The origin and composition of flysch deposits as an attribute to the excessive erosion of the Slani Potok Valley („Salty Creek“), Croatia

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1. INTRODUCTION

Flysch domains in Croatia occur along the elongated area of the External Dinarides (see overview in MARINČIĆ, (1981)). Although all Eocene flysch domains in the External Dinarides are exposed to a high degree of erosion (JURAK et al., 2002, 2003, 2005), erosion is unusually intense in the Slani Potok catchment. This catchment (with an area of 3 km²) is part of the Vinodol Valley (Fig. 1) where erosion is associated with intensive creeping and sliding processes. Accumulation of a colluvial soil-like mass, disposed to flowing,
forms badlands type terrain (Figs. 2 & 3). Such erosion represents a unique phenomenon within the Dinaridic flysch domain and has been investigated by JURAK et al. (1996, 2005, 2006), MILEUSNIĆ et al. (2004), BENAC et al. (2005). Previous investigations determined the occurrence of the mineral thenardite, \( \text{Na}_2\text{SO}_4 \) in the Slani Potok catchment. This mineral crystallizes by efflorescence at the surface of sedimentary rocks during the dry season (summer – July, August) – Fig. 4 and dissolves during wet seasons. Dissolved thenardite results in the salty taste of the Slani Potok Creek and is the origin of its name. According to MILEUSNIĆ et al. (2004) and JURAK et al. (2005, 2006) excessive erosion of the Slani Potok flysch complex occurs due to a lithological composition characterized by the prevalence of clay particles in pelitic flysch intervals, the presence of swelling minerals, sodium rich pore water, and occurrence of the sodium mineral thenardite. The aim of this study is to determine the source of sodium and sulphur needed for thenardite crystallization.

2. GEOLOGICAL SETTING

The Slani Potok catchment is part of the larger Mala Dubračina catchment in the elongated and irregularly shaped Vinodol Valley which has a NW-SE axis.

In the Vinodol Valley, the oldest rocks are Cretaceous platform carbonates. Tectonic movements at the end of Cretaceous formed the thrust fold belt of the External Dinarides (MARINČIĆ, 1981; BERGANT, 2003). In front of the uplifted thrusts, in a deep foreland basin, Early-Middle Eocene foraminiferal limestone and Middle Eocene flysch were deposited (ŠUŠNJAR et al., 1970; GRIMANI et al., 1973). Late Eocene limestone, fossiliferous conglomerates and sandstones, (equivalents of Late Eocene/Oligocene Promina...
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BLAŠKOVIĆ (1999), describes the Vinodol Valley as a syncline in which the axis is parallel to the valley strike. The syncline is mostly composed of Middle Eocene flysch deposits. Marginal rocks of the Vinodol Valley are represented by Upper Cretaceous limestones and Early-Middle Eocene foraminiferal limestone (ŠUŠNJAR et al., 1970) (Fig. 5). The Late Eocene limestone breccia and Quaternary deposits have a patchy occurrence in the Valley. Quaternary talus breccias occurred as a consequence of tectonic activity and were deposited on a foothill of steep cliffs (faults). The fault systems, that controlled the evolution of the Vinodol Valley morphology, have variable kinematic features that change along their strike and dip, merge into reverse or even over-thrust structures (BLAŠKOVIĆ, 1997).

The Middle Eocene flysch deposits constitute the central area of the Slani Potok catchment. Flysch is mostly represented by thick pelitic intervals interlayered with minor sandstones and biocalcirudites (‘nummulite breccias’). As a result of intensive processes of sliding, creep and formation of a colluvial soil mass (badlands), the flysch deposits are not currently in their original position, but instead exhibit a rather chaotic appearance with overturned, fragmented and deformed beds (Fig. 6).

The mineral thenardite occurs on the surface of all rock types in the Slani Potok area (MILEUSNIĆ et al., 2004; JURAK et al., 2005) – (Fig. 4). It has been documented as the first occurrence of this mineral in Croatia (MILEUSNIĆ et al., 2004). As there is no occurrence of salts in any of the flysch terrains, the appearance of thenardite seems to be a unique phenomenon of the Slani Potok flysch in the whole of the External Dinarides. Therefore we investigated a possible source of sodium and sulphur required for the crystal-
lization of thenardite. The petrographic and geochemical composition of all flysch rock types in Slani Potok has been studied in order to define the provenance of the detrital material. Therefore the geological framework of the hinterland has been taken into consideration as a potential source area.

The hinterland, located north of the Slani Potok area, consists of a Palaeozoic clastic complex (black shales, sandstones and quartz rich conglomerates), with barite and pyrite ore mineralization (JURKOVIĆ, 1959; ŠIFTAR, 1981; ALJI NOVIĆ et al., 2000), and a Mesozoic carbonate complex, with hornblende andesite (in the vicinity of Fužinski Benkovac (VRAGOVIĆ & GOLUB, 1969)). The hornblende andesite was attributed to intense low temperature (hydrothermal) alteration manifested as propylitized and albitized rock minerals with andesine, containing 33 vol. % of anorthite as well as pure albite as a common constituent (VRAGOVIĆ & GOLUB, 1969).

3. METHODS

The lithological, mineralogical and geochemical characteristics of the Flysch sedimentary rocks have been analyzed in order to determine the origin of sodium and sulphur ions necessary for the crystallization of thenardite. Several samples of sandstones and biocalcirudite have been studied micropetrographically and chemically. Some samples were taken randomly (due to the restricted occurrence of flysch in the original position) while some are from the 8 m thick section that has been measured and sampled (Fig. 7). Samples of pelitic flysch intervals from the section were analyzed for carbonate content, mineral and chemical composition. In order to compare the surface and internal chemical composition, two marl samples were taken from the same bed, one from the surface (sample number SPP 5a), and another from 0.5 m depth (SPP 5b). The mineral and chemical composition of calcitic platelets, accumulated at the surface of flysch rocks, has also been analyzed.

Petrographic investigation suggested further micropetrographic analyses of the samples and determination of the main constituents in sandstones using semi quantitative visual estimation (TERRY & CHILINGAR, 1955). The chemical composition (main macro- and microelements) has been determined in four rock samples (from 2 sandstones and 2 marls) as well as one sample of a calcitic platelet. Prior to analysis, samples were ground in an agate mortar followed by fusion with LiBO4/Li2B4O7. Their chemical composition was determined by inductively coupled plasma - emission spectroscopy (ICP-ES) in the ACME Analytical Laboratory, Canada. The carbonate content was determined according to Scheibler’s method (ISO 10693).

4. RESULTS

4.1. Petrological and mineralogical characteristics of flysch deposits

Flysch outcrops in the Slani Potok catchment area are represented by the prevalence of pelitic flysch intervals determined mainly as marls and silty marls, calcareous clayey siltstones, siltstones, and clayey siltstones (MILEUSNIĆ et al., 2004; JURAK et al., 2005). Subordinate flysch sequences include sandstones. Very restricted occurrences of biocalcirudite have also been observed within flysch deposits. A graphic log of a short flysch succession in its primary position is shown in Figure 7. Sandstones and marls of this section are arranged in fining upward sequences containing fine-grained sandstones at the base and marls at the top. Fine-grained basal sandstones exhibit small scale cross-lamination which can be attributed to the Tc intervals of turbidite sequences. Sandstones of Tc intervals are overlain by parallel laminated very fine-grained sandstones (Td interval), that gradually pass upwards into silty marl or marl of Te intervals. Six Tc–Te and two Td–Te sequences have been logged and are shown in Figure 7. Their recurrence in the vertical succession can be interpreted as deposition from several distal turbidity currents.

Sandstones have been determined as fine-grained lithic greywackes (Tc and Td intervals) with dominantly siliciclastic detritus (Fig. 8). Quartz grains are present with ca. 50 vol. %, followed by lithic fragments (ca. 30 vol. %), and feldspar grains (plagioclase, orthoclase and microcline) for ca. 20 vol. %. Quartz grains are mainly represented by monocrystalline undolose grains. Polycrystalline quartz grains are the dominant component among the lithic fragments. Subordinate grains with faintly preserved porphyry textures with plagioclase phenocrysts surrounded by microcrystalline
quartz or volcanic glass occur (Fig. 9). They are usually intensively altered and exhibit a brown clayey patina. Other lithic grain types correspond to quartzite, schists, shales, limestones and dolostones. Fossils are rarely present in all the examined samples. A clayey carbonate matrix fills the intergranular pore spaces. The primary matrix is partially recrystallized to chlorite.

Sandstone grains with porphyry or faint altered porphyry textures suggest a volcanic origin for these grains. Furthermore, grains showing a microcrystalline quartz matrix may
be interpreted as altered volcanic glass particles. The presence of volcanic, metamorphic and sedimentary rocks suggests a complex provenance for the sediments. Acidic or intermediate magmatic rocks are assumed as the main source of lithic particles.

The main constituent of the rather restricted biocalcirudite is fossil detritus, among which nummulites fragments are most common. In addition, fragments of echinoids and lithothamnium algae occur similarly as MAGDALENIĆ (1972) reported for similar rock types from the Istrian peninsula. Nevertheless, with the exception of fossil detritus in the biocalcirudite from Slani Potok, they contain an appreciable amount of coarse grained siliciclastic detrital material. It is worth mentioning that within the siliciclastic detritus, lithic fragments are the most common constituent, followed by quartz and feldspar grains. Lithic fragments clearly show a porphyry texture, whereas plagioclase phenocrysts are surrounded by altered microcrystalline quartz and a chlorite matrix (Fig. 10). Volcanic particles have been altered in a similar manner to the lithic grains described in sandstones. Metamorphic grains have also been discerned.

Pelitic flysch intervals in the Slani Potok area have been characterized mainly as marls, silty marls, calcareous clayey siltstones, siltstones, and clayey siltstones (MILEUSNIĆ et al., 2004; JURAK et al., 2005). The amount of clay in all the analyzed pelitic lithotypes varies from 2.5–36.9 wt. % where particles less than 2 μm prevail. Silty grains comprise 28.7–87.8 wt. %. The carbonate component varies from 3.8–60.0 wt. %. A small amount of sand grains (< 10 wt. %) is usually present in the pelitic rocks. Semiquantitative XRD analyses of the mineral composition showed that the main constituents of pelitic rocks are: muscovite and illitic material (<30 wt. %), quartz (<25 wt. %), calcite (<15 wt. %) and feldspar (<10 wt. %). Minor constituents include chlorite, kaolinite, smectite and pyrite (JURAK et al., 2005).

Thenardite, documented earlier by MILEUSNIĆ et al. (2004) and JURAK et al. (2005), seems to be the most characteristic feature of the Slani Potok flysch deposits. The biggest crystals observed by SEM have diameters of up to 2 μm (MILEUSNIĆ et al., 2004). Crystalization of thenardite (Fig. 4) has been interpreted as being due to efflorescence processes in the dry summer season. During the wet season, thenardite dissolves and therefore surface water is enriched in sodium and sulphate ions (MILEUSNIĆ et al., 2004; JURAK et al., 2005).

The surface of pelitic flysch intervals in Slani Potok has often been covered by calcitic platelets as loose detritus (Fig. 11). It is assumed that calcitic platelets were formerly a thin crust at the surface of sediments or soils. The calcite crust breaks due to creeping or sliding processes and forms angular calcitic platelets. The occurrence of calcitic platelets is a diageneric feature. XRD analyses indicate calcite as the only constituent of such platelets which are composed of elongated prismatic crystals. Calcite veins of similar appearance have not been found within the marls and sandstones.

4.2. Geochemical characteristics of flysch deposits

Results of macro- and microelement analysis of sandstones, marls and calcitic platelet samples are listed in Table 1.

All analyzed rock types have a high content of sodium and barium. Sandstones contain higher amounts of silicon and lower amounts of aluminium compared to marls. Amounts of magnesium and potassium are higher in marls, while the content of sodium is similar in both rock types. Calcium is higher in the sandstones, while trace elements are enriched in the marls.

It can be clearly seen that the composition of macro- and microelements of the marl sampled at the surface (SPP 5a)
summer period and dissolves during the wet seasons. The interrelationship of thenardite and the erosion of flysch rocks is two fold: 1) Thenardite transforms into mirabilite (sodium sulphate decahydrate) on contact with water, increasing its volume at least four-fold. This transformation can intensify erosion forming pressure in the host rock and 2) available sodium in solution acts as a dispersive agent to the clay particles of the pelitic flysch intervals. Both effects may be drivers for the creeping and sliding processes as well as the formation of a colluvial clay rich substratum subjected to mass flow.

The significant excessive erosion which has been interpreted as the influence of thenardite in the Slani Potok area resulted in a search for the source of sodium and sulphur needed for thenardite crystallization. The composition of flysch rocks was examined in an attempt to define the provenance of the flysch and a possible source of sodium and sulphur.

Flysch rocks were deposited by turbidity currents in the Middle Eocene in a deep water environment. Tectonic movements at the end of the Cretaceous form a complex foreland basin on the south-western side of the fault thrusts of the External Dinarides (MARINČIĆ, 1981; BERGANT, 2003). It is accepted that activation of the numerous Dinaridic (NW-SE) faults triggered immense gravitational flows and that flysch was deposited by turbidity currents.

Models for palaeo-transport of the turbidity currents have been discussed by numerous authors including MAGDALENIĆ (1972), MARINČIĆ (1981), TUNIS & VENTURINI (1992), and BABIĆ et al. (2007). As the flysch domain represents an elongated trough with NW-SE strike, MAGDALENIĆ (1972), proposed a longitudinal transport direction toward the ESE, which derived material from the Alps, and a transverse component toward the SW where the source area was the rising Dinarides in Palaeogene times. A similar pattern was proposed by MARINČIĆ (1981), but assumed the main transport paths were transverse toward the SW (from the Bosnian ridge), and deflection of the currents to the ESE in the deeper part of the basin. According to TUNIS & VENTURINI (1992) the main transport direction was transverse to the NW-SE strike of the uplifted fault thrust belt, while BABIĆ et al. (2007) explicitly reported transverse transport but with the direction toward the NE.

Considering the particular composition of the flysch deposits in Slani Potok (prevalence of siliciclastic particles versus carbonate grains and presence of thenardite), it was necessary to determine a potential provenance area and possible source of sodium and sulphur. The difference in flysch composition stems from the composition of adjacent terrains and distances from the source area. Flysch sequences derived dominantly from carbonate platforms contained mainly carbonate detritus (MAGDALENIĆ, 1972; TUNIS & VENTURINI, 1992; BABIĆ et al., 2007) which is not the case for the Slani Potok flysch units.

The hinterland (at the north of the Slani Potok area) consists of Palaeozoic shales, sandstones, and quartz rich conglomerates, with barite and pyrite ore mineralization (JUR-
KOVIĆ, 1959; ŠIFTAR, 1981; ALJINOVIĆ et al., 2000), and a Mesozoic carbonate complex, with hornblende andesite in the vicinity of Fužinski Benkovac. It was assumed that the Gorski Kotar might be the source area of the Slani Potok flysch rock units. Prior to deposition of the flysch by turbidity currents, Dinaridic land masses were subjected to intensive erosion. A high amount of pelitic detritus, forming thick Td-e flysch intervals, was possibly derived from the erosion of Palaeozoic shales. The detrital siliciclastic component of the flysch sandstones and bioclastic rudites may also have originated from Palaeozoic sandstones or conglomerates located in the Gorski Kotar area.

Analysed sandstones and bioclastic rudites from the Slani Potok catchment contain a significant amount of lithic fragments of volcanic origin, probably andesite, as well as altered volcanic glass particles. The hornblende andesite located in the Gorski kotar (vicinity of Fužinski Benkovac) north of the studied area, is considered as a source rock. This volcanic rock was attributed to the intense low temperature (hydrothermal) alteration manifested as propilitized and albitized rock minerals (VRAGOVIĆ & GOLUB, 1969). These authors also determined pure albite as a common constituent of andesite. Thus andesitic complexes from Fužinski Benkovac contain even more sodium content than usual. It is likely and possible that feldspar and volcanic particles derived from sodium rich andesite near Fužinski Benkovac could increase the sodium content in the sedimentary rocks of the Slani Potok area. Intermediate plagioclase as well as diagenetic albite and propylite from andesite can produce appreciable amounts of sodium during weathering. Thus the increased sodium content in the analyzed samples can stem from the specific composition of the flysch deposits.

The composition of macro- and microelements has been compared to the soil geochemical map data for the flysch area in Istria (PEH et al., 2003). Flysch samples from Slani Potok do not differ significantly from the flysch deposits in Istria, except for the sodium and barium contents. Mean concentrations of sodium in Istrian flysch are 0.55 %, while in the Slani potok flysch it is double this value. The mean concentration of barium in Istrian flysch is 232.58 mg/kg, while in Slani potok pelitic flysch intervals the mean concentration is higher (267–276 mg/kg).

It is worth pointing out that stream water has an appreciable amount of dissolved sodium while water at the spring of Slani potok creek has average sodium content, indicating a sodium source from flysch and not from the groundwater.

Sulphur is present in the pelitic flysch deposits in the form of pyrite (MAGDALENIĆ, 1972). Oxidation of pyrite by weathering processes at and near the surface can lead to the production of sulphate minerals.

The uplifted Palaeozoic ore complex from the Gorski Kotar region might have been influencing the composition of flysch deposits of the Slani Potok area. It is characterised by complex barite ore paragenesis where barite is the main ore mineral, accompanied by pyrite, quartz and celestine (JURKOVIĆ, 1959; ŠIFTAR, 1981; ALJINOVIĆ et al., 2000). ŠIFTAR (1981) indicated bacteriogenic dissolution of barite, and therefore also dissolution of barium, sulphur and strontium contained in barite. This evidence suggests that barium, sulphur and strontium could have been derived from the deteriorated ore complex in Gorski Kotar.

Complex recent diagenetic processes also influenced deposition in Slani Potok. A vast quantity of calcite crystallizes from solution saturated with carbonates as a thin crust at the surface of sediments or soils. The calcite crust breaks and forms angular calcite platelets. High values of barium and strontium in calcitic platelets, not typical for the primary sedimentary rocks, is possibly related to deterioration of the ore complex in the hinterland (Gorski Kotar region) and has a diagenetic origin.

If the Gorski Kotar region, located north of the Slani Potok valley, is considered the source area, it means that turbidity currents transported material from the uplifted hinterland (uplifted cordiller belt) and that palaeotransport was transverse to the strike of the foreland basin axis. Our observations show that the most likely transport directions are from the N-NE to the S-SW.

6. CONCLUSION

Flysch deposits that crop out in the Slani Potok catchment area, (as a part of Vinodol Valley), have been subjected to excessive erosion. A colluvial soil-like clayey mass attributed to creeping and sliding processes forms terrains of the badlands type. According to JURAK et al. (2002, 2005) and MILEUSNIĆ et al. (2004), the phenomenon of excessive erosion can be related to the occurrence of the mineral thenardite (Na2SO4). Increased concentrations of sodium and sulphate ions in surface water lead to the crystallization of thenardite in the dry and warm season. Water evaporating from the surface of sediment/soil in the dry season increases saturation of sodium and sulphate ions and thenardite occurs as efflorescence crusts on the surface of rocks/soils. When thenardite is later dissolved, sodium solutions act as a dispersing agent on the clay particles from flysch pelitic rocks types. As thenardite transforms into mirabilite (sodium sulphate decahydrate), there is a four fold increase in volume of the mineral. Frequent crystallization and dissolution of thenardite becomes the main driver for the erosion and this process results in mass wasting and disintegration of rock masses.

Surface waters in Slani Potok are enriched in sodium and sulphate, while the ground water does not have any appreciable amount of these ions. Geochemical analysis of marls and sandstones indicate a high amount of sodium and barium (0.93–1.09 % and 267–276 mg/kg, respectively). Together this suggests that increased sodium and sulphate concentrations can be ascribed to the particular composition of flysch rock units. The composition of Slani Potok flysch rocks differs from other flysch areas in the External Dinarides. The explanation for this was discovered in the complex composition of the provenance area – the Gorski Kotar region located in the hinterland of the Slani Potok.

In general, in the External Dinarides, flysch have been deposited in a deep foreland basin formed in front of the Di-
naricid thrust belt that has a longitudinal axis striking NW-SE. Turbidity currents transported flysch from the source area to the North of Slani Potok, in a direction transverse to the main axis of the foreland basin, (from the N-NE to the S-SW), depositing sediments in the study area. The particular composition of flysch deposits – prevalence of pelitic rocks, appreciable amounts of siliciclastic material in sandstones and biocalcireudites, with significant amounts of volcanic particles and feldspar grains, stems from the geological framework of the source area. It was assumed that a Palaeozoic clastic rock complex (black shales, sandstones and quartz rich conglomerates with barite ore mineralization), and Mesozoic carbonates with hornblende andesite cropping out in the Gorski Kotar region, hinterland of Slani Potok, was the provenance from where the clastic detritus has been derived. Thick pelitic flysch intervals are related possibly to derivation of vast quantities of fine grained material from black shales as well as sandy particles from Gorski Kotars’ Palaeozoic and Mesozoic sandstones, conglomerates, carbonates and andesite. Some sodium could be leached from the lithic and feldspar grains due to circulation of pore fluids while the increased amount of sulphur, barium and strontium in the flysch can be related to the barite ore complex in the source area of the Gorski Kotar region.

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