301
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HIGH TEMPERATURE CRYSTALLIZATION PROCESS INTO OPALIZED TUFF

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A b s t r a c t: White opalized tuff from the locality "Strmoš"– Probištip, is dominantly consisted of amorphous SiO_2 (over 90% mass), and a minor quantity of crystalline tridymite and quartz. Disordered structure of this material is consequence of its genesis. Fast transition from liquid to solid state enables existence of dominant amorphous state. This is confirmed by X-ray analysis and optical transmission microscopy. Thermal treatment of the material at 1200°C causes higher degree of structure stabilization – crystallization of tridymite. The basic mass remains in the same disordered amorphous state, while the process of crystallization extends only in the zones with higher order degree. At the same time minimal changes occurs in the porosity, resulting in insignificant decreasing of specific surface area.

Key words: opalized tuff;, crystallization; X-ray; optical microscopy; cluster

INTRODUCTION

Raw silica amorphous materials are widespread in Macedonia [1, 2, 3]. White opalized tuff which has been the subject of this research, was taken from the locality Strmoš, in the Kratovo–Zletovo volcanic area [4, 5].

Tuffs belong to the group of pyroclastic rocks, which have been created through sedimentation of ejected volcanic material. Under direct influence of the lower atmospheric temperature, fast cooling and solidification occure and there is not sufficient time for the molecular ordering process, which is the main reason for existence of the white opalized tuff in amorphous phase. At the same time, under the influence of lower atmospheric pressure, there is degasification – release of the gas phase (O_2, CO_2, sulfur gasses and other) from the basic mass [6, 7].

In the following stage of geological aging of the material, a process of opalization which includes incorporating of (X) molecules of H_2O in the structure of basic mass of amorphous SiO_2 begins, during its exposure to hydrothermal conditions.

EXPERIMENTAL AND DISCUSSION

Average chemical composition of the material from the locality, determined by a silicate chemical analysis, is presented in Table 1.

The variations in the chemical composition are consequence of natural changes within the place.

From mineralogical point of view, white opalized tuff is a raw material dominantly composed of amorphous SiO_2. Additionally containing minor quantities of crystalline modifications of SiO_2 – tridymite and quartz.

The crystalline phases of the material are determined by X-ray analysis. X-ray analysis (Figure 1). was realized on PHILIPS PW 1010 diffractometer (CuKα/Ni; 2θ = 2°– 60°; 38 kV; 18 mA;) (Fig. 1).

T a b l e 1

Average chemical composition of white opalized tuff

Chemical composition	Mass %
SiO_2	90 – 92
Al_2O_3	2 – 5
Fe_2O_3	0.2 – 0.5
TiO_2	0.2 – 0.4
CaO	1.5 – 4
MgO	0.4 – 1.2
Na_2O	0.1 – 0.4
K_2O	0.05 – 0.1
P_2O_5	max 0.1
MnO	tr.
SO_3	0.4 – 0.8
l.w	2 – 4

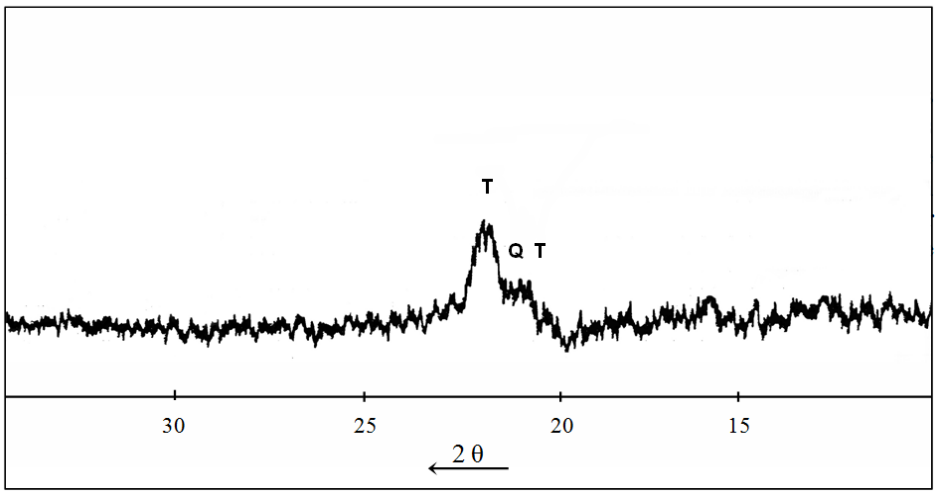

Fig. 1. X-ray diffractogram of white opalized tuff

From micro-level point of view according to the law of probabilities, there is an equal probability for the initiation of the crystallization process in any microspot, as the whole basic mass is homogeneous in composition. Every microcenter could be the begetting of a spot which remains longer under the higher temperature and pressure than the rest in the surrounding. The structure of the basic silica material starts with molecular ordering process, to provide primary structural crystalline phases appropriate and characteristic for the conditions at that moment.

The microscopic examinations have been realized by transmission optical method, on the microscope SM-POL, Letz-Wetzlar, Germany. Characteristic clusters which contains, a large number of centers of crystallization, surrounded by amorphous mass, are clearly visible on micrographs (N+). The crystallization centers are homogeneously distributed to all levels of dimensions through basic mass of amorphous SiO_2, and their aggregating originates from the naturally defined self-similarities system in the forming phase. They increase as a consequence of aggregation with other granules, and the spherical form furthers into a quasi-spherical to irregular form. The mutual borders in the aggregates define shape, with higher discrepancy of the spherical form. Clusters which contain a larger number of crystallization centers are formed, surrounded by basic amorphous mass Crystal segments of the clusters widen in space at thermal treatment, thus connecting with each other and forming a macrocrystal (Figures 2 and 3)..

White opalized tuff has been exposed under thermal treatment at the temperature of 1200°C in duration time of 1, 3 and 5 hours.

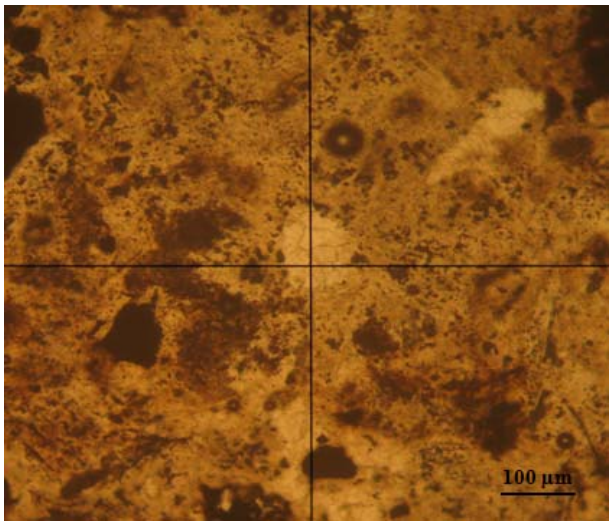

Fig. 2. Micrograph of cluster after thermal treatment of 1200°C in duration time of 3 hours (bar = 100 µm)

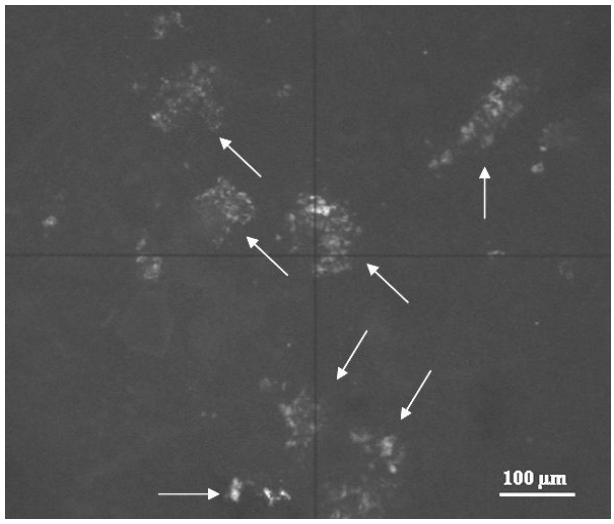

Fig. 3. Micrograph of cluster after thermal treatment of 1200°C in duration time of 3 hours (N+) (bar = 100 µm)

During heating, there is a partial morphological consolidation. The finest particles in the unformed macropores aggregate with each other or blend to the wall of the pore, thus emphasizing the space form of the pore (Figures 4 and 5). In the end, it results with minimal decreasing of porosity and increasing of specific mass (Table 2).

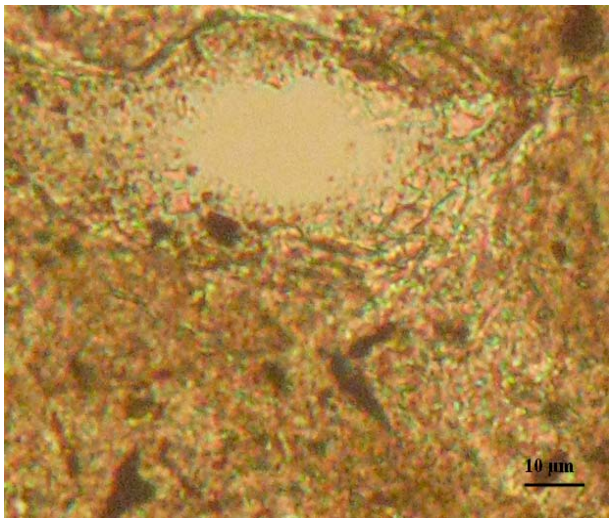

Fig. 4. Micrograph of unformed macropore (bar = 10 µm)

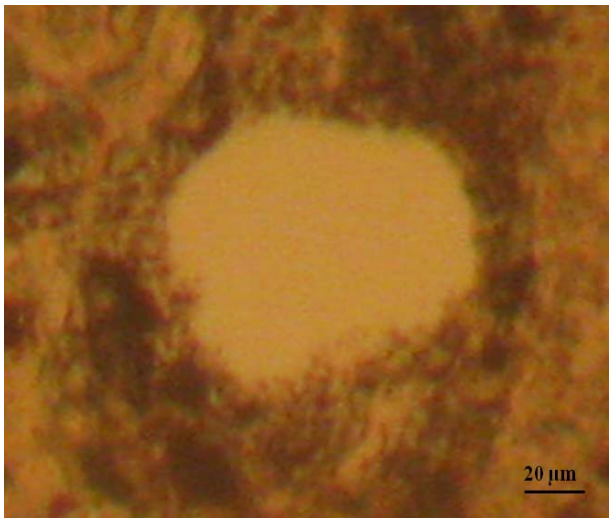

Fig. 5. Micrograph of unformed macropore after thermal treatment of 1200°C in duration time of 3 hours (bar = 20 µm)

T a b l e 2

Specific mass and porosity after thermal treatment of 1200°C in duration time of 1 and 3 hours

	γ g/cm^3	θ (%)
Initial material	2.302	42.01
1 h, 1200°C	2.315	41.04
3 h, 1200°C	2.320	40.82

A more intensive change of porosity (1,03%) occurs at primary thermal treatment of 1200°C in a duration time of 1 hour. With increasing of duration time, there is only minor change of porosity (0,22%), which indicates that the described process resulting in decreasing of total porosity is completed at the initial exposure of the material at the thermal treatment of 1200°C. This points to the fact that the thermal treatment hasn't got any significant influence upon porosity (Figures 6 and 7), i.e. closure of the space between microgranules occurs only in microzones previously morphologically prepared for consolidation, which makes the primary thermal treatment at the temperature of 1200°C in duration of 1 hour sufficient.

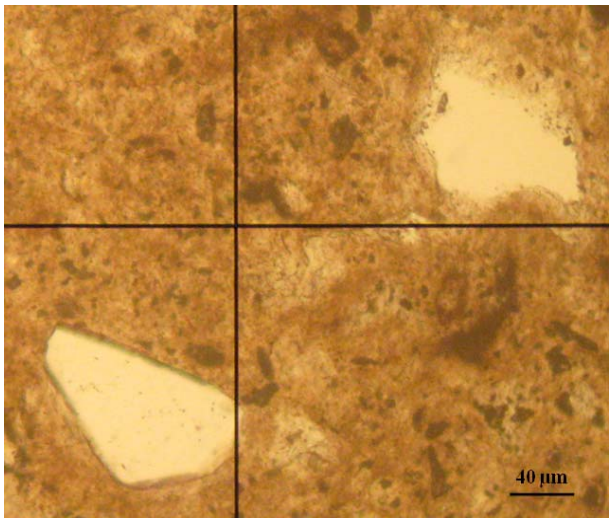

Fig. 6. Micrograph of grain of quartz and pore after thermal treatment of 1200°C in duration time of 3 hours (bar = 40 µm)

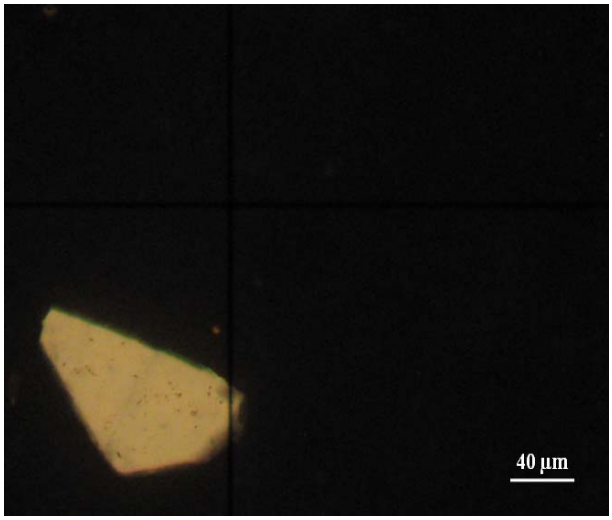

Fig. 7. Micrograph of grain of quartz and pore after thermal treatment of 1200°C in duration time of 3 hours (N+) (bar = 40 µm)

These results are in high correlation with the results of specific surface whose basic value most of all depends on porosity (Table 3).

T a b l e 3

Monolayer capacity and specific surface after thermal treatment of 1200°C in duration time of 1, 3 and 5 hours

	n^a_m mol/kg	S m^2/g
Initial material	0,4199	26.01
1 h, 1200°C	0.3794	24.220
3 h, 1200°C	0.3730	23.800
5 h, 1200°C	0.3694	23.581

Thermal treatment of the material provides a minor higher level of crystallization, depending on temperature and its duration [8–11].

After thermal treatment of 1–5 hours, at 1200°C, the material shows that the level of crystallization increases. The evidence is simultaneously sightseeing X-ray diffractograms for variously duration time. With increasing of the duration time of the thermal treatment of 1200°C, there is a minimum decrease in the intensity of quartz's peak, as a consequence of a polymorphic transformation of crystal modifications from quartz to tridymite (Figure 8).

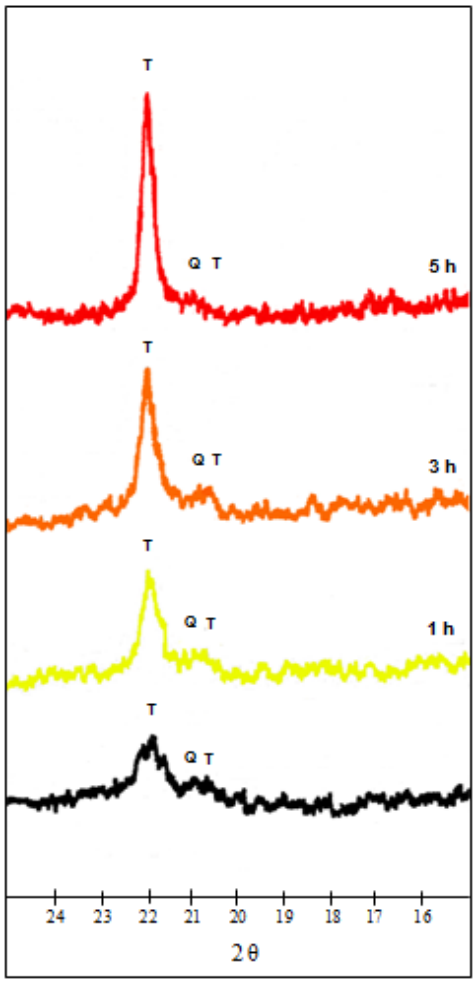

Fig. 8. X-ray diffractogram of white opalized tuff after thermal treatment of 1200°C in duration time of 1, 3 and 5 hours

CONCLUSION

The level of crystallization process (molecular ordering) of white opalized tuff from the locality "Strmoš" – Probištip, increases after thermal treatment. By comparison of X-ray diffractograms we can conclude that with the increase of the duration time of thermal treatment of 1200°C the level of molecular arrangement in trydimite crystal phase is also increased. There isn't a rapid increase of the level of crystallization because only those zones of the basic amorphous mass with higher level of arrangement crystallize, which is an addition of the primary crystallization process. The rest of the amorphous mass (the dominant part) further remains into amorphous state (thermally stable).

The influence of thermal treatment upon morphology, microstructure and texture is evident in sphering of macropores and blocking of micropores, which results in a change of specific surface area.

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Р е з и м е

ВИСОКОТЕМПЕРАТУРЕН ПРОЦЕС НА КРИСТАЛИЗАЦИЈА КАЈ ОПАЛИЗИРАН ТУФ

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Клучни зборови: опализиран туф; кристализација; рендгенска анализа; оптичка микроскопија:, кластер.

Белиот опализиран туф од локалитетот Стрмош – Пробиштип, главно е составен од аморфен SiO_2 (преку 90% масени), и минимални количини на кристални тридимит и кварц. Неподредената структура на материјалот е последица на неговата генеза. Поради брзата трансформација од течна во цврста состојба, во материјалот доминантно егзистира аморфната фаза. Ова се потврдува со примена на рендгенска анализа и оптичка микроскопија. Термичкиот третман на материјалот на температура од 1200°C предизвикува повисок степен на структурна стабилизација – кристализација на тридимитот. Основната маса останува во неподредена аморфна состојба, додека кристализираат само зоните со повисок степен на подреденост. Доаѓа и до минимални промени во порозноста, што резултира со незначително намалување на специфишната површина.