Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia with a grant from the CEI-ES Know How Programme organize

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1st INTERNATIONAL WORKSHOP ON THE PROJECT

Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)

PROCEEDINGS

Edited by:
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Language: English for presentations and papers

THE IMPACT OF THE VOLCANIC ACTIVITY OVER THE DEVELOPMENT OF LAKE DIATOMITE IN KOZHUF REGION, REPUBLIC OF MACEDONIA

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Abstract

This paper presents the influence of volcanic activity in Kozhuf region over the development of diatoms existing in Tikvesh Neogene Lake.

As of the latest research it is stated that, the diatomaceous earth, at Veshje and Barovo sites consists rich and diverse association of benthic and plankton diatomite. The presence of this rich and diverse diatomite flora is caused by the conditions during the Upper Pliocene volcanic products from the immediate vicinity, which enabled forming of a mineral resource - Diatomaceous earth on these sites.

Key words: diatoms, Kozuf district, Diatomaceous earth, Tikvesh basin, Neogene

Introduction

Many researchers throughout the world perform research on the impact of volcanic activity on the development of diatoms living in lake environments (Telford et al., 2004, Jones and Gislason 2008, Elmas and Bentli I., 2013) by focusing on the role of volcanic ash in aquatic environment. Therefore the increasing potential of volcanic ash depends on the type of eruption, the size of the particles, and the distance of the volcanic centers from the lake environment. Volcanic ash is one of the main sources for the influx of Si and composition of diatoms(Barker et al., 2005).

The study area

Kozhuf area represents a relatively large volcanic complex located in the southern part of Macedonia (mountain massif of Kozhuf). In geotectonic regionalization at this part of the Balkan Peninsula, this complex enters Vardar zone. The localization of this volcanic complex at transversal zone Kozuf - Kukush (Arsovski M., Ivanov T., 1977) with the intersection of Vardar Zone is indicating on appearance of volcanism of central type. This tectonic knot is formed at the intersection of reactivated regional fault structures towards Vardar direction NW-SE to N-S and newly formed fault structure Kozuf - Kukush in Neotectonic period.

The sites with diatomaceous earth-Veshje and Barovo is located in Southeast of Veshje and Barovo villages, near the town of Negotino and spatially lie on the northeastern slopes of the volcanogenic plateau - Vitacevo. In geological terms they belong to Tikvesh Neogene basin, located in the central part of Vardar Zone.

Geological structure of the surrounding researched area

Kozhuf area is the second volcanic surface area in Republic of Macedonia in extent of about 600 km2 ground covered by pyroclastic purely volcanic and sedimentary volcanogenic material (Fig. 1). The average thickness of the pyroclastic material is about 400 m. The volcanic rocks in this area are a product of diorite and monzonite - to granite and syenite magma. The presence of different varieties, from intermediate to acidic, is a result of contamination and assimilation of the original magmatic melt originating from the border area of the upper layer and continental crust (Boev B., 1990).

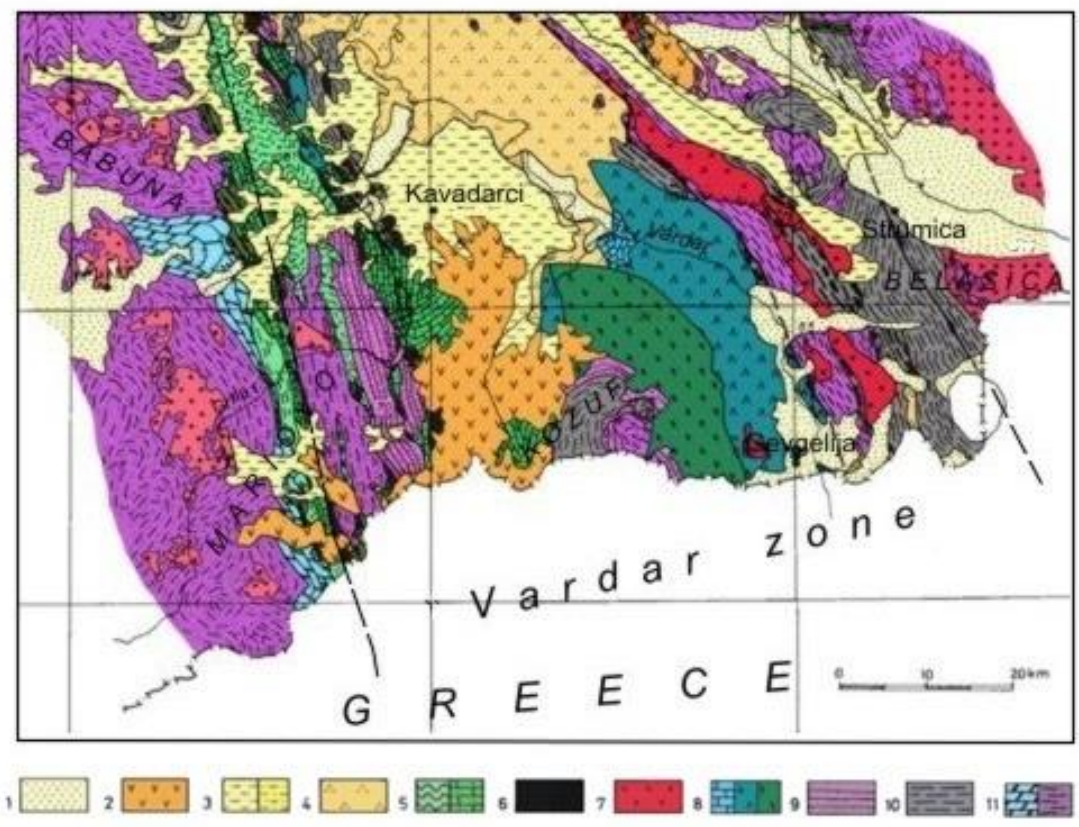

Fig. 1. Geological map of the wider area of Kozhuf district

1 – Pliocene-Quaternary deposits; 2 - Pyroclastic and volcanic rocks; 3 - Mio-Pliocene deposits; 4 – Eocene flysh; 5- Albian-Cenomanian-Turonian deposits; 6 – Jurassic ultrabasic rocks; 7 – Jurassic granite; 8 – Jurassic ophiolite (gabbros, massive basalts and pillow lavas, flysh and limestones); 9 – Triassic deposits; 10 – Paleozoic low metamorphic rocks; 11 – Proterozoic.

According the isotopic studies, this volcanic activity began at the end of the upper Miocene, and took place mainly in Pliocene to the Pleistocene (Kolios et al. 1980 4±1.8 8 Ma, and according to Boev in 1988 and Karamata et al. 1992 6±1.8 Ma).
The multiphase activity of the volcanism is due to the very characteristics of volcanoes and the nature of the magma in volcanoes of this type. This magma by nature is intermediate to acidic, poorly mobile, while relatively rich in easily volatile components. In an explosive phase of such activity it results to disposal of large quantities of volcanic material which

directly spills into Lake Tikvesh, which conducted its filling. Deposition of most of the volcanic material is performed in water, or is successively filled at big Lake Tikvesh. The most significant traces of Tikvesh Neogene Lake levels at peneplain in Vitacevo at the elevation of 900 m. Inside the lake as a result of the processes of sedimentation, reaches to the primary sedimentation pyroclastic material (lacustrine deposited tuffs and epiclastics) , and the presence of pumice in certain horizons of Epiclastics indicates over-deposition of the most primary pyroclastic material. The termination of volcanic activity is marked by the appearance of diatoms in developing of Tikvesh Lake, which is now represented by a horizon of Diatomaceous earth within epiclastic sediments.

Within the geological structure at Veshje and Barovo sites the lithological members of volcanogenic and sedimentary complex participate to the plateau of Pliocene age - Vitacevo. Mostly represented are the pyroclastic creations presented with andesite agglomerates and andesite volcanic breccia, less stratified pelit tuffs to tuffits, diatomaceous earth, rarely tufa limestone and quaternary (diluvia) sediments.

Evolution of neogene tikvesh graben

In terms of Neotectonic evolution in Republic of Macedonia, alike in other parts of Central Balkan Peninsula , has started approximately at late lower Miocene period and further on took place more intensively in Baden (Middle Miocene) when first ditches were formed. Then, within the ditches, first freshwater basins (Skopje, Kumanovo, Kocani and Probistip) were formed. Significant intensification of vertical movements occurred in late Sarmatia (Middle Miocene) and early Meot (Upper Miocene) when the existing ditches and freshwater basins were extended, and created a number of new pools such as Tikvesh basin. Tikvesh basin is formed on the territory of Vardar zone. In its northern part is stretches NW - SE, and the southern extension is N - S (Fig. 2).

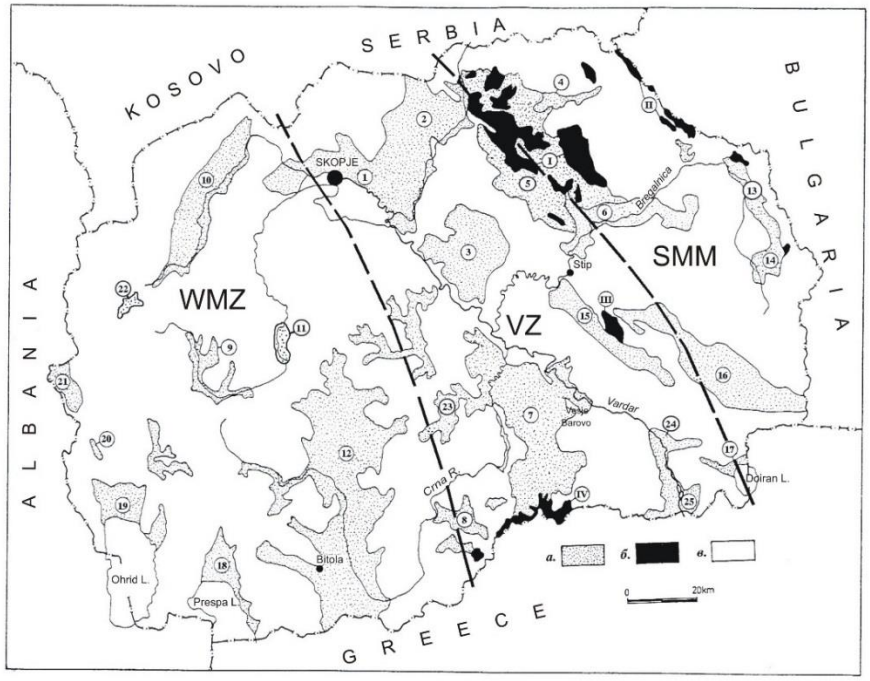

Fig. 2. Relicts from the Neogene and Pleistocene basins in Macedonia
7 - Tikves basin, IV - Kozuf volcanic complex, SMM - Serbian – Macedonian massif, VZ - Vardar zone, ZMZ - Western Macedonian zone,

The ditch has started its forming in the late Middle Miocene and Upper Miocene - Pliocene was associated with Central Macedonian Lake (Skopje - Kumanovo, Veles, Tikvesh). At the Upper Pliocene there was a significant expansion of the lake, where there is a multiple shifting sands, gravel and sandy clays with tufa plates of Pliocene and Pleistocene age. In lithographic profile of Tikvesh ditch there are three separate formations: Nerezi Vitacevo and Mariovo formation (Dumurdzhanov N., etc. 2002). The horizon of Diatomaceous earth is in Vitacevo formation and by Ognjanova - Rumenova (2000) the Diatomaceous earth has a Miocene Association of *Actinocyclus* Ehr., and *Cyclotella castracanei*, and the upper levels of the profile *Cyclotella macedonica* Jur. and *Stephanodiscus careonensis* Ehr. that confirm Pliocene age of formation.

Results and discussion

The connection of Neogenic tectonic evolution and intense volcanic activity at Kozhuf region, as well as the multiple repetition of volcanic stages of middle Miocene to Pleistocene, have a major influence on the development of diatoms living in Tikvesh Neogene Lake.

Diatoms are a class of microscopic Silicic algae (Bacillariophyta) who live , grow and flower in different types of water and different depths , and are quite sensitive organisms to environmental change (chemical condition of the water, yield of nutrients, etc.). The diatomaceous activity is mainly due to the influx of silica and nutrients in the aquatic environment. Silicon is an essential element that is required to form the skeleton of diatoms, and is derived from several sources.

As one of the main sources of Si is volcanic ash that is erupted from nearby and distant eruptions of volcanoes, and it is deposited on the lake bottom. The volcanic ash contains high concentrations of silicon and deposition in aquatic environment changes the chemical composition of water and the ecosystem (Telford et al., 2004)

Based on contemporary studies on the growth of diatoms, today it is considered that except Si, a very important nutrient is the phosphorus (P). Deposition of ash rich in P can also contributes to the introduction of a larger amount of P in the lake. Quantitative increase of diatoms comes after the deposition of volcanic ash, as a result of changing the ratio Si: P in the aquatic environment (Telford et al., 2004). The Silicon and phosphorus are factors that directly affect the proliferation of diatoms, depending on the concentration of volcanic ash, there is a change of the ratio Si: P of the water, resulting in a change in the number and types of diatoms. The various relationships of Si:P, the diatom types react differently in terms of their environment (Holm and Armstrong, 1981).

The increase in the yield of volcanic material in the aquatic environment has detrimental effects on diatoms, because if the concentrations of elements such as P, Mn and Pb, are very high, they may inhibit biological growth of diatoms (Jones and Gislason, 2008).

Another source of Si in the watery environment is the surrounding land located near the lake, and the reaction with water releases silica and silica also dissolved by the streams is carried into the lake. As a good source of Si are the rainfalls, which create water currents that carry a silica (SiO_2) and other nutrients (such as phosphorus) in the lake from the surrounding highlands.

Light is one of the important factors that directly affect the existence and prevalence of diatoms. The solar energy from the sun needed for photosynthesis, directly affect the development and blooming of diatoms (Fig. 3).

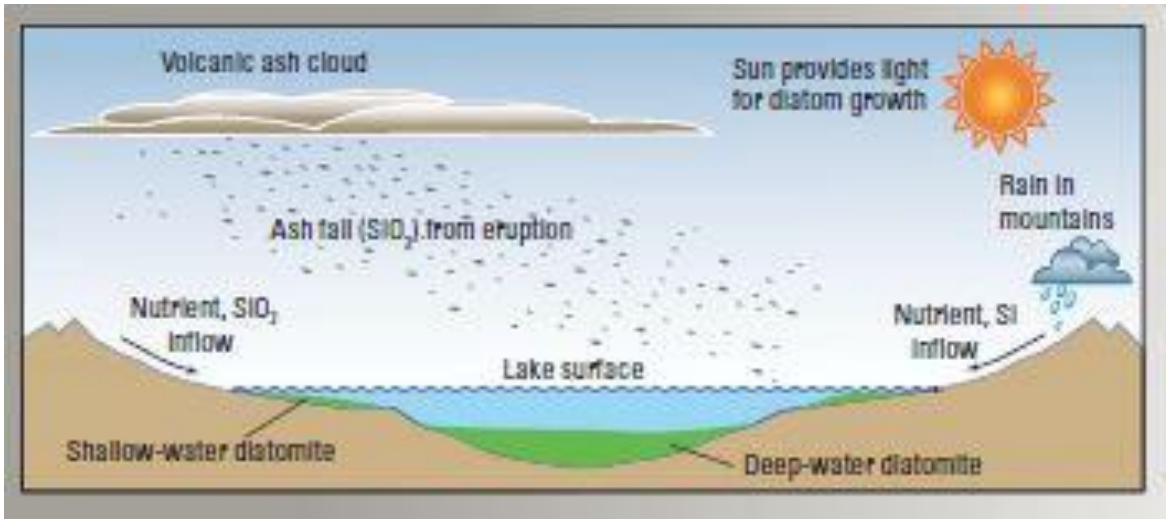

Fig. 3. Scheme for formation of diatomite deposits in a lake and some of the processes that are important in their formation

After the death of diatoms, silicon skeleton falls to the bottom of the lake which forms biogenic - silicate layer (Bsi), and through the geological history, comes to accumulation and formation of Diatomaceous earth.

As of the research over Diatomaceous earth in Veshje and Barovo sites it can be concluded that there is a connection between the volcanism of Kozhuf complex and diatomaceous earth at Tikvesh pool, and diatomite was deposited in shallow freshwater lake but also rich in silica.

The analysis of a large number of samples taken from the drillings of diatomaceous layer in Veshje site, diverse association of diatomite flora was found. The association diatomaceous flora is predominantly consisted of freshwater species of benthic diatoms such as: *Epithemia ad. saxonica* (Kütz.) Patrick, *Epithemia sorex* Kützing, *Epithemia hyndmanii* W. Smith, *Cymbella cistula* (Hempr.) Grunow, *Cymbella leptoceras* (Ehr.) Grunow, *Epithemia adnata* (Kütz.) Breb., *Navicula aff. invicta* Husted, *Navicula oblonga* Kützing, *Pinnularia aff. brevicesta* Cleve, *Pinnularia aff. stomatophora* Grunow, *Diploneus elliptica* Cleve, *Epithemia sp., Cymbella girodi* (Hėr.) Krener, *Navicula aff. orangiana* Patrick, *Cymbella affinis* Kützing, *Cymbella cymbifor. nonpunctata* Fontell, *Epithemia turgida* Kützing, *Fragilaria construens* (Ehr.) Grunow, *Melosira inslandica helvetica* Müller, *Navicula aff. placenta* Ehrenberg, *Navicula radiosa* Kützing, *Synedra sp, Epithemia argus protracta* A. Mayer, *Epithemia turgida granulata* (Ehr.) Brun., *Epithemia adnata proboscidea* Patrick, *Epithemia muelleri* Fricke, *Navicula aff. lacistricus gibbosa* Husted, *Navicula sp, Melosira sp., Pinnularia aff. cardinaliculus* Cleve, *Cymbella aff. helvetica* Kützing, *Diploneus ovalis* (Hilse) Cleve, *Diploneus ovalis oblongella* (Nae.) Cleve, *Fragilaria cons*truens (Ehr.) Grunow, *Melosira cf. distans* lirata (Ehr.) Betbge, *Diploneus sp., Epithemia adnata* (Kütz.) Breb., *Melosira distans* (Ehr.) Kützing, *Melosira italica* (Ehr.) Kützing, *Rhopalodia gibba* (Ehr.) O. Müller, *Navicula aff. radiosa*

subrostrata Cleve, *Pinnularia sp.* where all samples dominanting species *Epithemia hyndmanii* W. Smith.

Diatomaceous plankton flora is represented by gender representative *Cyclotella meneghiniana* Kützing, and is a poorly represented in terms of benthos. Neogene freshwater diatoms show great diversity and include many forms, which are virtually identical to modern species (Round et al. 1990).

The rich and numerical representation of diatomite flora and conditions that were present in the lake basin during the upper Pliocene, are the main factors for the formation of the productive layer of Diatomaceous earth. Lake basin was poor in carbonates, while the nearby volcanoes (Kozhuf Region) accumulated material and ash tuffs, which gave large amounts of inorganic substances and silicon free acid, which was necessary for fast development and building shells of diatoms.

Diatomaceous productive horizon in Veshje site has shaped layer that lies between the andesite tuffs and agglomerates. The appearance of fine andesite tuffs grain are considered as the beginning of a quieter phase, when freshwater lake could developed diatoms, which later gave the material to create diatomaceous layer .

Diatomaceous layer thickness is variable, from 0.35 m in the peripheral parts in the 1-1.25 m in the central parts. This layer of Diatomaceous earth is sub-horizontal, with a general decline in the SW angle of 2-3°, which in many places has wedging frequent as a result of erosive action of waves in relatively shallow lake environment

The deposition of diatomaceous earth was aborted by the launch of a new volcanic activity, with more explosive nature, characterized by the creation of andesite agglomerates, andesite agglomerate tuffs, and rarely andesite breccia. Andesite agglomerates almost everywhere lie directly over the layer of Diatomaceous earth, and they occur in many layering of andesite agglomerative tuffs, and in some places medium- grain andesite tuffs as well. The visible signs of stratifying the series indicate that it was created (deposited) in the aquatic environment. The wedging of diatomite is associated with a relatively short period of shallowness of the Lake basin, as well as explosive volcanism, which has probably put an end to the development of microorganisms - diatoms and other wildlife in the lake.

Conclusion

The diatomaceous rich flora and volcanic activity in the Kozhuf area in Neogene Tikvesh lake were essential prerequisites for creating of favorable environmental conditions (water rich in dissolved silica) to form deposits of Diatomaceous earth in Veshje and Barovo sites.

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