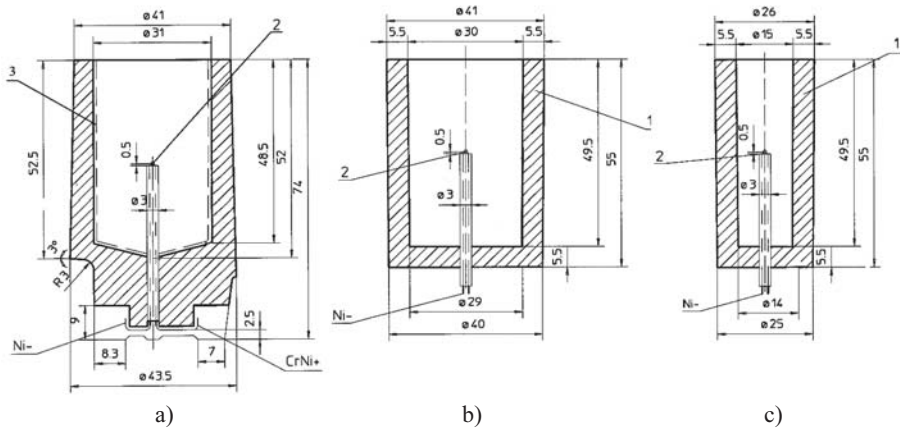
Thermodynamic equilibrium of the alloys Z1, Z2 and Z3 of three different manufacturers were simulated with the computer Thermo-Calc application. A suitable database in the program and the elements that composed our alloy were chosen. Our next step was to determine the amount of elements and to define the temperatures and pressures of the simulated equilibrium. The program has recorded all the thermodynamically possible phases that were present at defined conditions, and it constructed the equilibrium binary phase diagram. For all the alloys, the phases of completed solidification were simulated.

The chemical analyses of starting materials made by the Z1, Z2 and Z3 manufacturers and of the specimens after the TSTA were made. The specimens for the metallographic

**Table 3.** Chemical composition of alloy from three different manufacturers; mass %.

**Tabela 3.** Kemijska sestava zlitin treh različnih proizvajalcev; mas. %.

|    | Al      | Cr1    | Mg     | Mn1    | Cu     | Zn     | Ti     | Ni3    | Fe2    | Si2     | Pb     |
|----|---------|--------|--------|--------|--------|--------|--------|--------|--------|---------|--------|
| Z1 | 88.4888 | 0.0484 | 0.2999 | 0.1198 | 0.0815 | 0.0415 | 0.0092 | 0.0249 | 0.6504 | 10.2216 | 0.0067 |
| Z2 | 87.5246 | 0.0018 | 0.3458 | 0.0209 | 0.0239 | 0.0175 | 0.0137 | 0.0035 | 0.4593 | 9.9959  | 0.0086 |
| Z3 | 88.0195 | 0.0034 | 0.3631 | 0.0176 | 0.0728 | 0.0626 | 0.0065 | 0.0221 | 0.4556 | 10.9168 | 0.0503 |



**Figure 3.** Measuring cells: a) made by Croning sand, b) made by cast iron 30 mm diameter and c) made by cast iron 15 mm diameter; 1 - cast iron, 2 - thermocouples and 3 - coated.  
**Slika 3.** Merilni lončki: a) iz Croning peska, b) iz sive litine premera 30 mm ter c) iz sive litine premera 15 mm; 1 - siva litina, 2 - termoelementi in 3 - s premazom.

analyses were cut from the specimens after the completed TSTA. The samples for the optical microscopy were prepared by the standard metallographic procedure. Prepared samples were observed and photographed in the Nikon Microphot FXA optical microscope that was equipped with the 3CCD-videocamera Hitachi HV-C20A and the analySIS computer program to analyze metallographic pictures.

## RESULTS AND DISCUSSION

Cooling curves and suitable microstructures of alloys from three different manufacturers are shown in Figures 4 - 6. Table 4 presents average temperatures of the TSTA. Table 4 reveals that the temperatures of the starting solidification, the minimum and maximum liquidus temperatures, and the minimum and maximum eutectic temperatures are

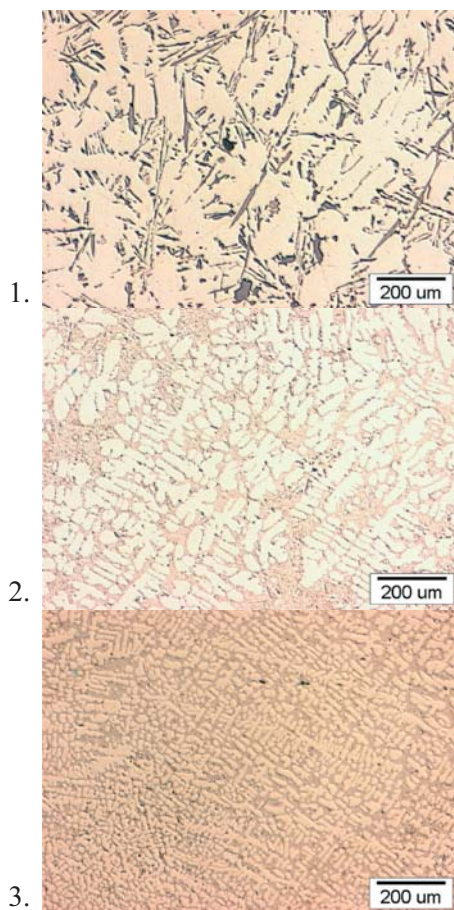
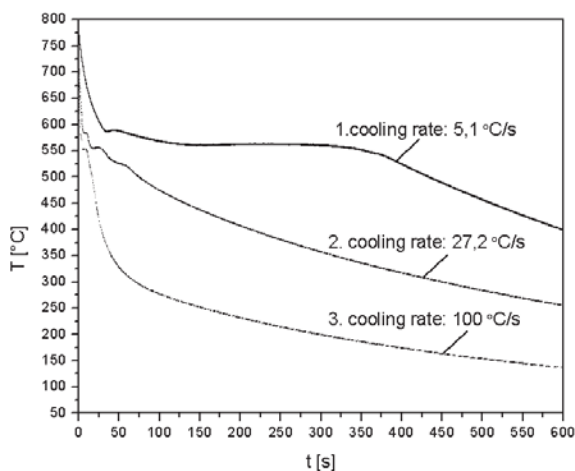
**Table 4.** Characteristic temperatures from triple simple thermal analyses; °C.  
**Tabela 4.** Značilne temperature trojne enostavne termične analize; °C.

| Alloy       | Z1    |       |       | Z2    |       |       | Z3    |       |       |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|             | a     | b     | c     | a     | b     | c     | a     | B     | C     |
| $T_N$       | 640.5 | 633.0 |       | 647.5 | 639.3 | 631.0 | 629.8 | 626.3 | 633.5 |
| $T_L$       |       |       | 588.0 |       |       | 578.5 |       |       | 575.5 |
| $T_{L/min}$ | 582.3 | 581.8 | 576.5 | 584.5 | 582.3 | 577.3 | 575.3 | 575.2 | 571.5 |
| $T_{L/max}$ | 586.5 | 584.0 | 579.8 | 589.0 | 584.5 | 579.5 | 579.8 | 581.7 | 575.8 |
| $dT_L$      | 4.2   | 2.2   | 2.2   | 4.5   | 2.2   | 1.5   | 4.5   | 6.5   | 2.8   |
| $T_E$       |       |       | 556.0 |       |       |       | 567.0 | 567.0 | 566.5 |
| $T_{E/min}$ | 563.5 | 556.8 | 553.3 | 558.8 | 554.0 | 551.3 | 566.8 | 567.3 | 565.8 |
| $T_{E/max}$ | 566.3 | 559.4 | 557.0 | 562.3 | 556.2 | 552.5 | 569.0 | 569.0 | 567.0 |
| $dT_E$      | 2.8   | 2.6   | 2.5   | 3.5   | 2.2   | 1.2   | 1.5   | 1.2   | 0.8   |
| $T_K$       | 542.8 | 550.2 | 531.0 | 548.8 | 545.0 | 531.0 | 542.8 | 550.8 | 533.0 |

decreasing with the increasing cooling rate. The highest liquidus undercooling was observed at the alloy Z3, the highest eutectic crystallizations undercooling at the alloy Z2.

With the STA, where the cooling rate was 10 K/min, temperatures of the starting solidification or liquidus temperature at cooling, and the temperatures of the initial melting or solidus temperature, at heating were determined. During cooling, the first

to begin to solidify was the alloy Z1 (585.3 °C), then the alloy Z2 (585 °C), and the lowest liquidus temperature corresponded to the alloy Z3 (581.3 °C) (Figure 7a). Heating curves showed that the alloy Z3 had the lowest solidus temperature (543 °C), the alloy Z2 had a little higher solidus temperature (550 °C), and the highest solidus temperature belonged to the alloy Z1 (557 °C) (Figure 7b).



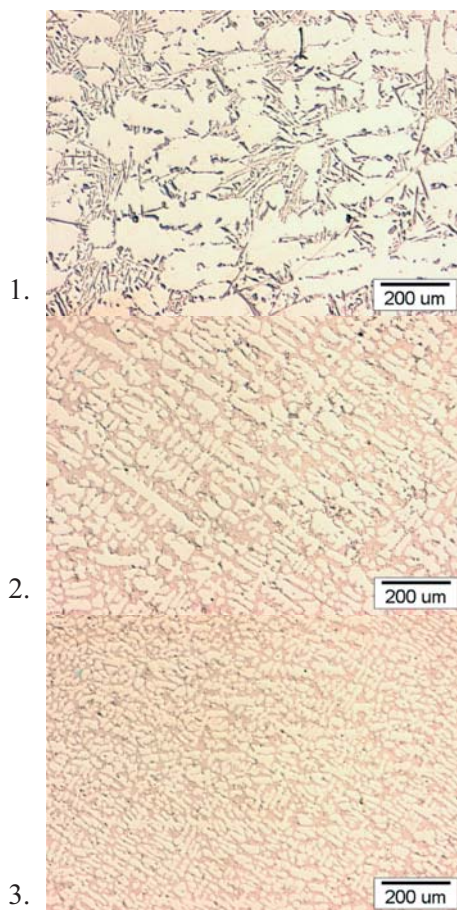
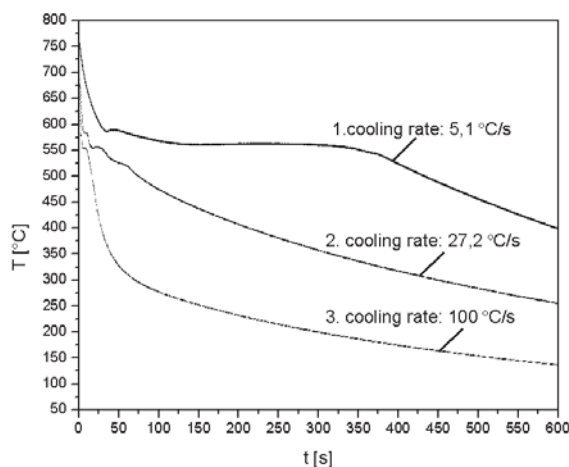
**Figure 4.** Cooling curves of AlSi10Mg alloy Z1 at three different cooling rates and their corresponding micro-structure; 1. sand mould,  $\Phi$  30 mm; 2. cast iron mould,  $\Phi$  30 mm; 3. cast iron mould,  $\Phi$  15 mm.

**Slika 4.** Ohlajevalne krivulje zlitin AlSi10Mg Z1 pri treh ohlajevalnih hitrostih ter njihove ustrezne mikrostrukture; 1. peščena kokila,  $\Phi$  30 mm; 2. jeklena kokila,  $\Phi$  30 mm; 3. jeklena kokila,  $\Phi$  15 mm.

Using the Thermo-Calc program, the course of equilibrium solidification of the AlSi10Mg alloy was determined. The  $\text{Si}_2\text{Ti}$  phase started to solidify the first, followed by the  $\alpha_{\text{Al}}$  phase (primary mixture crystals of solid solution based on aluminium). We can define the temperature of solidification of  $\alpha_{\text{Al}}$  crystals as liquidus temperature of the alloy. From the melt, the Si and  $\text{Al}_{13}\text{Fe}_4$  phases began to precipitate. When the eutectic temperature

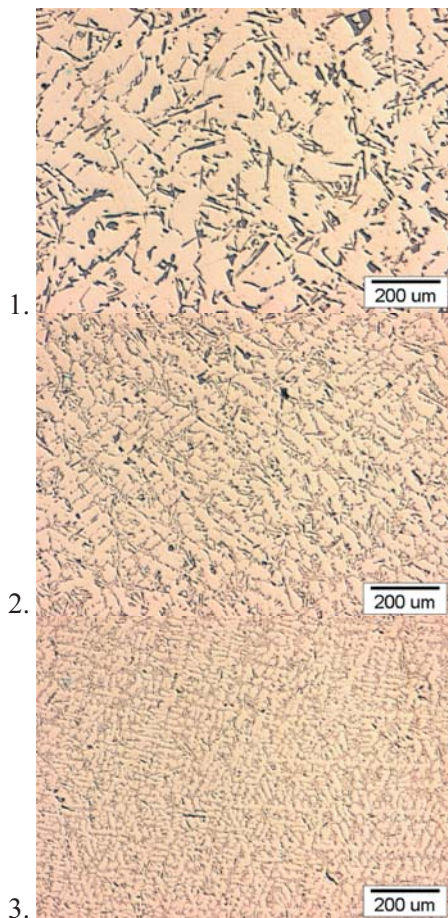
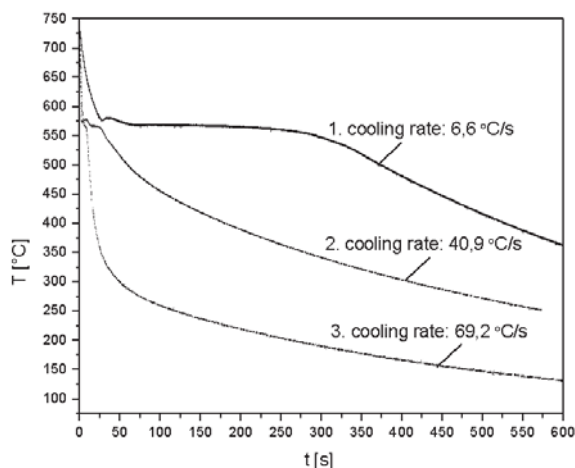
was reached, the remaining melt solidified as eutectic ( $\alpha_{\text{Al}} + \beta_{\text{Si}}$ ). At the end, the  $\text{Mg}_2\text{Si}$  phase and  $\text{Al}_{12}\text{Mn}$  and  $\text{Al}_2\text{Cu}$  phases precipitated from the solid solution.

Figure 8 shows characteristic temperatures at different cooling rates. Cooling rate of  $0.01^\circ\text{C/s}$  represented the equilibrium solidification that was achieved with the Thermo-Calc program. With STA the cooling



**Figure 5.** Cooling curves of AlSi10Mg alloy Z2 at three different cooling rates and their corresponding microstructure; 1. sand mould,  $\Phi$  30 mm; 2. cast iron mould,  $\Phi$  30 mm; 3. cast iron mould,  $\Phi$  15 mm.

**Slika 5.** Ohlajevalne krivulje zlitine AlSi10Mg Z2 pri treh ohlajevalnih hitrostih ter njihove ustrezne mikrostrukture; 1. peščena kokila,  $\Phi$  30 mm; 2. jeklena kokila,  $\Phi$  30 mm; 3. jeklena kokila,  $\Phi$  15 mm.



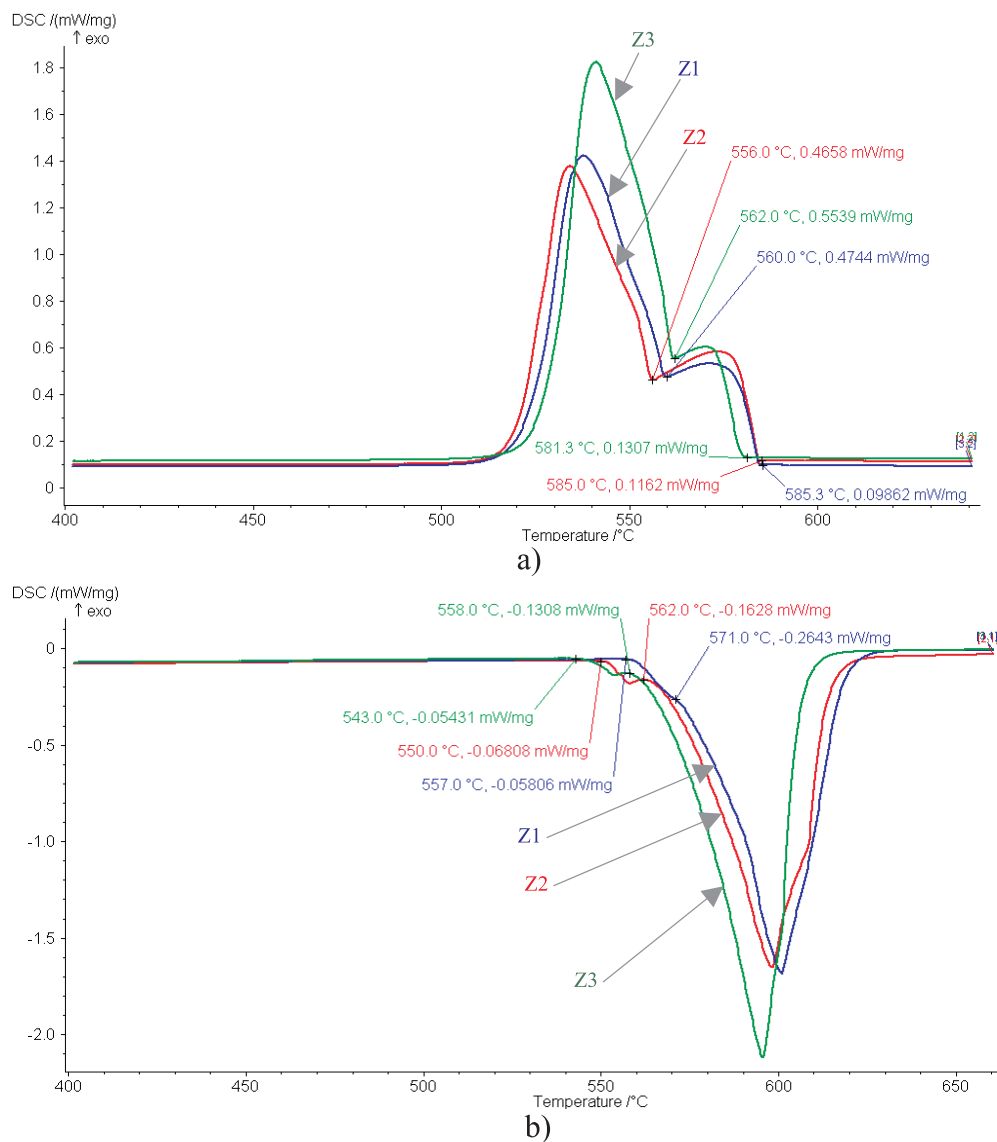
**Figure 6.** Cooling curves of AlSi10Mg alloy Z3 at three different cooling rates and their corresponding micro-structure; 1. sand mould,  $\Phi$  30 mm; 2. cast iron mould,  $\Phi$  30 mm; 3. cast iron mould,  $\Phi$  15 mm.

**Slika 6.** Ohlajevalne krivulje zlitine AlSi10Mg Z3 pri treh ohlajevalnih hitrostih ter njihove ustrezne mikrostrukture; 1. peščena kokila,  $\Phi$  30 mm; 2. jeklena kokila,  $\Phi$  30 mm; 3. jeklena kokila,  $\Phi$  15 mm.

rate of  $0.17\text{ }^{\circ}\text{C/s}$  was achieved. Cooling rates of approximately  $5\text{ }^{\circ}\text{C/s}$ ,  $40\text{ }^{\circ}\text{C/s}$ , and  $100\text{ }^{\circ}\text{C/s}$  were achieved with the TSTA. At equilibrium cooling rate, only liquidus temperature  $T_L$  and the temperature of completed solidification  $T_E$  (the lowest temperature where the melt still exists or solidus temperature) were determined.

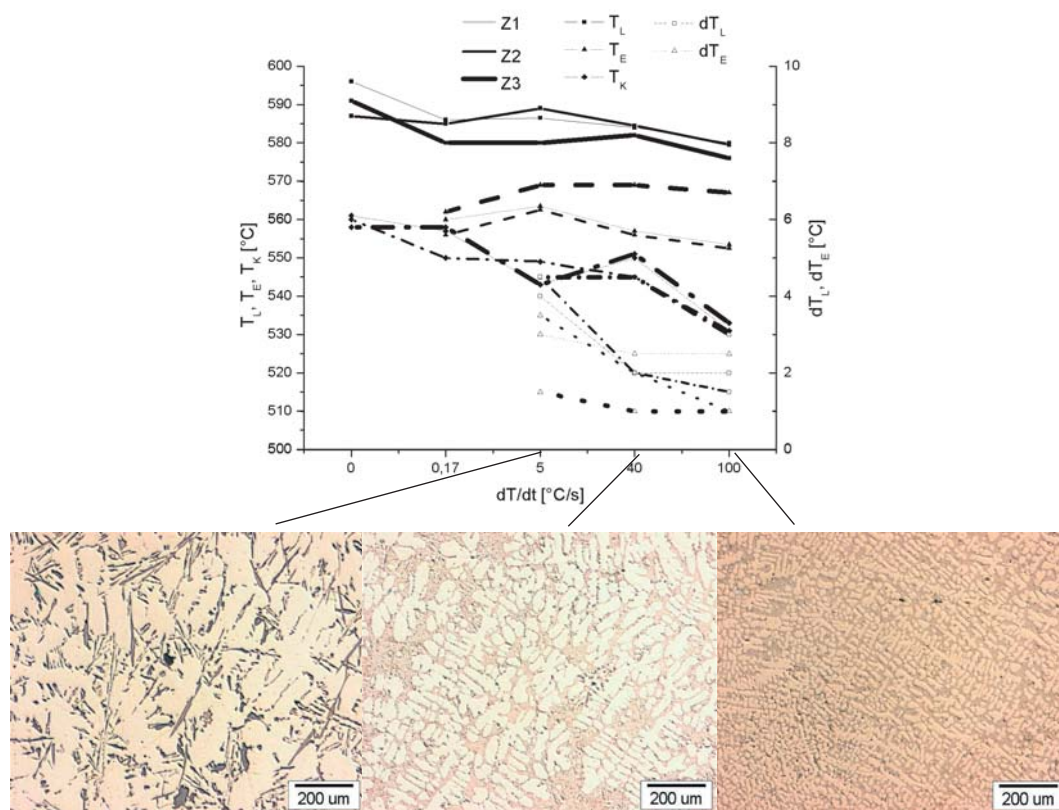
The differences in  $T_L$  and at  $T_E$  appeared because of different chemical compositions

of alloys of researched alloys. The tendency is indicated that characteristic temperatures of solidification are dropping with the increasing cooling rate. If all three materials are compared, it can be noticed that the greatest deviation appeared at the alloy Z3. The solidification of eutectic took always place the first with the alloy Z3, followed by the alloy Z1, the last was the alloy Z2. The widest solidification range had the alloy Z2 and the narrowest the alloy Z3. The level of



**Figure 7.** Cooling (a) and warming (b) curves of specimens from the simultaneous thermal analysis taken from the block.

**Slika 7.** Ohlajevalne (a) in ogrevne (b) krivulje simultane termične analize vzorcev vzetih iz blokov zlitin Z1, Z2 in Z3.



**Figure 8.** Graphic review of the main temperatures during solidification of alloy at triple simple thermal analyses (5 °C/s, 40 °C/s in 100 °C/s), simultaneous thermal analysis (0.17 °C/s) and at Thermo-Calc (0.01 °C/s) and their corresponding microstructures.

**Slika 8.** Grafični prikaz značilnih temperatur pri strjevanju zlitine iz trojne enostavne termične analize (5 °C/s, 40 °C/s in 100 °C/s), simultane termične analize (0,17 °C/s) ter Thermo-Calca (0,01 °C/s) in ustreznih mikrostruktur.

undercooling at liquidus temperatures and at eutectic temperature increased with the increasing cooling rates. The alloy Z2 had the highest liquidus and the smallest eutectic undercooling.

## CONCLUSIONS

Examinations of three commercial AlSi10Mg alloys with the TSTA, STA, computer Thermo-Calc program, chemical

analyses and metallographic analyses enabled several conclusions.

The variation in chemical composition of three commercial alloys has been reflected on the characteristic temperatures of the TSTA. Silicon and magnesium reduced not only liquidus temperatures, but also the temperatures of eutectic solidification ( $\alpha_{Al} + \beta_{Si}$ ).

Among the metal inclusions, the most frequent in the AlSi10Mg alloy is iron that

precipitates in a shape of needles, which represents intermetallic  $\beta\text{-Al}_5\text{FeSi}$  phase that worsen the properties of the alloy<sup>[10]</sup>. The manganese present in the alloy prevents formation of  $\beta\text{-Al}_5\text{FeSi}$  phase and forms less harmful labyrinthine,  $\alpha\text{-Al}_{15}(\text{MnFeMe})_3\text{Si}_2$  (Me=Cr,Cu), phase<sup>[10]</sup>. The alloy Z1 contained more a suitable amount of manganese with regard to iron; therefore the smallest amount of the harmful  $\beta\text{-Al}_5\text{FeSi}$  phase was found in alloy Z1, while the amount of  $\alpha\text{-Al}_{15}(\text{MnFeMe})_3\text{Si}_2$  phase was the highest. In the alloys Z2 and Z3 with less manganese it had to be alloyed.

Solidification in usual practice takes place under non-equilibrium conditions, mainly because of high cooling rates. The development of microstructure depends on the chemical composition, the cooling rate and the addition of modifying elements. Highest cooling rate causes reduction of the liquidus temperatures and the temperatures of binary eutectic solidification. Small primary crystals of multicomponent solid solution based on aluminium,  $\alpha_{\text{Al}}$  dendritic shape, and equable distribution of eutectic are formed at higher cooling rates, which improves the mechanical properties of the castings, and conditions closer to the die-casting conditions are achieved. The alloy Z2 had a larger amount of silicon, and thus the microstructure primary phase  $\alpha_{\text{Al}}$  and binary eutectic is equally distributed, but during the solidification it formed primary silicon crystals, which is caused by the fluctuations in the melt.

The best results with the TSTA were obtained with the alloy Z3, but the microstructure was the most favorable with the alloy Z1, due to small primary crystals. Binary eutectic end

$\alpha\text{-Al}_{15}(\text{MnFeMe})_3\text{Si}_2$  (Me=Cr,Cu) and  $\beta\text{-Al}_5\text{FeSi}$  phases were equally distributed among the interdendritic spaces of primary crystals  $\alpha_{\text{Al}}$ . There was less  $\beta\text{-Al}_5\text{FeSi}$  phase because of the suitable amount of manganese. For use in the casting production the alloy Z1 can be recommended.

## POVZETEK

### Termodinamična analiza zlitine AlSi10Mg

Pri ulivanju pogosto prihaja do napak, ki povzročijo, da je ulitek neuporaben. Vzroke za livarske napake in napake v zgradbi materiala lahko iščemo v tehnologiji priprave taline na litje in v postopku litja ali pa že v samem vhodnem materialu.

Preiskovali smo zlitino AlSi10Mg proizvajalcev Z1, Z2 in Z3 in sicer s trojno enostavno termično analizo, simultano termično analizo, z računalniško simulacijo Thermo-Calc ter metalografsko analizo.

Za vsako zlitino različnih proizvajalcev smo preizkus trojne enostavne termične analize ponovili trikrat. Glede na hitrost ohlajanja smo oznakam pripisali končnico a za ohlajanje v peščeni kokili, b za ohlajanje v veliki jekleni kokili ter c za ohlajanje v mali jekleni kokili.

Kemijsko analizo smo opravljali na vhodnih materialih Z1, Z2 in Z3 ter na vzorcih po končani trojni enostavni termični analizi.

Meritve trojne enostavne termične analize so potekale v treh različnih lončkih hkrati. Uporabili smo dva merilna lončka (kokili) iz sive litine z notranjim premerom 30 mm

in z notranji premer 15 mm, tretji merilni lonček pa je bil izdelan po postopku Croning premera 30 mm. V vsak merilni lonček smo v isti višini namestili na sredino termoelement tipa K (Ni-CrNi) ter jih priključili na merilno kartico National Instruments DAQPad-MI0-16XE-50, le-to pa na osebni računalnik na katerem smo s pomočjo programskega paketa LabVIEW 5.0 zajemali merilne vrednosti ter jih sproti grafično in tabelarično beležili. Pripravljene zlitine, mase približno od 230 g do 250 g, smo stalili v grafitnem lončku s pomočjo indukcijske peči. Ko je talina dosegla temperaturo 750 °C, smo odkrili lonček, odstranili oksidno plast in vlili talino v vse tri merilne lončke.

Z računalniško aplikacijo Thermo-Calc smo izdelali simulacijo termodinamičnih ravnotežij zlitine Z1, Z2 in Z3. V programu smo izbrali ustrezno bazo podatkov, iz periodnega sistema pa izbrali elemente, ki so sestavljali našo zlitino. Program nam je izpisal vse termodinamično možne faze, ki so prisotne pri določenih pogojih in skonstruiral binarni ravnotežni fazni diagram.

Vzorci zlitin Z1, Z2 in Z3 so bili preiskani s simultano termično analizo. Na platinasti senzor aparature STA 449 firme NETZSCH smo vstavili dva enaka lončka. V en lonček smo dali preiskovani material, v drugega pa primerjalni (inertni) vzorec. Meritve smo opravljali v zaščitni atmosferi zaščitnega plina 99,999 % N<sub>2</sub>. Vzorce smo segrevali do temperature 720 °C s hitrostjo 0,17 °C/s in jih ohlajali z enako hitrostjo do sobne temperature.

Vzorce za metalografske preiskave smo

pripravili iz vzorcev od trojne enostavne termične analize. Ustrezno razrezane vzorce smo vroče vložili v umetno maso ter jih nato mehansko pripravili (brusili in polirali). Pripravljene vzorce smo nato opazovali in slikali z optičnim mikroskopom Nikon Microphot FXA, ki je opremljen s 3CCD-videokamero Hitachi HV-C20A in računalniškim programom analySIS za analizo metalografskih slik.

S termično analizo določene povprečne vrednosti hitrosti ohlajanja znašajo v peščenem lončku izdelanem po postopku Croning v območju med 4 in 6 °C/s, v jeklenem lončku premera 30 mm v območju med 30 in 45 °C/s in v jeklenem lončku premera 15 mm v območju med 90 in 110 °C/s. Ugotovili smo, da z naraščajočo ohlajevalno hitrostjo karakteristične temperature trojne enostavne termične analize padajo, podhladitve pa se večajo.

Pri ohlajanju zasledimo s pomočjo diferenciranih ohlajevalnih krivulj izločanje faze Mg<sub>2</sub>Si, ki se začne pri temperaturi 537 °C. Računalniška simulacija s programom Thermo-Calc nam potrdi nastajanje te faze pri temperaturi 535 °C pri Z1, pri 549 °C pri Z2 ter pri 556 °C pri Z3. Literaturni viri navajajo izločanje faze Mg<sub>2</sub>Si pri temperaturi 554 °C.

Literaturni vir navaja možnost nastanka faze  $\alpha\text{-Al}_{15}(\text{Fe,Mn,Me})_3\text{Si}_2$  (Me=Cr,Cu), ki jo zasledimo v mikrostrukturi kot labirintasti heterogeni zlog, z naraščajočo temperaturo litja pa je te faze manj.

Z metalografsko analizo ugotovimo, da se mikrostrukture glede na proizvajalca razlikujejo med seboj. V vzorcu iz zlitine Z2

je mikrostruktura izločenega evtektika bistveno enakomerneje razporejena v primerjavi z vzorcem iz zlitine Z1. Z naraščajočo hitrostjo ohlajanja dosežemo manjše izoblikovane primarne zmesne kristale  $\alpha_{Al}$ , izognemo pa se nastanku iglic faze  $\beta-Al_5FeSi$ , ki neugodno vplivajo na mehanske lastnosti končnih ulitkov.

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## Plinsko in ionsko nitriranje orodij iz AISI H10 in H13 za toplo ekstruzijo aluminija ter njihova stabilnost kakovosti

## Gas and ion nitriding of dies for aluminium hot extrusion made from AISI H10 and H13 steels and their stability of quality

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**Izvleček:** Orodja z ozkimi in globokimi režami, izdelana iz jekla AISI H10 in H13, so bila nitrirana pri različnih proizvajalcih naprav za ionsko in plinsko nitriranje, pri čemer so proizvajalci sami izbrali parametre nitiranja. Dobljene mikrostrukture kažejo na razlike glede na prisotnost ali odsotnost spojinske plasti (bele plasti), njene debeline in variiranja faznega razmerja  $\epsilon/\gamma$  v tej plasti ter glede na globino nitiranja (difuzijsko cono) in trdotni profil. Dobljene globine nitiranja, maksimalne vrednosti za trdote in  $\epsilon/\gamma$  fazno razmerje so ponavadi podobni za orodja nitrirana pri istem proizvajalcu, medtem ko za različne proizvajalce naprav te vrednosti variirajo. Ugotovljene so bile manjše razlike med mikrostrukturami v 1 mm in 4 mm reži, ki so tudi posledica različnega strujanja plinske mešanice. Nitirani vzorci so bili testirani na obrabo z "blok na cilinder" testno napravo. Strukture spojinskih plasti, ki so bližje monofazni, ob dovolj veliki trdoti in globini nitiranja, izkazujejo njeno poznejše luščenje. To rezultira v daljši življenski dobi orodja, saj spojinska plast ščiti površino orodja pred kemičnim reagiranjem z vročim Al.

**Abstract:** A specially shaped die (AISI H10 and H13) with 1 and 4 mm narrow gap was developed to analyse the efficiency of nitriding process in narrow gaps. The dies were gas or ionic nitrided at various manufacturers of nitriding equipments. The manufacturers themselves, based on their experience with extrusion dies, chose the optimal nitriding parameters. The microstructure obtained showed differences with regard to the presence or absence of a compound layer, its thickness and  $\epsilon/\gamma$  phase ratio (XRD), nitriding depth and microhardness values. The nitriding depths obtained, the maximum microhardness of the nitrided surfaces and  $\epsilon/\gamma$  phase ratio are usually similar on dies of the same manufacturer, while for different manufacturers these values differ. The different characteristics of the nitrided microstructures resulted in various times of compound layer spalling (removal) during testing for wear resistance. On the sites of compound layer removal accelerated chemical attack took place that increased wear on the die surface. The compound layer is chemically more resistant to hot aluminium in comparison to nitrided base material. Earlier removal of the compound layer consequently results in decreased die life and later removal leads to prolongation of die life.

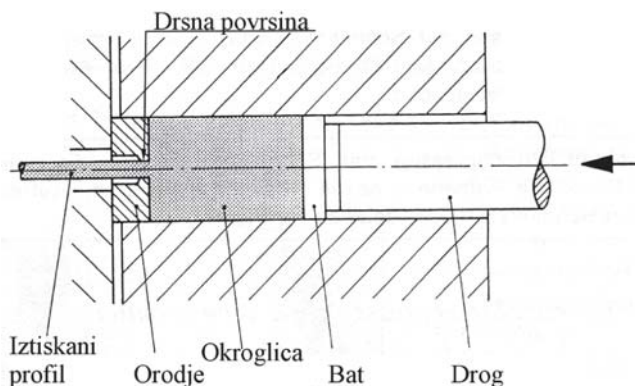
**Ključne besede:** Topla ekstruzija Al, AISI H10, AISI H13, nitriranje, spojinska plast, obraba.  
**Key words:** Al hot extrusion, AISI H10, AISI H13, nitriding, compound layer, wear.

## 1. Uvod

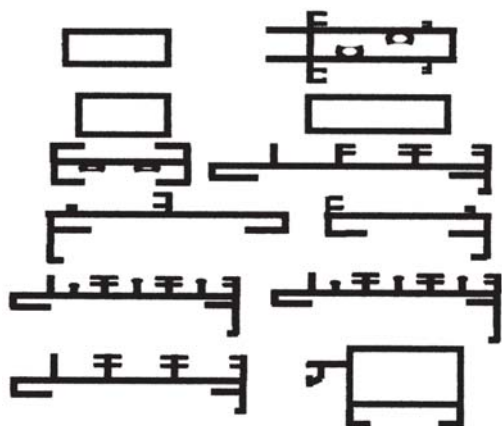
Toplo stiskanje aluminija (slika 1) je postopek, pri katerem se na cca. 450-500°C ogreta okroglica iztiskuje skozi odprtino na orodju, ki daje profilu želeno obliko. Potrebne sile stiskanja so v območju med 10-55 MN, izstopne hitrosti profila pa do 100 m/min. Poškodbe in tribološke razmere na drsni površini omenjene odprtine orodja vplivajo na kakovost površine ekstrudiranca. Kontaktni pritiski na drsni površini orodij dosegajo vrednosti do 100 MPa, temperature pa lahko lokalno porastejo celo nad 600°C, saj se med procesom ekstruzije generira veliko toplote, ki je posledica volumskega stiskanja okroglice in trenja na kontaktu iztiskovanega profila in površine orodja. Najpogosteje uporabljeno orodno jeklo za izdelavo matrice je AISI H13, pa tudi H11 in H10. Življenjska doba orodja je determinirana z dopustnimi tolerancami prečnega preseka, kot tudi z lepim izgledom površine ekstrudiranca [1-4].

Od orodij za toplo ekstruzijo aluminija zahtevamo, da imajo čim večjo odpornost proti abraziji, adheziji in mehanskemu utrujanju ter kemično obstojnost. Več o

kemičnih reakcijah med vročim Al in orodjem si bralec lahko prebere v literaturi [14-15]. Boljšo obrabno obstojnost in s tem daljšo življenjsko dobo orodij dosegamo z dodatnim oplemenitjenjem površine orodja in sicer s plinskim nitiranjem, ionskim nitiranjem, nitiranjem v kopeli, s CVD ali PVD prevlekami, dupleks postopki, itd [5-12]. Slabost nitiranja v kopeli je predvsem škodljiv vplivu tega postopka na okolje, omejitev PVD postopka pa je vezana na težave učinkovitega oplaščevanja površin, ki ležijo v ozkih in dolgih režah. Na orodjih so omenjene ozke in globoke reže zelo pogosto prisotne; ekstrudirani profili so namreč zaradi težnje po čim večjem vztrajnostnem momentu in tankih stenah posledično tudi zelo kompleksnih oblik (slika 2). Zaradi slednjega je plinsko nitiranje še vedno aktualno, saj je učinkovito tudi v ozkih in dolgih režah orodij. Pri nitiranju orodnih jekel (AISI H13, H11 in H10) pogosto nastaja spojinska plast (bela plast). Kemična sestava orodij in stanje površine, ki jo želimo nitirati, kot tudi pravilna nastavitve parametrov žarjenja in nitiranja (plinska mešanica in njen pretok, temperatura, čas, itd.), vplivajo na nastanek in rast spojinske plasti (bele plasti), na razmerje faz ( $\epsilon$  in  $\gamma'$ ) v njej ter na difuzijo dušika v jekleno matico [5-8,12]. Mnenja



Slika 1. Princip tople ekstruzije aluminija in drsna površina na orodju.



**Slika 2.** Raznolikost ekstrudiranih profilov z ozkimi režami.

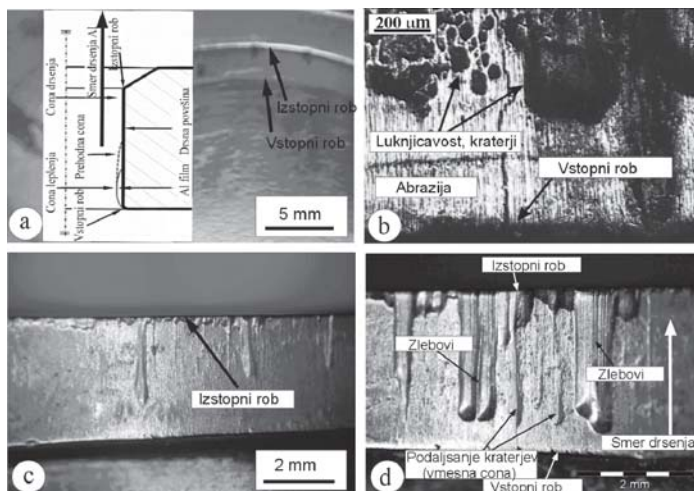
v literaturi o tem, ali spojinska plast pozitivno oz. negativno vpliva na obrabno obstojnost površine orodij so zelo deljena. Tudi proizvajalci naprav za ionsko in plinsko nitiranje niso enotnega mnenja o tem, katera mikrostruktura jekla nastala pri nitiranju je obrabno najbolj obstojna. Tako nekateri belo plast odklanjajo, nasprotno pa drugi želijo nitrirane plasti s tankimi (3-5  $\mu\text{m}$ ) belimi

plastmi <sup>[1]</sup>. Iz prakse je tudi znano, da življenjska doba nitriranih orodij, celo pri ekstrudiranju enakega profila, zelo niha.

V prispevku so podane in analizirane mikrostrukture površin v zato posebej izdelanih ozkih in globokih režah orodij iz jekel AISI H10 in H13, ki so bila nitrirana pri različnih proizvajalcih naprav za ionsko in plinsko nitiranje, nadalje je podana njihova fazna analiza (XRD), trdote, itd. Opravljeni preizkusi obrabe na nitriranih površinah so fokusirani na pojasnjevanje vloge spojinske plasti glede njene kemične odpornosti v kontaktu z vročim aluminijem.

## 2. POTEK (ANALIZA) OBRABE NITRIRANE DRSNE POVRŠINE NA REALNEM ORODJU

Na drsni površini orodja (slika 3a) nastopajo tri različne cone in sicer cona lepljenja, prehodna (tranzicijska) cona in cona



**Slika 3.** Faze napredovanja obrabe na nitrirani drsni površini orodja (a.) za toplo ekstruzijo okroglega profila, kemično reagiranje (luknjicavost) v coni tranzicije in formiranje kraterjev (b.) ter širitve (podaljševanje) kraterjev proti izstopnemu robu drsne površine (c.) - (d.).

drsenja <sup>[13]</sup>. Obrabi je najbolj izpostavljena prehodna cona, saj prav na tem mestu pride do občasnega sprijemanja (lepljenja) ekstrudiranega materiala s površno orodja in s tem tudi do kemičnih reakcij (aktivnosti) ter do ločitve omenjene zveze. Posledica tega je tvorba luknjičavosti (eng. pitting), ki pozneje vodi do tvorbe majhnih kraterjev (slika 3b), kateri se med nadaljnjim procesom ekstruzije počasi razširijo (podaljšajo) v smeri drsenja Al profila na celotno drsno cono vse do izstopnega roba drsne površine (slika 3c-d). Pri tem so prisotni obrabni mehanizmi kot kemično reagiranje aluminija s površino orodja, abrazija in adhezija.

### 3. IONSKO IN PLINSKO NITRIRANJE ORODIJ Z OZKIMI IN GLOBOKIMI REŽAMI

Naša študija temelji na analizi nitriranih mikrostruktur orodij z 1 mm in 4 mm režo (slika 4).

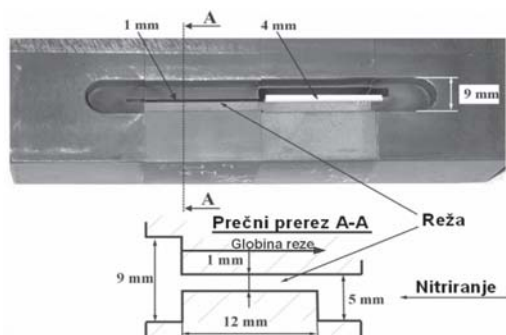
Kemična sestava uporabljenih orodnih jekel iz AISI H10 in H13, ki so bila nitrirana pri osmih različnih proizvajalcih naprav za ionsko (proizvajalec I-II) in plinsko nitiranje (proizvajalec IV-VIII), je podana v tabeli 1. Od proizvajalcev naprav (tabela 2) se je zahtevala izpolnitev dveh pogojev in sicer:

- celoten čas postopka nitiranja ne sme presegati 12 ur,
- minimalna globina nitiranja lahko znaša 120  $\mu\text{m}$ .

Proizvajalci so sami izbrali parametre nitiranja (vrednosti parametrov ne želijo posredovati) t.j. optimalno plinsko mešanico in pritisk, temperaturo, čas nitiranja, ohlajanje, itd. Iz nitiranega orodja smo potem s pomočjo elektroerozije izrezali

manjše bloke za analizo mikrostrukturne in meritve trdote difuzijske plasti, opravili fazno analizo in izmerili debelino spojinske plasti ter eksperimentalno indentificirali obrabo. Orodje z ozkimi in globokimi reži je bilo izbrano za primerjavo učinkovitosti plinskega z ionskim nitiranjem; namreč, ozke reže so na orodjih za ekstruzijo preje omenjenih kompliciranih oblik profilov pogosto prisotne in predstavljajo omejitev pri uporabi ionskega nitiranja. Ionsko nitiranje je namreč relativno neučinkovito v omenjenih ozkih in globokih režah orodij.

Tako za plinsko, kot tudi za ionsko nitrirana orodja, je značilna možnost nastanka spojinske plasti, na kar pri plinskemu nitiranju vplivajo sledeči parametri: temperatura in čas nitiranja, vrsta orodnega jekla, kemična sestava plinske mešanice in strujanje plina v peči (parcialni tlak dušika), čas nitiranja, itd. Dostopna literatura še ne poroča o učinkovitosti plinskega nitiranja v ozkih in globokih režah oz. kako na to vpliva intenziteta lokalnega strujanja plinske mešanice. Pri vplivu spojinske plasti na obrabno obstojnost je potrebno upoštevati, da ta nima enotne debeline, ampak se le-ta spreminja. To ima za posledico povečanje hrapavosti na mestu njenega luščenja in s tem tudi površine za cca. 100% <sup>[12]</sup>.



Slika 4. Orodje z 1 in 4 mm režo ter prečnim presekom A-A.

**Tabela 1.** Kemčna sestava uporabljenih orodnih jekel, (AISI, METAL Ravne), [mas.%].

| Metal Ravne | AISI | C    | Si   | Mn   | Cr   | Mo   | V    | Fe   |
|-------------|------|------|------|------|------|------|------|------|
| Utop 33     | H10  | 0.30 | 0.30 | 0.38 | 3.0  | 2.80 | 0.45 | Ost. |
| Utop Mo2    | H13  | 0.40 | 1.0  | 0.40 | 5.05 | 1.28 | 0.95 | Ost. |

**Tabela 2.** Seznam proizvajalcev za ionsko (ION) in plinsko (GSN) nitiranje orodij, debeline spojinske plasti (DSP), globine difuzijske plasti (GDP), in maksimalne vrednosti trdote (MHRD) v 1 mm in 4 mm visoki reži na orodjih iz jekel H10 in H13.

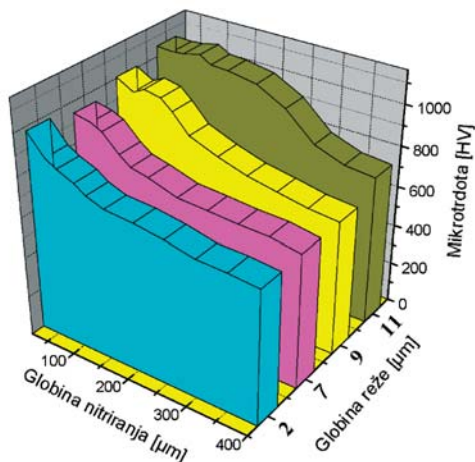
| Proizvajalec    |      | I.                     | II.      | III. | IV.  | V.   | VI.  | VII. | VIII. |
|-----------------|------|------------------------|----------|------|------|------|------|------|-------|
| Način nitiranja |      | ION                    | ION      | PLN  | PLN  | PLN  | PLN  | PLN  | PLN   |
|                 | Reža | Glavni parametri - H10 |          |      |      |      |      |      |       |
| DSP[μm]         | 1mm  | /                      | /        | 4-12 | 4-12 | 8-14 | 8-12 | 4-10 | 5-10  |
|                 | 4mm  | /                      | 0-5      | 4-8  | 6-13 | 8-14 | 8-12 | 6-12 | 6-12  |
| GDP [μm]        | 1mm  | 170-30                 | 150-70   | 120  | 160  | 180  | 120  | 160  | 150   |
|                 | 4mm  | 150-70                 | 340-100  | 110  | 180  | 180  | 130  | 170  | 150   |
| MHRD [Hv]       | 1mm  | 1200-700               | 934-819  | 1135 | 1120 | 1130 | 1020 | 1092 | 1120  |
|                 | 4mm  | 1185-1065              | 1054-945 | 1146 | 1130 | 1130 | 1035 | 1100 | 1146  |
|                 | Reža | Glavni parametri - H13 |          |      |      |      |      |      |       |
| DSP[μm]         | 1mm  | /                      | /        | 4-12 | 4-12 | 5-8  | 8-12 | 4-10 | 3-7   |
|                 | 4mm  | /                      | /        | 8-16 | 6-13 | 8-12 | 8-12 | 6-12 | 5-8   |
| GDP [μm]        | 1mm  | 170-30                 | 150-70   | 120  | 130  | 150  | 120  | 140  | 130   |
|                 | 4mm  | 150-70                 | 340-100  | 110  | 140  | 150  | 120  | 150  | 140   |
| MHRD[Hv]        | 1mm  | 1200-500               | 850-790  | 1050 | 1100 | 1150 | 1020 | 1090 | 1080  |
|                 | 4mm  | 1185-700               | 1054-900 | 1070 | 1100 | 1150 | 1035 | 1100 | 1080  |

#### 4. MIKROSTRUKTURA, FAZNA SESTAVA IN TRDOTA JEKLA NA POVRŠINI

##### 4.1 Ionsko nitiranje

Na orodjih iz obeh uporabljenih jekel in nitriranih pri proizvajalcih I in II, smo ugotovili (izmerili) razlike tako v globini nitiranja (difuzijska cona) v 1 mm in 4 mm reži, kot tudi v zvezi s spojinsko plastjo (prisotnost oz. neprisotnost). Globina nitiranja je bila določena na osnovi merjenega profila trdot. Boljša učinkovitost nitiranja v 4 mm reži, v primerjavi z 1 mm režo, je značilna za oba proizvajalca. Proizvajalec II je bil uspešnejši v obeh primerih, čeprav uspešnost nitiranja v 1mm

reži ne zadošča postavljenim pogojem. Na sliki 5 je prikazan profil trdote (globina nitiranja) za proizvajalca št. II v 4 mm reži in orodje iz jekla H10. Vidimo lahko, da je globina nitiranja med cca. 340 μm na začetku, in cca. 100 μm na koncu 12 mm reže. V 1mm reži pa dobimo 150 μm na začetku, in 70 μm na koncu reže, kar so prenizke vrednosti za orodja za toplo ekstruzijo Al. Za proizvajalca I velja, da so mikrostrukture v 1 in 4 mm reži brez spojinske plasti. Enako velja za 1 mm režo pri proizvajalcu II medtem ko smo v 4 mm reži dobili 0-5 μm debelo belo plast. Dejstvo, da smo v 4 mm reži dobili spojinsko plast, v 1mm reži pa ne, lahko pripišemo različnemu strujanju (histrosti) plinske mešanice znotraj 1 in 4 mm reže in temu posledično tudi različnemu gradientu vplivnih parametrov



**Slika 5.** Potek trdotne pod površino ionsko nitiranega jekla H10 v štiri milimetrski reži, proizvajalec II.

(tlak, temperatura, itd). Tudi pri drugem orodju obeh proizvajalcev smo dobili podobne rezultate za globino nitiranja in maksimalne trdote na površini. Proizvajalec II bi torej lahko zadovoljivo nitiral v 4 mm režah le v primeru, če so te krajše (cca. 5 mm). Iz prakse je znano, da je dolžina drsnih površin ponavadi v območju med 3,5 mm do 12 mm.

Za orodje iz jekla H13 so bili dobljeni podobni mikrotrdotni profili, le da so bile vrednosti za trdote še nekoliko nižje.

## 4.2 Plinsko nitiranje

Orodja iz jekel H10 in H13 so bila nitrirana pri šestih različnih proizvajalcih naprav za plinsko nitiranje. Dobili smo precej podobne vrednosti tako za maksimalne trdote, kot tudi za globine nitiranja na orodjih nitriranih pri istem proizvajalcu. To velja za obe orodni jekli, pri čemer smo za jeklo iz H10 dobili nekoliko višje globine nitiranja in maksimalne vrednosti za trdote (tabela 2). Naslednja značilnost je, da večina orodji za jeklo iz H10 posedujejo belo plast, katere

debelina pa se ponavadi malo razlikuje glede na 1 mm in 4 mm režo (tabela 2). V 1 mm reži smo dobili manjše trdote. V isti tabeli so podane še globine nitiranja za 1 in 4 mm režo. Pri orodjih iz jekla H13 je bilo opaziti večjo variabilnost glede prisotnosti oz. neprisotnosti spojinske plasti saj je bila na nekaterih orodjih prisotna na drugih pa ne. Na slikah 6a-l so podane tipične mikrostrukture tako brez spojinske plasti, kot tudi z spojinsko plastjo na površini orodja iz jekla H13, katere debelina se rahlo spreminja od orodja do orodja, še bolj pa od proizvajalca do proizvajalca. V nekaterih primerih ni spojinske plasti. To nas napeljuje na sklep, da je proces nitiranja zelo občutljiv; strujanje plinske mešanice namreč ni konstantno po celotnem volumnu peči kar pomeni, da so relevantni parametri za nitiranje odvisni od pozicije orodja v peči oz. od razmer na lokalnem nivoju, kar rezultira v različnih dobljenih mikrostrukturah nitriranih plasti. Debeline spojinske plasti, maksimalne trdote in globine nitiranja so za orodno jeklo H13 prav tako podane v tabeli 2.

Tudi fazna analiza nitriranih površin kaže na podobno razmerje faz  $\alpha/\alpha'$  med orodji nitriranih pri istih proizvajalcih in sicer tako za orodja iz jekla H10 (slika 7) kot tudi za orodja iz jekla H13.

### Orodja iz jekla H10:

Kot je bilo že omenjeno, smo pri jeklu H10 skoraj pri vseh nitriranih orodjih dobili spojinsko plast na površini. Proizvajalec III je v 1 mm reži dosegel relativno majhno globino nitiranja, ki znaša cca. 120  $\mu\text{m}$ , maksimalna vrednost trdote pa cca 1146 HV, debelina spojinske plasti pa 4-12  $\mu\text{m}$ . V 4mm

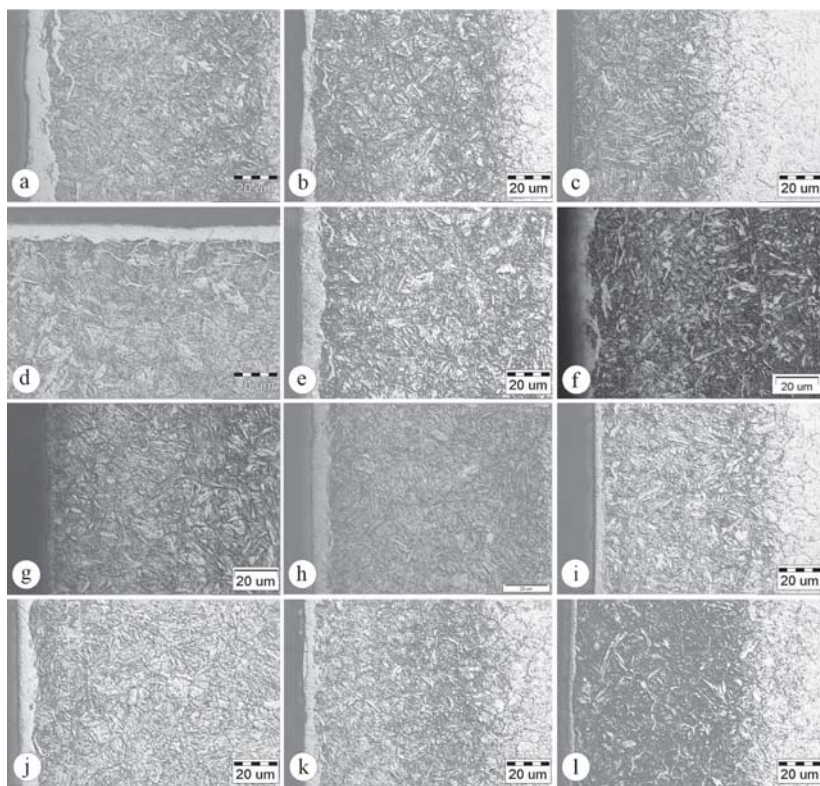
reži je bila dosežena globina nitiranja cca. 110  $\mu\text{m}$ , debelina spojinske plasti cca. 4-8  $\mu\text{m}$ , maksimalna trdota je cca. 1135 HV. Fazna analiza (XRD) na nitirani površini (slika 7) razkriva precej večji delež faze  $\epsilon$  kot faze  $\gamma$  ter železove okside. Ocenjeno  $\epsilon/\gamma$  fazno razmerje znaša cca. 6, kar pomeni, da je sestava spojinske plasti relativno blizu  $\epsilon$  monofazni mikrostrukturi.

Proizvajalec IV je v 1 mm reži dosegel relativno veliko globino nitiranja, t.j. cca. 160  $\mu\text{m}$ , maksimalna trdota je cca. 1120 HV, debelina spojinske plasti pa cca. 4-12  $\mu\text{m}$ . V 4 mm reži je bila namerjena globina nitiranja cca. 180  $\mu\text{m}$ , malenkostno večja debelina

spojinske plasti, t.j. cca. 6-13  $\mu\text{m}$ , in maksimalna trdota cca. 1130 HV. XRD (slika 7) nam razkriva velik delež  $\epsilon$  in nekoliko več faze  $\gamma$  glede na orodja pri proizvajalcu III. Ocenjeno fazno razmerje  $\epsilon/\gamma$  znaša cca. 3 (slika 7), kar je manj kot v pri proizvajalcu III.

Za proizvajalca V je značilna velika globina nitiranja cca. 180 mm za obe reži, debelina spojinske plasti cca. 8-14 mm ter maksimalna trdota cca. 1130 HV. Ocenjeno fazno razmerje  $\epsilon/\gamma$  znaša cca. 0,7 (slika 7), kar pomeni, da je v spojinski plasti več faze  $\gamma$ .

Za proizvajalca VI je značilna relativno majhna globina nitiranja cca. 120-130  $\mu\text{m}$ ,



**Slika 6.** Variabilnost mikrostruktur iz jekla H13 med orodji in različnimi proizvajalci: (a-c) - proizvajalec III, (d) - proizvajalec IV, (e-g) - proizvajalec V, (h) - proizvajalec VI, (i-j) - proizvajalec VII, (k-l) - proizvajalec VIII, OM, jedkano z nitalom.

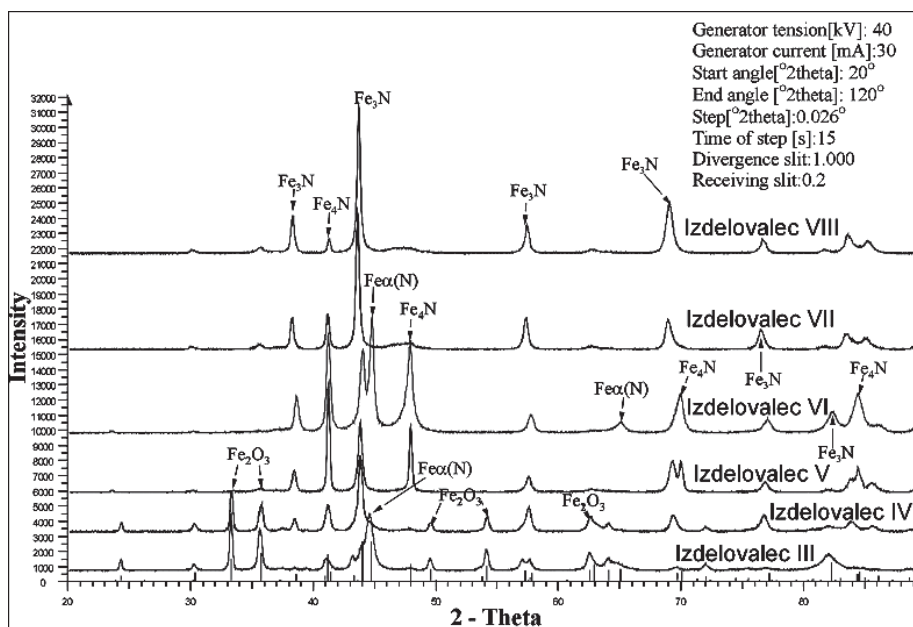
debelina spojinske plasti cca. 8-12  $\mu\text{m}$ , ter maksimalna trdota cca 1030 HV. XRD nam pokaže veliko faze  $\gamma'$  (ocenjeno fazno razmerje  $\epsilon/\gamma'$  znaša cca. 0,8) ter tudi vrh  $\alpha_{(\text{Fe})}$  kar pomeni, da spojinska plast verjetno ni prekrila celotne nitrirane površine ali pa je ta pretanka. To posledično odpira vprašanje o učinkovitosti plinskega nitiranja v ozkih in globokih režah tega proizvajalca.

Za proizvajalca VII je značilna relativno velika globina nitrirane plasti in sicer v 1 mm reži znaša cca. 160  $\mu\text{m}$ , debelina spojinske plasti pa cca. 4-10  $\mu\text{m}$  ter 170  $\mu\text{m}$  oz. 6-12  $\mu\text{m}$  v 4 mm reži. Maksimalne trdote so cca. 1100 HV. XRD nitrirane plasti pokaže na veliko faze  $\epsilon$  ter malo faze  $\gamma'$ . Ocenjeno fazno razmerje  $\epsilon/\gamma'$  znaša cca. 4.

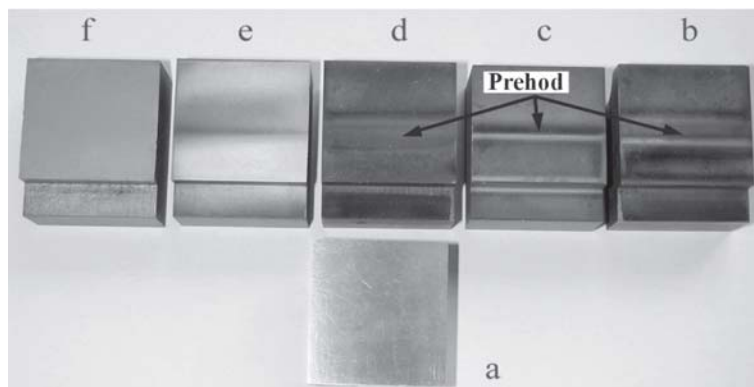
Za proizvajalca VIII je značilna nekoliko nižja globina nitiranja v obeh režah t.j. cca.

150 mm, debelina spojinske plasti pa znaša 5-10  $\mu\text{m}$  v 1 mm reži in 6-12  $\mu\text{m}$  v 4 mm reži. Maksimalne trdote so cca. 1120-1150 HV. XRD analiza razkrije skoraj monofazno mikrostrukturo spojinske plasti, saj ima ocenjeno fazno razmerje  $\epsilon/\gamma'$  znaša cca. 10.

Vzroke za prisotnost oz. neprisotnost spojinske plasti in ponavadi malenkostno večjo globino nitiranja in debelino spojinske plasti v 4 mm reži je treba iskati v že omenjenem različnem strujanju plinske mešanice tako v peči za nitiranje, kot tudi v 1 in 4 mm reži. Na sliki 8 so prikazani površinski izgledi nitriranih površin nekaterih blokov, kjer je jasno viden prehod iz 9 mm reže na 1 oz. 4 mm režo, kar nakazuje na vpliv lokalnega strujanja (hitrost, pritisk, itn.) plinske mešanice na nitiranje.



Slika 7. Fazna analiza (XRD) nitriranih površin orodij iz jekla H10 pri proizvajalcih III-VIII.



**Slika 8.** Izgled nekaterih plinsko nitriranih površin z jasnim prehodom iz 9 mm reže v 1 oz. 4 mm režo.

## 5. INDIVIDUALNO TESTIRANJE OBRABE NITIRANIH MIKROSTRUKTUR

Posebna izvedba "blok na cilinder" naprave za študij obrabe (slika 9) je omogočilo testiranje pri povišanih temperaturah in visokih kontaktnih pritiskih, ki so značilni za toplo ekstruzijo Al; testni pogoji so podani v tabeli 3. Dimenzije ogretyh cilindrov iz zlitine AA 6063 (0.5 Mg, 0.5 Si, 0.19 Fe, 0.05 Mn), ki predstavljajo ogreti ekstrudiranec, so bile premera  $\Phi 146$  mm x 35 mm, dimenzije testiranih blokov pa so bile 30 mm x 30 mm x 20 mm. Ogrevanje Al cilindrov je induktivno s pomočjo tuljave s samo polovico ovoja. Na obeh straneh Al cilindra sta nameščena bakrena diska, preko katerih je tudi posredno kontrolirana temperatura Al (sevalni koeficient bakra znaša cca. 0,8); namreč, sevalni koeficient Al je zelo nizek in napake meritev na Al cilindru bi posledično lahko bile zelo velike. Nadalje, omenjeni bakreni diski omogočajo testiranje pri visokih kontaktnih pritiskih, kar ima za posledico krajše potrebne čase testiranja, sočasno pa onemogočajo plastično defor-

macijo Al cilindrov. V realnem procesu tople ekstruzije drsenje med površino orodja in ekstrudirancem poteka v skoraj neoksidativnih pogojih, zato med testiranjem v komoro dovajamo argon (kemična sestava v volumskih ppm:  $O_2$  max 5 ppm,  $H_2O$  max 10 ppm,  $CO_2$  max 0,5 ppm,  $N_2$  max 20 ppm). Testiranje obrabe z vročim Al sodijo med najbolj zahtevna tribološka testiranja, zato so objave s tega področja v literaturi tudi zelo redke. Pri topli ekstruziji so eksperimentalni podatki o vlogi spojinske plasti pri življenjski dobi orodja še posebej zaželeni, saj je študij v industrijskih pogojih zelo otežen.

Pri laboratorijskem testiranju (testni pogoji 1, tabela 3) nas je zanimal predvsem vpliv spojinske plasti na obrabno obstojnost: in sicer njena odpornost proti kemičnemu reagiranju z vročim aluminijem, način njene odstranitve z nitrirane površine ter odziv tako nanovo nastale površine na kontakt z vročim Al. Začetno stanje površine je podano na slika 10a. Opazili smo, da je za odstranitev spojinske plasti bistven proces nastanka razpok na njeni površini (slika 10b) kar vodi do njenega postopnega (delnega) luščenja

(40-60 %), kot je prikazano na slika 10c. To nas tudi napeljuje na dejstvo, da je duktilnost spojinske plasti zelo pomembna karakteristika, ki bo vplivala na čas njene odstranitve. Nadalje, na mestu odstranitve spojinske plasti začne vroč aluminij (cca. 570 °C, relativno blizu tališča) pospešeno reagirati z novo nastalo površino (slika 10c). Vzrok za to lahko pripišemo povečanju hrapavosti na mestu odstranitve spojinske plasti, kar ima za posledico povečanje (cca. 100 % <sup>[12]</sup>) površine, potencialno primerne za kemično reagiranje s toplim Al; spojinska plast namreč ni enakomerne debeline, kot je to vidno iz slik 6a-f ter iz tabele 2. Proces delnega luščenja spojinske plasti in pospešenega kemičnega reagiranja smo opazili na vseh testiranih blokih, razlikoval se je le čas, ko je prišlo do pojava luščenja (tabela 4). Iz slike 10c je tudi razvidno, da je spojinska plast kemično bolj obstojna proti vročemu Al kot osnovni material, saj so ta mesta (Ang. pitting) na spojinski plasti komaj opazna. Poslabšanje kvalitete površine v poznejši fazi testiranja je verjetno posledica intenzivnega kemičnega reagiranja z razkrito površino, pa tudi adhezije (slika 10d).

V tabeli 4 so podani približni časi delnega luščenja (cca. 40-60 %) spojinske plasti za nekatere proizvajalce oz. za nekatere tipične lastnosti nitriranih mikrostruktur in sicer za H10 in H13. Manj krhke so monofazne spojinskih plasti, pri čemer pa je vsekakor bolj zaželjena  $\gamma'$ , ki je manj krhka kot  $\epsilon$ . S tega vidika je bila dobljena spojinska plast proizvajalca III relativno ugodna, vendar je

zaradi manjše globine nitriranja in manjših maksimalnih trdot prišlo do delnega luščenja (cca. 40-60 %) že po eni uri testiranja (tabela 4). Isto je bilo opaženo tudi pri proizvajalcu V, z relativno neugodno fazno sestavo spojinske plasti, kljub relativno veliki globini nitriranja in visokih maksimalnih vrednosti trdote.

Delno luščenja spojinske plasti po dveh urah (tabela 4) pa je bilo opaženo pri proizvajalcu VII. Omenjena mikrostruktura namreč poseduje strukturo spojinske plasti, ki vsebuje malo  $\gamma'$  faza in relativno zelo globoko difuzijsko plast. Spojinska plast proizvajalca VIII je skoraj monofazna ( $\epsilon$ ), poleg tega pa ima še relativno veliko globino difuzijske plasti (150  $\mu\text{m}$ ), kar je rezultiralo z delnim luščenja po 2 dveh urah testiranja (slika 10c).

Kot je bilo že omenjeno so rezultati delnega luščenja spojinske plasti za obe nitrirani jekli podani v tabeli 4.

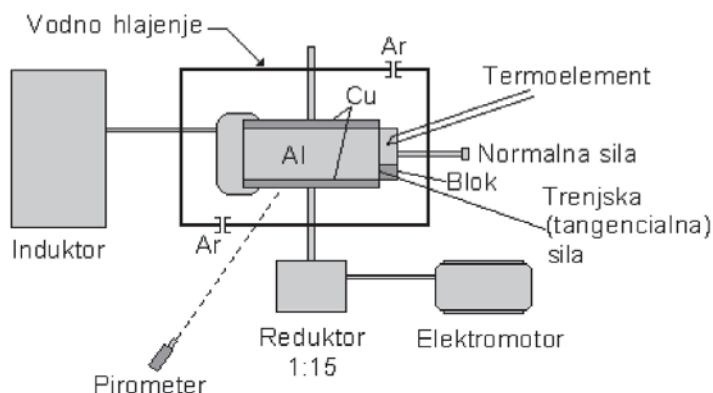
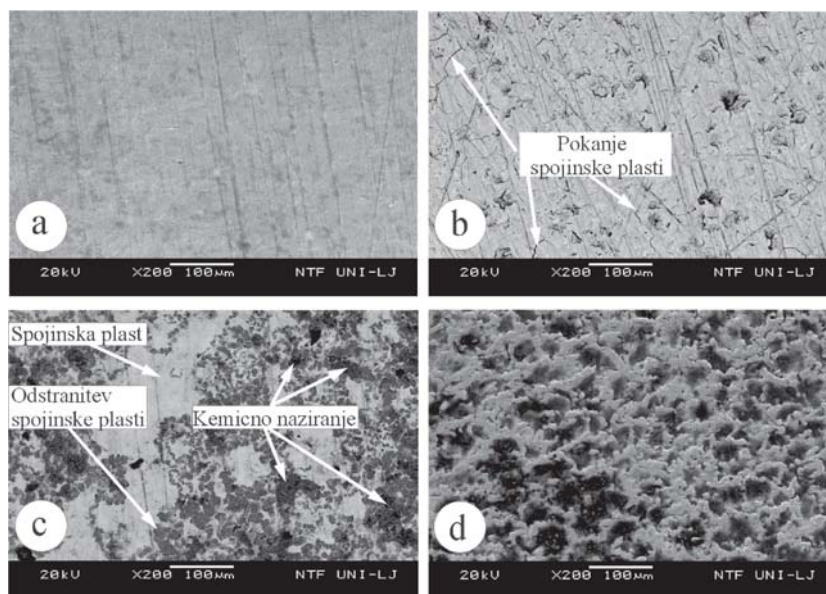
Potek obrabe površin, kot je prikazan na slika 10a-d, je značilen za vse testirane mikrostrukture. Karakteristike spojinske plasti in difuzijske cone pa pogojujejo dinamiko obrabnih procesov na testirani površini oz., kdaj bo nastopilo določeno stanje na površini, kot je prikazano na prej omenjeni sliki. Kdaj bo prišlo do luščenja spojinske plasti je odvisno od predvsem od njene mikrostrukture (zaželena monofazna mikrostruktura) in nosilnosti difuzijske plasti (zaželena čim večja nosilnost).

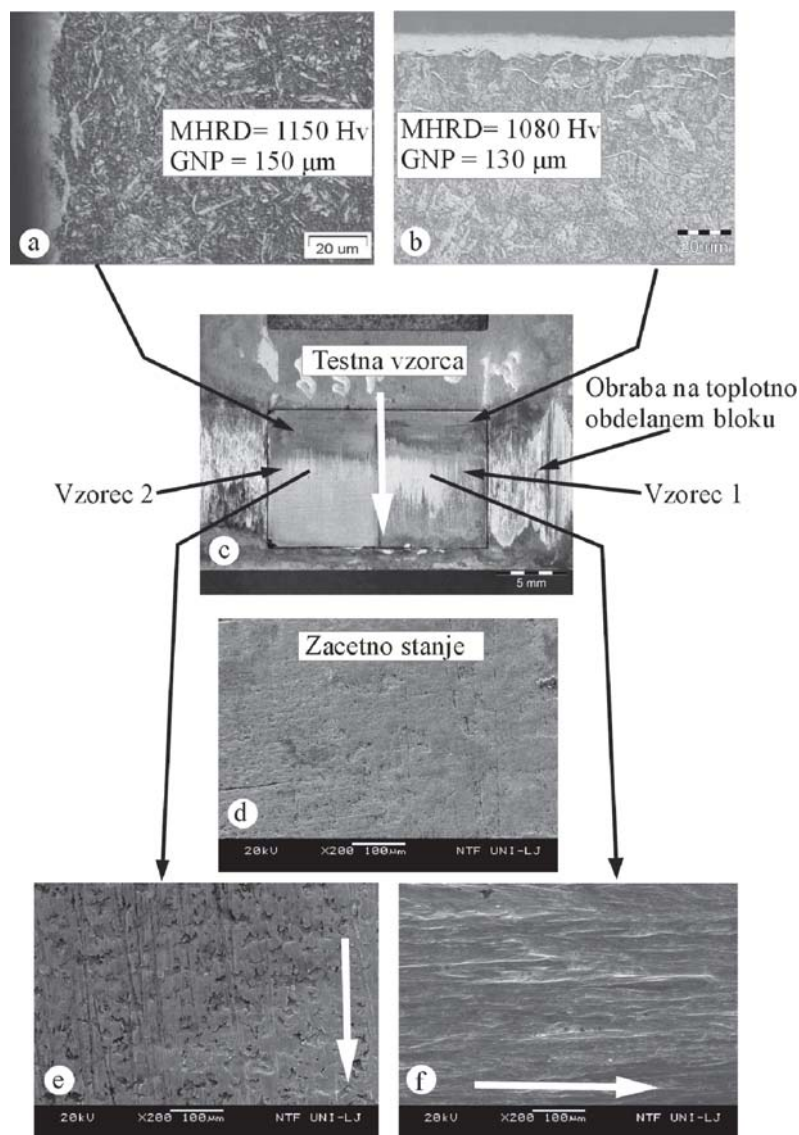
**Tabela 3.** Testni pogoji.

| Orodno jeklo | Čas          | 1h         | 2h            |
|--------------|--------------|------------|---------------|
| H10          | Proizvajalec | III, V, VI | IV, VII, VIII |
| H13          | Proizvajalec | III, VI    | V, VII, VIII  |

**Tabela 4.** Približni časi delnega (40-60 %) luščenja spojinske plasti, testni pogoji 1.

|                                   | Testni pogoji 1 | Testni pogoji 2 |
|-----------------------------------|-----------------|-----------------|
| Normalna sila [N]                 | 2200            | 1920            |
| Naležna površina [mm x mm]        | 30 x 10         | 30 x 5          |
| Povprečni kontaktni pritisk [MPa] | 7,5             | 15              |
| Relativna hitrost zdrsa [m/min]   | 25              | 25              |
| Temperatura Al cilindra [°C]      | 510             | 510             |

**Slika 9.** Shema naprave "blok na cilindru"**Slika 10.** Časovni potek obrabe nitiranih površin: začetno stanje, SEI (a.), pokanje spojinske plasti, SEI (b.), delna odstranitev spojinske plasti in pospešena obraba (najverjetneje zaradi kemičnega reagiranja z vročim Al) na mestu njene odstranitve, BEC (c.) in kemično reagiranje in adhezija na mestih brez spojinske plasti, SEI (d.), (testni pogoji 1).



**Slika 11.** Primerjalno testiranje ( $t=3h$ ) vzorcev z različnimi mikrostrukturama: vzorec 2 (a.), vzorec 1 (b.), toplotno obdelani blok z vstavljenima vzorcema in makro posnetek obrabljenih površin (c.), začetno sanje površine (d.), površina vzorca 2 posneta v SEI (e.), površina vzorca 1 posneta v SEI (f.), (testni pogoji 2), smer drsenja označena s puščico.

Debelina spojinske plasti pri različnih proizvajalcih in orodjih ni nihala v takem obsegu, da bi iz tega lahko izpeljevali

enolične zaključke. V povprečju je znašala okrog 4-15  $\mu m$ .

## 6. PRIMERJALNO TESTIRANJE OBRABE

Na osnovi individualnega testiranja smo ugotovili, da ohranjanje spojinske plasti na drsni površini podaljšuje življenjsko dobo orodja. Znano je tudi, da večja trdota in globlja difuzijska cona povečuje obrabno obstojnost orodij. Za pojasnjevanje dileme, kaj bolj povečuje obrabno obstojnost, ali srednje debela spojinska plast z ugodno fazno sestavo (proizvajalec IV, H13, vzorec 2, slika 11a,c) ob zadostni globini difuzijske cone in velikosti trdot ali tanka spojinska plast z manj ugodno sestavo ob večji trdoti (proizvajalec V, H13, vzorec 1, slika 11b-c) in globini difuzijske cone, smo izvedli primerjalno ( $t=3h$ ) testiranje obrabe omenjenih vzorcev pri večjih kontaktnih pritiskih (testni pogoji 2, tabela 3). Makrografske posnetke površin na sliki 11 c nam kaže, da je drugi vzorec, kljub manj ugodni sestavi spojinske plasti, vendar z njeno tanjšo debelino ter z večjo trdoto in globino difuzijske cone, obrabno bolj obstojen (sliki 11c,f).

Daljšo življenjsko dobo orodij lahko torej povečujemo tudi z večjo globino nitiranja; smo pa z globino nitiranja tudi omejeni, saj to lahko privede do prenitiranja, če ta postopek večkrat ponovimo.

## 7. Zaključki

Izdelana so bila laboratorijska orodja iz jekel H10 in H13 z ozkimi (1 mm oz. 4 mm) in dolgimi (12 mm) režami, ki so bila nitrirana pri različnih proizvajalcih za plinsko in ionsko nitiranje, pri čemer so slednja služila za primerjavo uspešnosti obeh postopkov

nitiranja po dolžini različno ozkih rež. Dobljene mikrostrukture jekla plinsko nitriranih površinah se precej razlikujejo, tako glede globine difuzijske cone in maksimalne vrednosti dobljenih trdot, kot tudi glede sestave oz. deleža  $\epsilon$  ali  $\gamma'$  spojinske plasti. Globine difuzijskih plasti nihajo v območju med 110-190  $\mu m$ , fazno razmerje  $\epsilon/\gamma'$  pa se spreminjal od proizvajalca do proizvajalca od skoraj monofazne  $\epsilon$  sestave do  $\epsilon/\gamma'$  razmerja cca. 0,7. Pri nobenem od proizvajalcev ni bila dobljena čista monofazna  $\gamma'$  sestava spojinske plasti. Debeline spojinskih plasti so se gibale v območju cca. 4-16  $\mu m$ . V 1 in 4 mm reži istega orodja so bile opažene manjše razlike, tako v globini nitiranja, kot tudi v debelini spojinske plasti. Te razlike bi lahko pripisali različnemu strujanju plinske mešanice v 1 mm in 4 mm reži. Različne, zgoraj karakterizirane mikrostrukture so rezultirale tudi v različnih časih luščenja spojinske plasti med tribološkim simuliranjem vroče ekstruzije aluminija. Spojinska plast je kemično bolj obstojna proti vročemu aluminiju. Na mestih njenega luščenja zaradi povečanja hrapavosti pride najverjetneje do pospešenega kemičnega reagiranja z vročim aluminijem, kar pospeši obrabo. Zato v primeru, ko se spojinska plast odluči v zelo zgodnji fazi procesa tople ekstruzije, to luščenje negativno vpliva na življenjsko dobo orodja. V primeru kasnejšega luščenja spojinske plasti, pa zaradi njene večje kemične stabilnosti do vročega Al, to rezultira v daljši življenjski dobi orodja. Sestava spojinske plasti, ki se približuje enofazni, je bolj odporna proti luščenju. Fazna razmerja cca. 1:1 povečujejo krhkost spojinske plasti in s tem zmanjšujejo življenjsko dobo orodja. Orodja z relativno neugodno sestavo spojinske plasti ter večjo

difuzijsko cono in trdoto so v primerjalnem testiranju izkazale boljšo obrabno obstojnost v primerjavi z orodjem z ugodno sestavo spojinske plasti, vendar manjšo difuzijsko cono in manjšo trdoto.

Pri ionskem nitriranju so bile dobljene večje razlike v učinkovitosti nitriranja, tako glede na geometrijo rež 1 in 4 mm, kot tudi glede na proizvajalca. V 1 mm reži nihče od proizvajalcev ni bil uspešen. V primeru, da ima orodje z 4 mm ozko režo krajšo drsno površino (do cca. 5 mm), bi bila učinkovitost drugega proizvajalca lahko zadovoljiva.

V primerjavi dobljenih mikrostruktur na orodjih iz jekel AISI H10 in AISI H13, ki so bila nitrirana pri istih proizvajalcih, bi lahko sklepali, da je slednje bolj nagnjeno k tvorbi spojinske plasti.

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