RESEARCH ON PROPERTIES OF MOLTEN BASALT – PART II

Phase 2

1. Preparation of a basalt bath sample for analysis

For analysing the basalt, the initially obtained bath was thoroughly mixed. Hereafter a few samples were chosen, the combination of which resulted in an average sample. The samples were extracted from two different locations: from the surface and from the lower layer of basalt bath.

2. Producing glass

The chemical analysis of an average sample of basalt rock was carried out by the means of X-ray fluorescence analysis. The X-ray fluorescence analysis of basalt was performed using the Axios Advanced device by PANanalytical. An X-ray tube with Rh-anode with 4 kW capacity served as excitation source for characteristic emission. The measurements were made in vacuum of approx. 3 Pa. The ground samples to be tested were pressed to tablets with polystyrol at the ratio of 1:12. The total amount of iron is represented as Fe_2O_3. The margin of error was ±0.1%.

Chart 1. Chemical analysis of basalt rock, mass percent

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Basalt	44,4	15,3	2,3	10,4	10,4	10,9	2,0	4,3

Based on the chemical composition of the submitted sample, the composition of glass was defined (see Chart 2). Obtained samples of rock were crushed and then ground up in a mill to fine powder. A modified version of basalt glass was obtained by adding 35 mass percent of dolomite ($CaCO_3$•$MgCO_3$) to the bath.

Chart 2. Chemical composition of basalt glass with modified content, mass percent

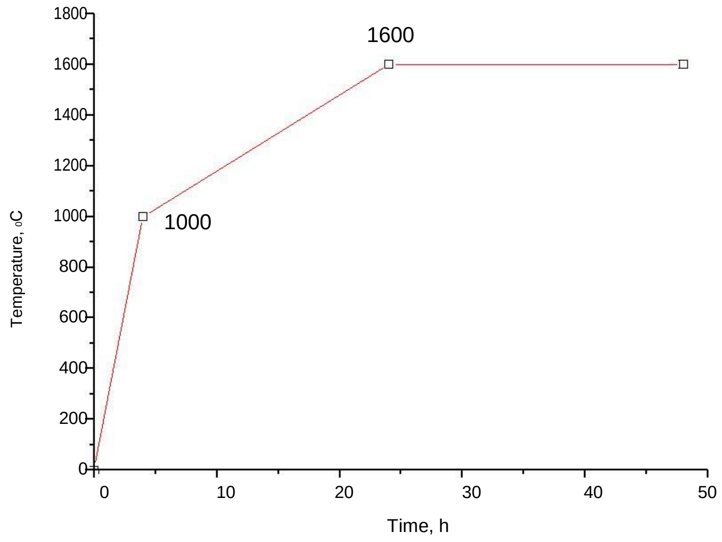
Type of glass	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Basalt	34,7	11,9	8,1	1,8	20,9	17,6	1,6	3,4

The formula of bath is given in the chart below.

Chart 3. The formula of bath

Raw material	Amount, g
Basalt sample	100
$CaCO_3$•$MgCO_3$	54

The bath was heated up in a platinum crucible in a high-temperature furnace according to the temperature setting outlined below. Slow heating within the temperature range of 1000-1600 ^oC was necessary to prevent a strong gas release by non-dissolved components of bath.

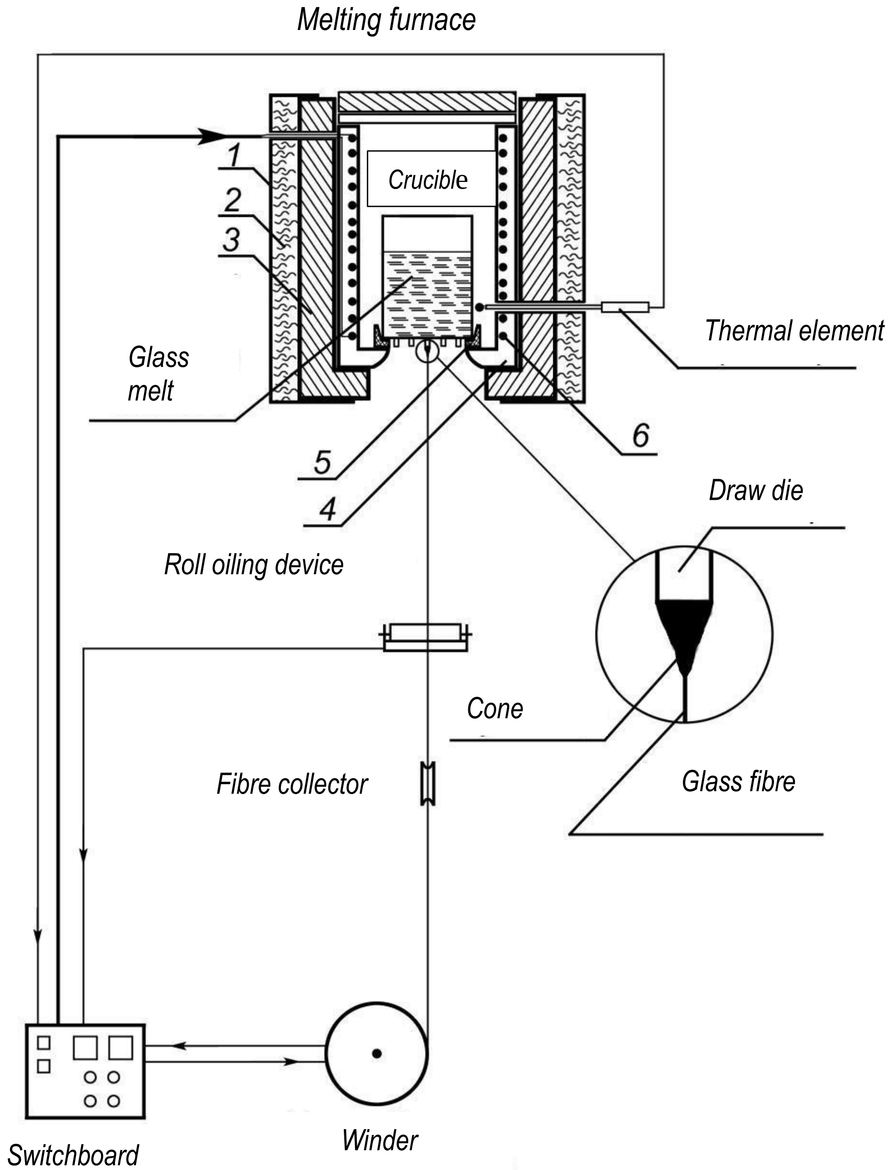


Picture 1. Temperature setting for producing glass with added 35 mass percent of dolomite

The crucible with liquid glass melt was withdrawn from the furnace with pincers at the temperature of 1570-1590 °C. The hardening of obtained glass was done by fast pouring out of the glass melt into water of room temperature. Obtained glass with the composition to be analysed was completely boiled at 1590 °C for 24 hours and had no foreign gas inclusions.

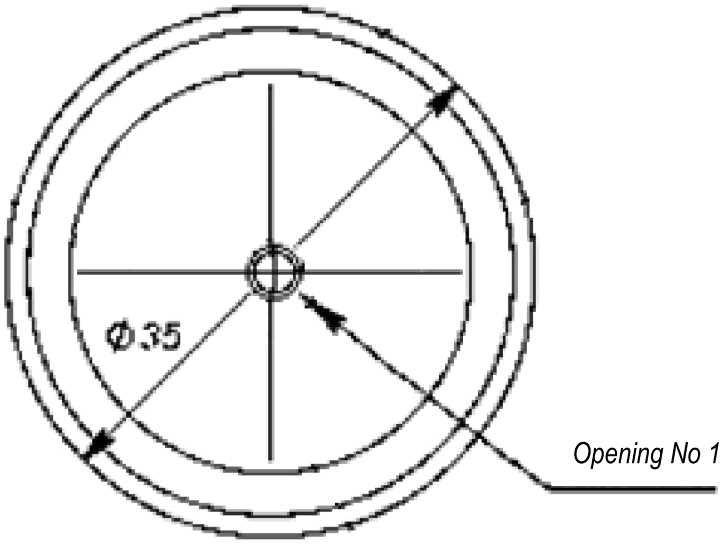
3. Defining the viscosity of basalt melt with added 35 mass percent of dolomite

The viscosity of basalt melt was defined at a laboratory facility (Picture 2). The experiment method used for defining the viscosity of melt was based on the change in rate of flow through a tubular channel with a circular cross-section with known diameter at given temperature. A pre-weighed sample of basalt glass (70g) was placed into a platinum/rhodium crucible (Picture 3) with inner diameter of ~30 mm and one 2-mm-long draw die with a diameter of ~2 мм. Hereafter the crucible was fixed in the furnace in vertical position. The heating of the crucible was performed automatically at the rate of 300 °C/hour to the temperature of 1100 °C. Then the heating was continued manually until a drop of melt appeared at the draw die and further kept at given temperature till an alignment of the temperature field in the melt was reached.



1. Metal lining; 2. Kaoline wool; 3. Light weight ceramic coating;
4. Ceramic coating; 5. Ceramic leg for multi-die crucible;
6. Pt – thermal element

Picture 2. Chart of a laboratory facility for obtaining continuous fibre



Picture 3. Platinum/rhodium crucible with a draw die

Chart 4. Crucible data

Outer diameter of crucible	35 mm
Diameter of draw die (№1)	2 мм
Length of draw die	2 мм

In the course of experiment the temperatures of the upper and lower limits of the fiberization were defined. The temperature of the lower limit of fiberization is the temperature, which allows to obtain fibre with a diameter of up to 20 µm for 30 minutes without break-off of fibre. The temperature of the upper limit of fiberization (TUL) is the temperature of the flowingout of basalt melt and of flowing into the drawing field of the crucible. At this temperature no further fiberization is possible.

Chart 5. Conditions of the fiberization

Type of fibre	TLL, °C	TUL, °C	T, °C
Basalt	1450±10	1480±10	30±10

Based on the results of measuring the mass of discharged glass melt at particular temperature, a dependence of the volume of discharged melt (V) on time (t) can be build up. The obtained dependency V(t) = Q is the main parameter, which hereafter allows to define the viscosity of melt.

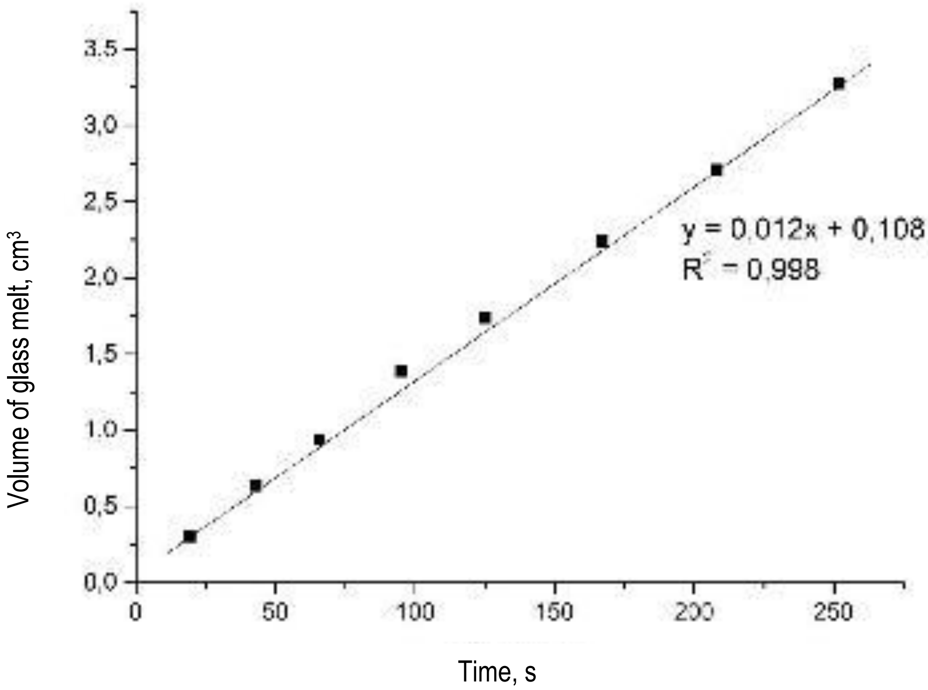
The viscosity of melt was derived from the Poiseuille law:

$$\eta = \frac{\pi R^4}{8Ql}\Delta p$$

where $\Delta p = p_1 - p_2$ is a differential pressure at the ends of capillary tube, Pa;

- volume flow rate of melt, m^3/sec.;
- radius of draw die, m;
- length of draw die, m.

Picture 4 outlines the dependency of the volume of glass outflow at the temperature of the upper limit of fiberization (1480 °C) on time, where the volume flow rate of the melt (Q) was defined based on slope ratio.



Picture 4. Change dependency of the volume of glass outflow with added 35 mass percent of dolomite on time (35,27% MgO + CaO)

The density of obtained glass was defined using a hydrostatic weighing method on Sartorius YDK 01 scales equipped with YDK 01 LP (accuracy 0,1 мг). Water was used as immersion liquid. The density of glass was calculated according to the formula below:

$$\rho = \rho_l \frac{m_a}{m_a - m_l},$$

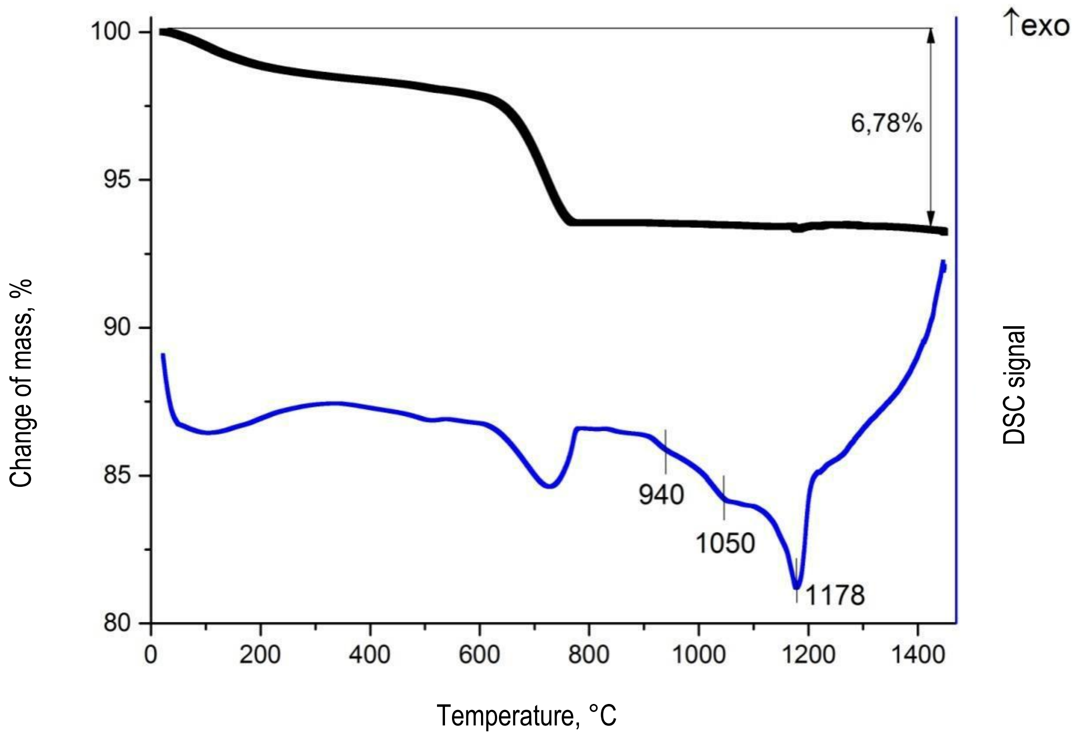
where ρ is the glass density, g/cm^3; ρ_l is the density of immersion liquid, g/cm^3; m_a is the mass of sample in air, g; m_l is the mass of sample in immersion liquid, g.

The density of obtained glass amounted to 2,71 g/cm^3.
The viscosity of basalt melt at 1480 °C was 9.6 Pa*sec.

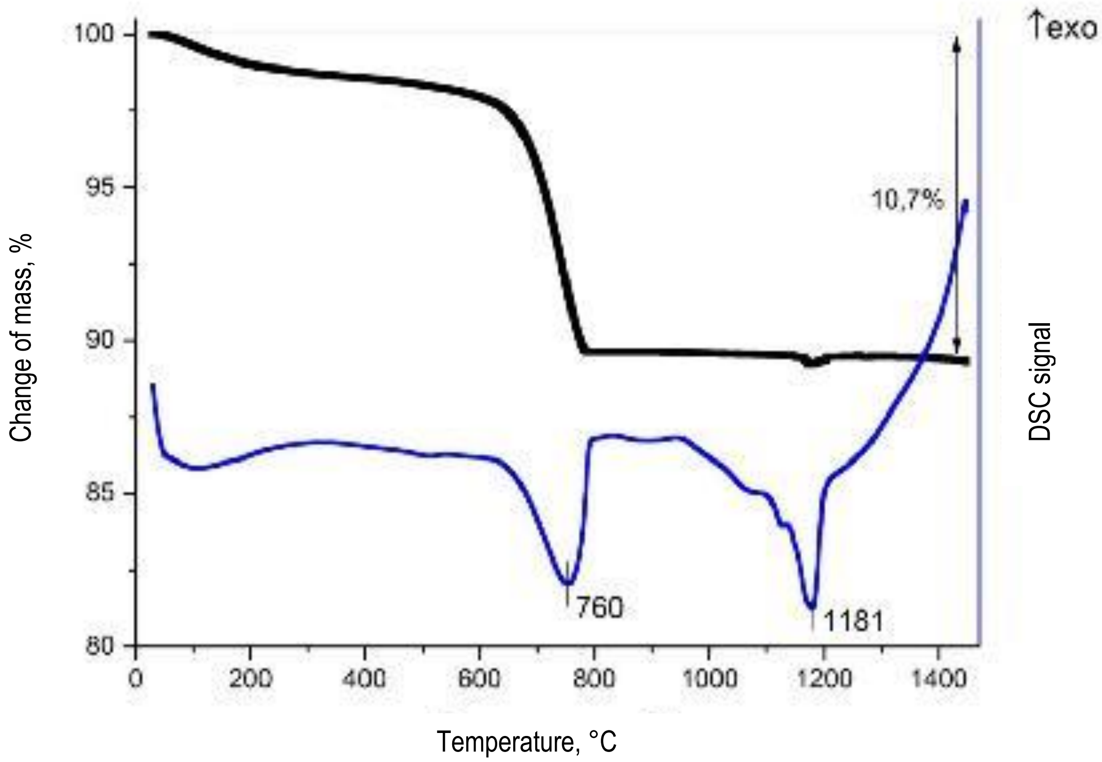
3. Thermal properties

The thermal analysis of basalt rock with added 10, 20 resp. 35 mass percent of dolomite was performed by means of a synchronous thermal analyser STA Jupiter 449C by NETZSCH with a high-temperature furnace (operating temperature = 20-1500°C). A supersensitive sample holder with Pt/Pt-Rh thermocouples was used for testing. Platinum pots (working pot and comparison pot) were used in the experiment. During the testing the samples were heated at the rate of 10 °C/min between 20 °C and 1450 °C. The mass of weighed amount summed up to more than 80mg. Method error of the temperature evaluation was ±2 °C.

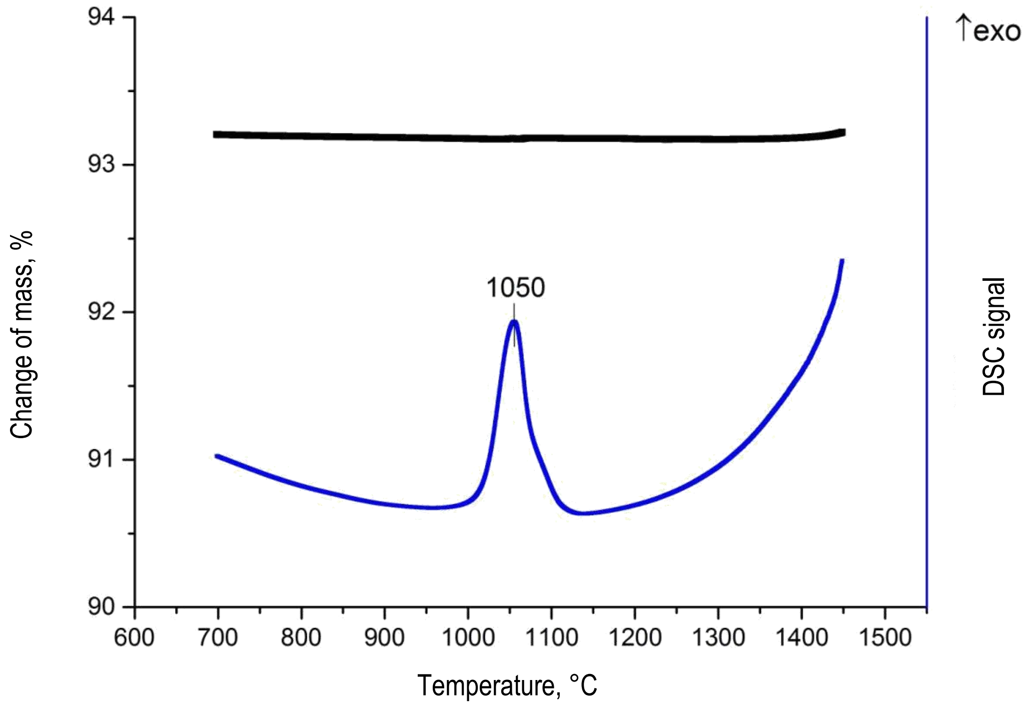
The DSC curve shows a series of endothermal effects at the temperature of approx. 175°C, which are related to the removal of bound moisture (Pictures 5, 6). A thermogravimetric curve (TG-curve) in the temperature interval of 600-800°C depicts a sharp mass reduction. This effect is related to the decomposition of dolomite. Above the melting temperature the sample exists in liquid state, and the temperature dependence of its heat capacity differs from that in crystalline state. Therefore, the slope of DSC curve changes after melting. The pictures below demonstrate that the additions of dolomite do not result in change of melting temperature of the initial basalt.



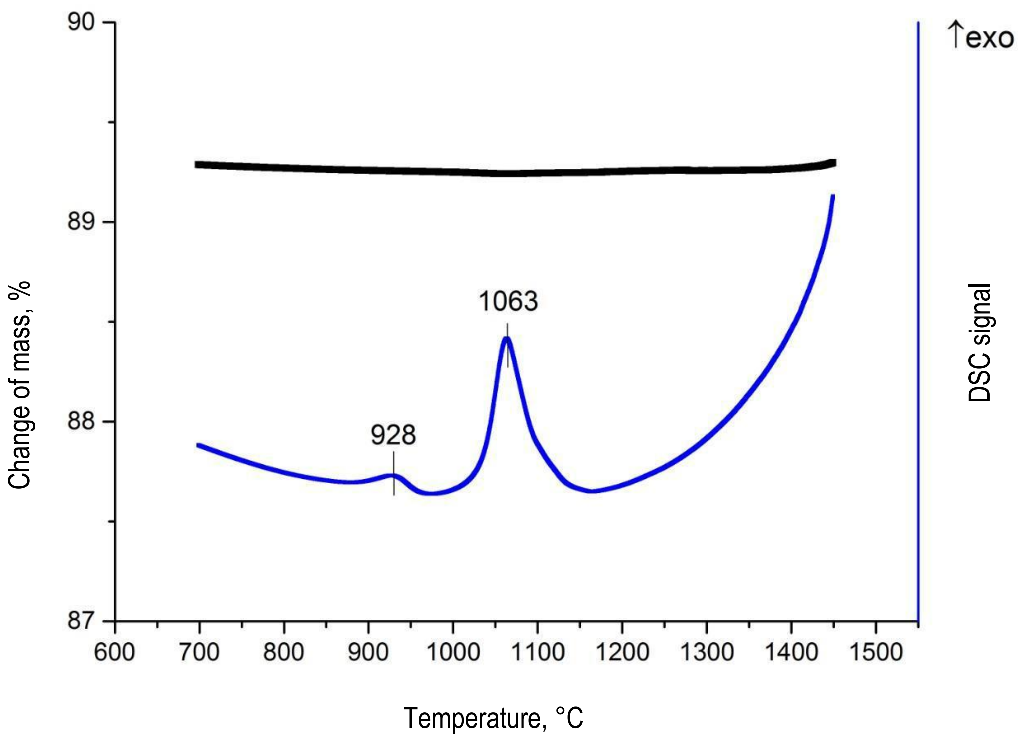
Picture 5. Heating curves DSC (blue) and TG (black) of basalt rock with added 10 mass percent of dolomite ((24.4%MgO+CaO)), produced in air at the heating rate of 10°/min



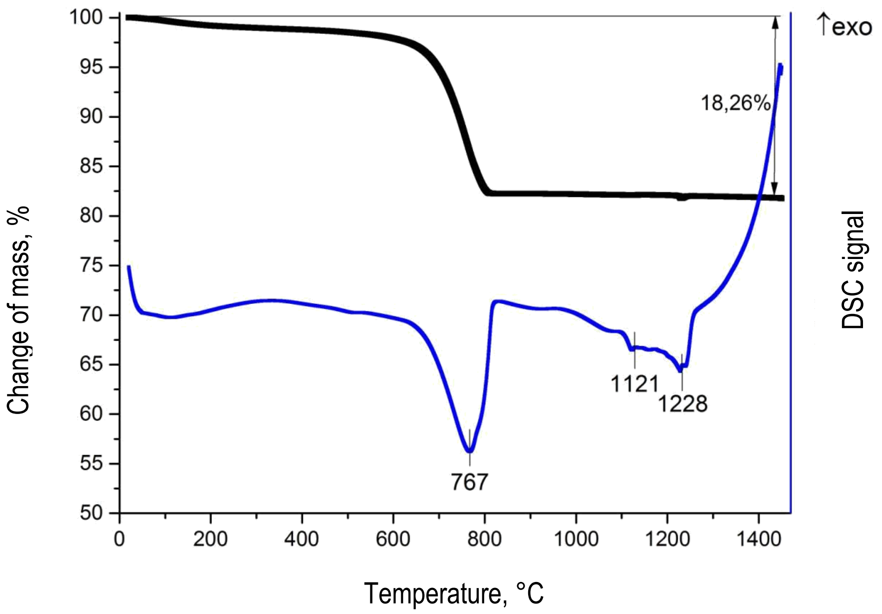
Picture 6. Heating curves DSC (blue) and TG (black) of basalt rock with added 20 mass percent of dolomite (27.5%MgO+CaO), produced in air at the heating rate of 10°/min



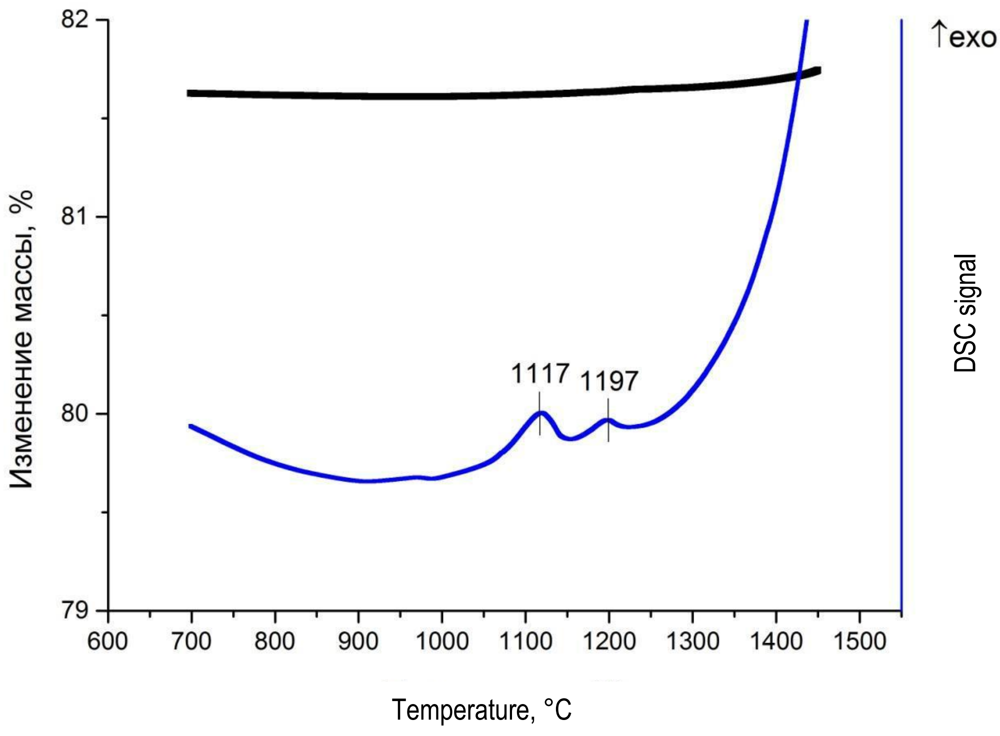
Picture 7. Cooling curves DSC (blue) and TG (black) of basalt with 10 mass percent of dolomite, produced in air at the cooling rate of 10 °/min



Picture 8. Cooling curves DSC (blue) and TG (black) of basalt with 10 mass percent of dolomite, produced in air at the cooling rate of 10 °/min



Picture 9. Heating curves DSC (blue) and TG (black) of the basalt rock with 35 mass percent of dolomite (32.14%(MgO+CaO)), produced in air at the heating rate of 10 °/min

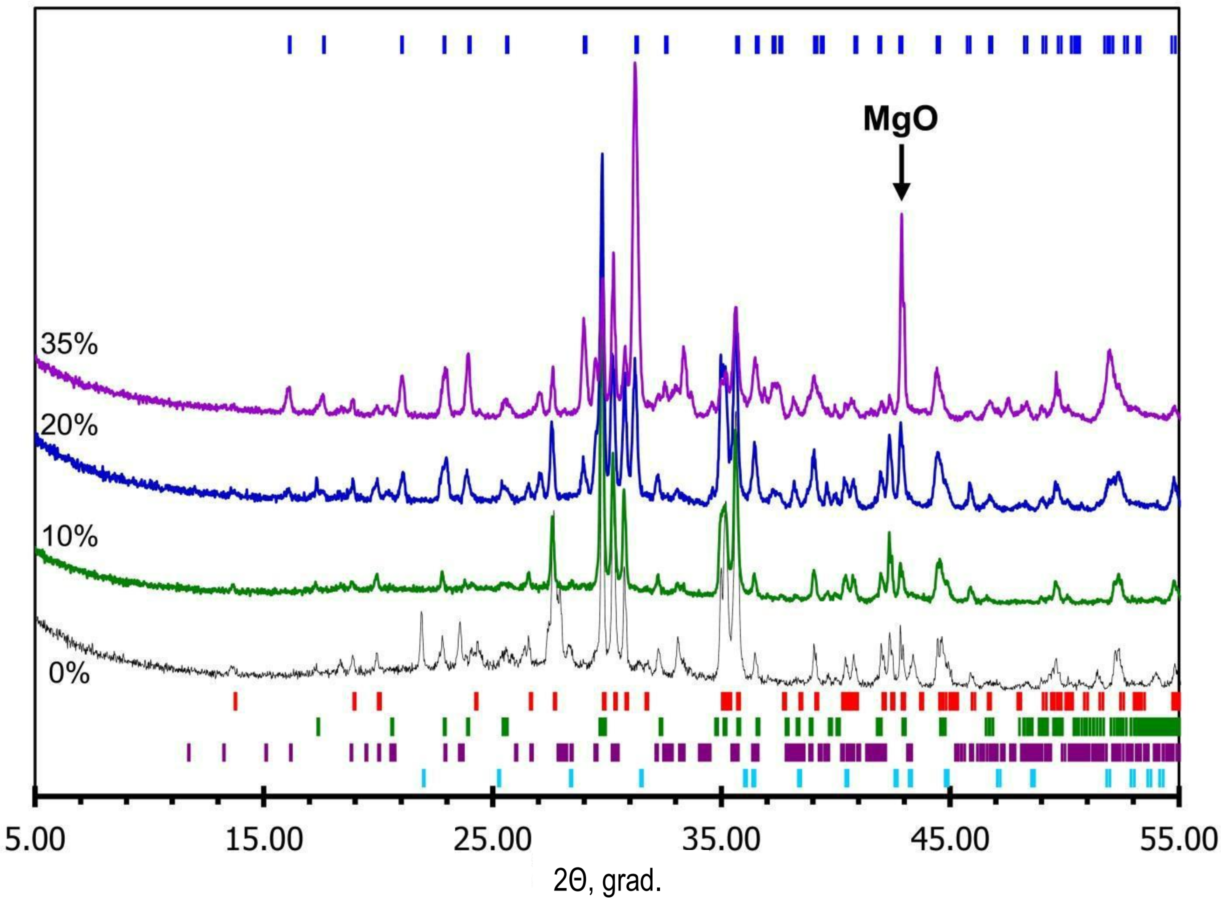


Picture 10. Cooling curves DSC (blue) and TG (black) of the basalt rock with 35 mass percent of dolomite, produced in air at the cooling rate of 10 °/min

4. Phase composition of basalt samples with dolomite additions (CaMg(CO3)2)

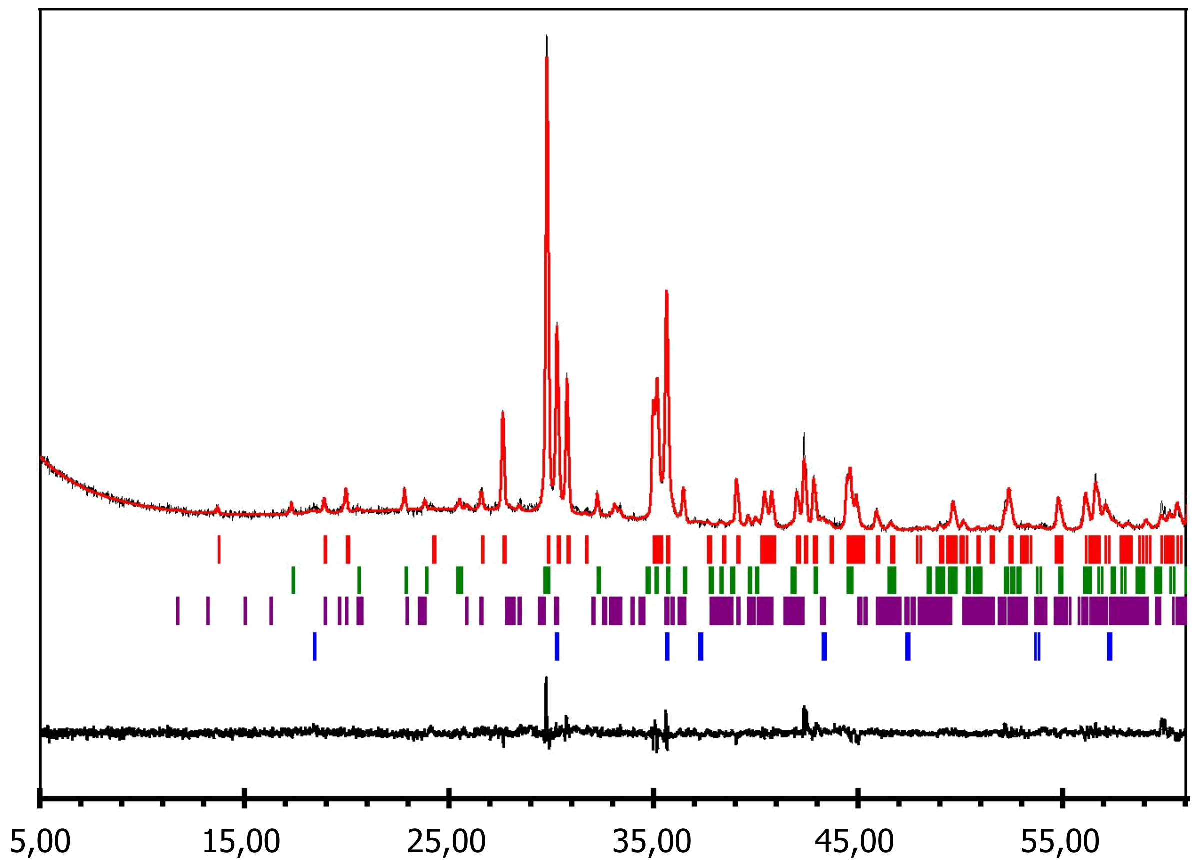
Chart 6. Phase composition of basalt samples with various percentage of dolomite ($CaMg(CO_3)_2$), annealed at 1200 ^oC for 1 hour

0 % $CaMg(CO_3)_2$						
Augite *C2/c grid*	Akermanite $Ca_2MgSi_2O_7$ *P-42₁m grid*	Periclase MgO, *Fm3m grid*	Cristobalite $P4_12_12$ grid	Forsterite *Pnma grid*	Kyanite - *P1 grid*	Magnetite *Fd3m grid*
a = 9.7447 *b* = 8.8706 *c* = 5.2976 β = 106.12			*a* = 4.984 *c* = 6.916	*a* = 10.213 *b* = 5.979 *c* = 4.755	*a* = 7.076 *b* = 7.853 *c* = 5.588 α = 90.12 β = 100.85 γ = 105.72	*a* = 8.397
64 %			**2 %**	**11 %**	**13 %**	**11 %**
10 % $CaMg(CO_3)_2$						
a = 9.7554 *b* = 8.8795 *c* = 5.3040 β = 106.116				*a* = 10.224 *b* = 5.992 *c* = 4.762	*a* = 7.119 *b* = 7.872 *c* = 5.548 α = 89.66 β = 100.75 γ = 105.97	*a* = 8.359
75 %				**10 %**	**9 %**	**6 %**
20 % $CaMg(CO_3)_2$						
a = 9.7476 *b* = 8.8736 *c* = 5.2986 β = 106.051	*a* = 7.770 *c* = 5.044			*a* = 10.222 *b* = 5.985 *c* = 4.760	*a* = 7.077 *b* = 7.881 *c* = 5.548 α = 90.04 β = 100.94 γ = 105.71	*a* = 8.396
54 %	**15 %**			**16 %**	**13 %**	**2 %**
35 % $CaMg(CO_3)_2$						
a = 9.736 *b* = 8.870 *c* = 5.2944	*a* = 7.7622 *c* = 5.0216	*a* = 4.2126		*a* = 10.230 *b* = 6.003 *c* = 4.773	*a* = 7.03 *b* = 7.827 *c* = 5.593	
β = 106.026					α = 89.59 β = 101.38 γ = 107.24	
31 %	**34 %**	**9 %**		**4 %**	**21 %**	



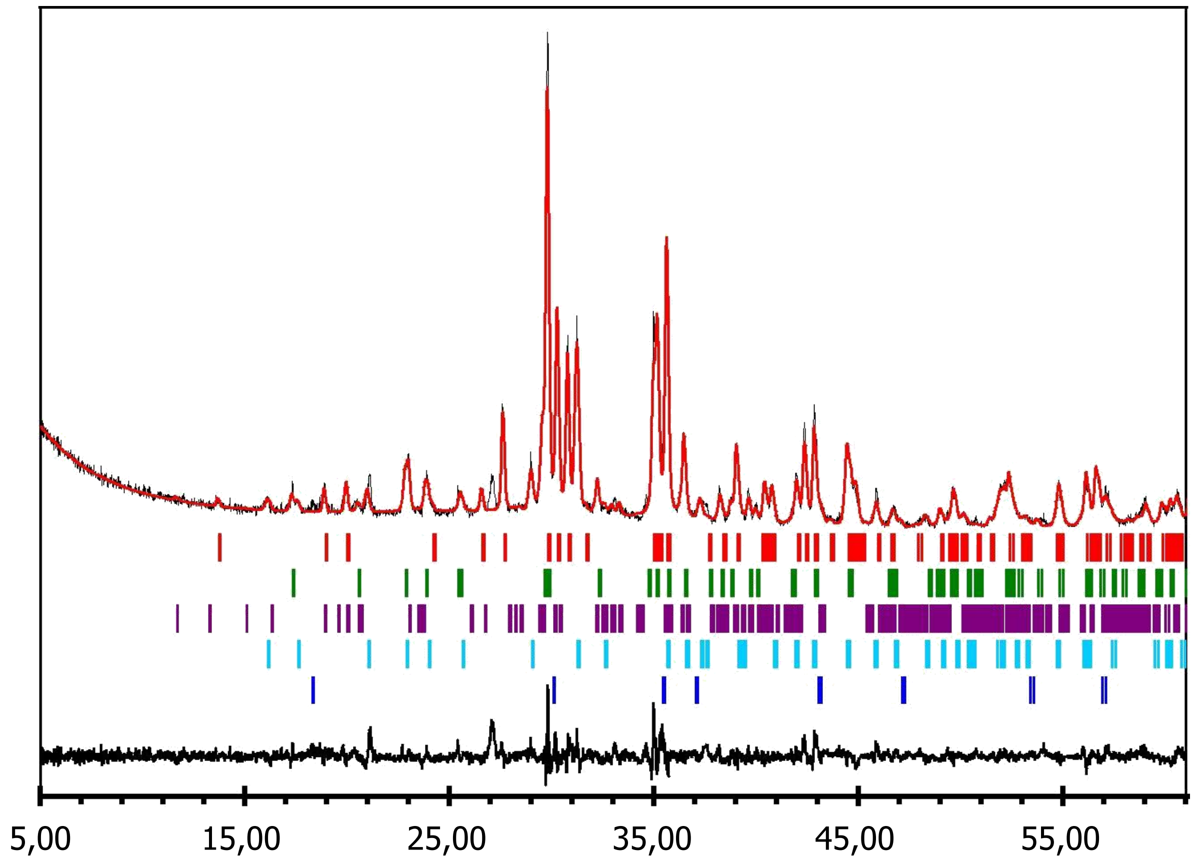
Picture 11. X-ray charts of the samples of initial basalt, mixed with various amounts of dolomite ($CaMg(CO_3)_2$) (0%, 10%, 20% and 35 %) and annealed at 1200 ^oC for 1 h. Vertical lines show locations of reflexes for:

1. *Augite*, $(Mg,Ca,Fe)_2(SiO_3)_2$ (red),
2. *Forsterite*, Mg_2SiO_4 (green),
3. *Kyanite*, $Al_2(SiO_4)O$ (purple),
4. *Cristobalite low*, SiO_2 (light blue),
5. *Akermanite*, $Ca_2MgSi_2O_7$ (blue).



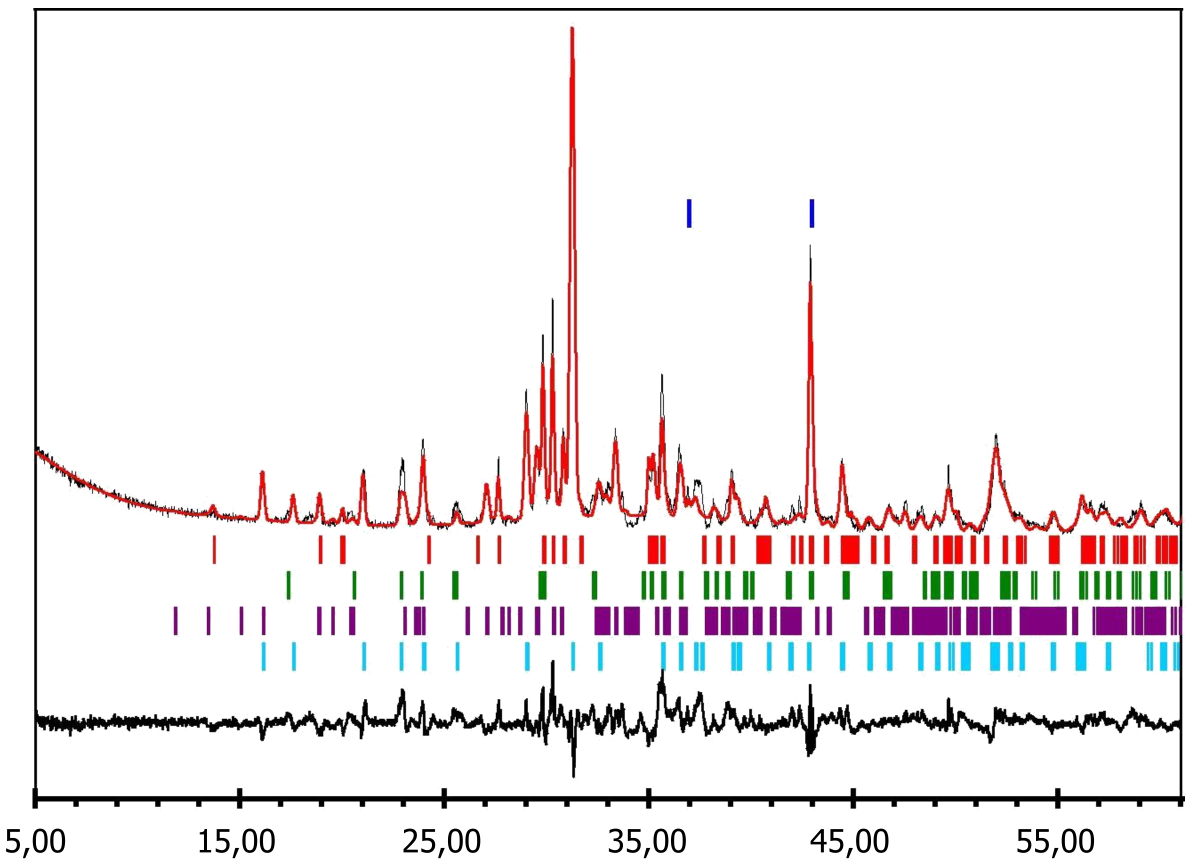
Picture 12. X-ray chart of the sample of initial basalt with 10% of dolomite ($CaMg(CO_3)_2$), annealed at 1200 ^oC for 1 h, and the results of Rietveld quantitative phase analysis. Experimental (black), calculated (red) and differential (lower) charts. Vertical lines show locations of reflexes for:

1. *Augite*, $(Mg,Ca,Fe)_2(SiO_3)_2$ (red),
2. *Forsterite*, Mg_2SiO_4 (green),
3. *Kyanite*, $Al_2(SiO_4)O$ (purple),
4. *Magnetite*, Fe_3O_4 (blue).



Picture 13. X-ray chart of the sample of initial basalt with 20% of dolomite ($CaMg(CO_3)_2$), annealed at 1200 ^oC for 1 h, and the results of Rietveld quantitative phase analysis. Experimental (black), calculated (red) and differential (lower) charts. Vertical lines show locations of reflexes for:

1. *Augite*, $(Mg,Ca,Fe)_2(SiO_3)_2$ (red),
2. *Forsterite*, Mg_2SiO_4 (green),
3. *Kyanite*, $Al_2(SiO_4)O$ (purple),
4. *Akermanite*, $Ca_2MgSi_2O_7$ (light blue).
5. *Magnetite*, Fe_3O_4 (blue).

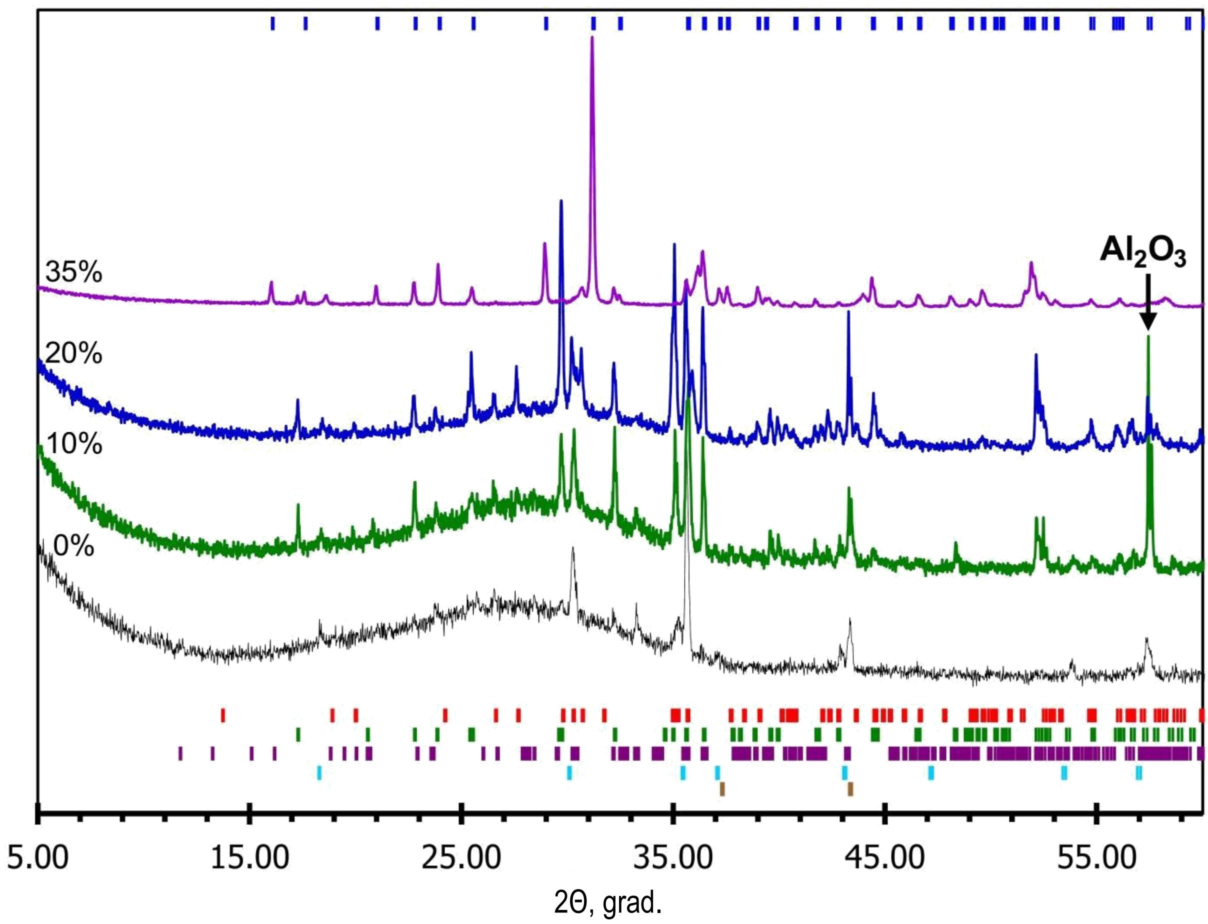


Picture 14. X-ray chart of the sample of initial basalt with 35% of dolomite ($CaMg(CO_3)_2$), annealed at 1200 ^oC for 1 h, and the results of Rietveld quantitative phase analysis. Experimental (black), calculated (red) and differential (lower) charts. Vertical lines show locations of reflexes for:

1. *Augite*, $(Mg,Ca,Fe)_2(SiO_3)_2$ (red),
2. *Forsterite*, Mg_2SiO_4 (green),
3. *Kyanite*, $Al_2(SiO_4)O$ (purple),
4. *Akermanite*, $Ca_2MgSi_2O_7$) (light blue),
5. *Periclase*, MgO (purple).

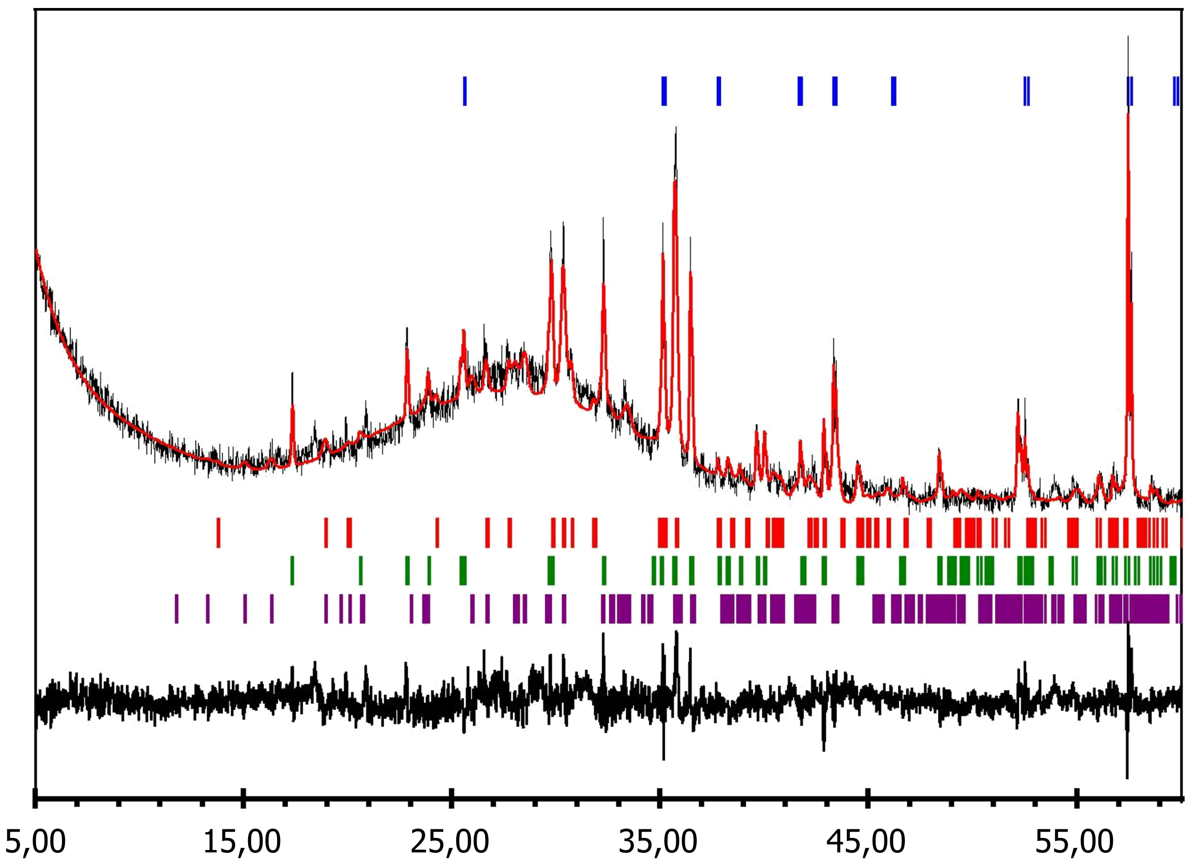
Chart 7. Phase composition of basalt samples with various percentage of added dolomite ($CaMg(CO_3)_2$), annealed at 1300°C for 1 h

0 % $CaMg(CO_3)_2$						
Augite grid $C2/c$	Akermanite $Ca_2MgSi_2O_7$ grid $P\bar{4}2_1m$	Periclase MgO, grid $Fm3m$	Forsterite Mg_2SiO_4 grid $Pnma$	Kyanite grid $P\bar{1}$	Magnetite Fe_3O_4 grid $Fd3m$	Hematite Fe_2O_3
					a = 8.323	a = 5.074 c = 14.34
					95 %	**5 %**
10 % $CaMg(CO_3)_2$						
Augite grid $C2/c$	Akermanite $Ca_2MgSi_2O_7$ grid $P\bar{4}2_1m$	Periclase MgO, grid $Fm3m$	Forsterite grid $Pnma$	Kyanite grid $P\bar{1}$	Ringwoodite Fe_2SiO_4 grid $Fd3m$	Corundum Al_2O_3 grid $R3c$
a = 9.762 b = 8.844 c = 5.323 β = 106.36			a = 10.226 b = 5.999 c = 4.762	a = 7.093 b = 7.847 c = 5.539 α= 89.73 β = 100.95 γ = 106.11		a = 4.763 c = 12.996
28 %			**27 %**	**33 %**		**12 %**
20 % $CaMg(CO_3)_2$						
a = 9.780 b = 8.868 c = 5.320 β = 106.27		a = 4.174	a = 10.238 b = 5.998 c = 4.758		a = 8.284	
48 %		**7 %**	**34 %**		**11 %**	
35 % $CaMg(CO_3)_2$						
	a = 7.7930 c = 5.0281		a = 10.256 b = 6.0075 c = 4.7590		a = 8.233	
	66 %		**20 %**		**14 %**	



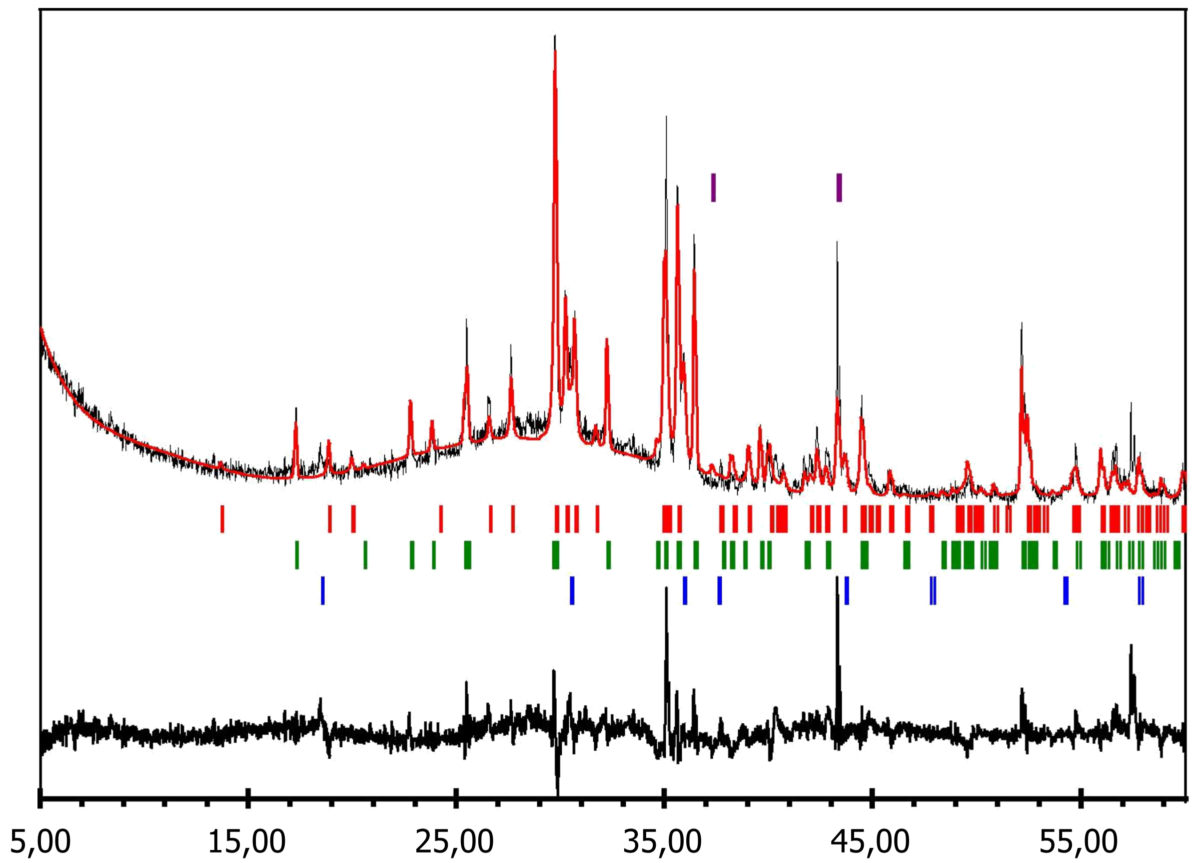
Picture 15. X-ray charts of the samples of initial basalt, mixed with various amounts of dolomite ($CaMg(CO_3)_2$) (0%, 10%, 20% и 35 %) and annealed at 1300 ^oC for 1 h. Vertical lines show locations of reflexes for:

1. *Augite*, $(Mg,Ca,Fe)_2(SiO_3)_2$ (red),
2. *Forsterite*, Mg_2SiO_4 (green),
3. *Kyanite*, $Al_2(SiO_4)O$ (purple),
4. *Magnetite*, Fe_3O_4 or *Ringwoodite*, Fe_2SiO_4 (light blue),
5. *Akermanite*, $Ca_2MgSi_2O_7$ (blue).
6. *Periclase*, MgO (brown).



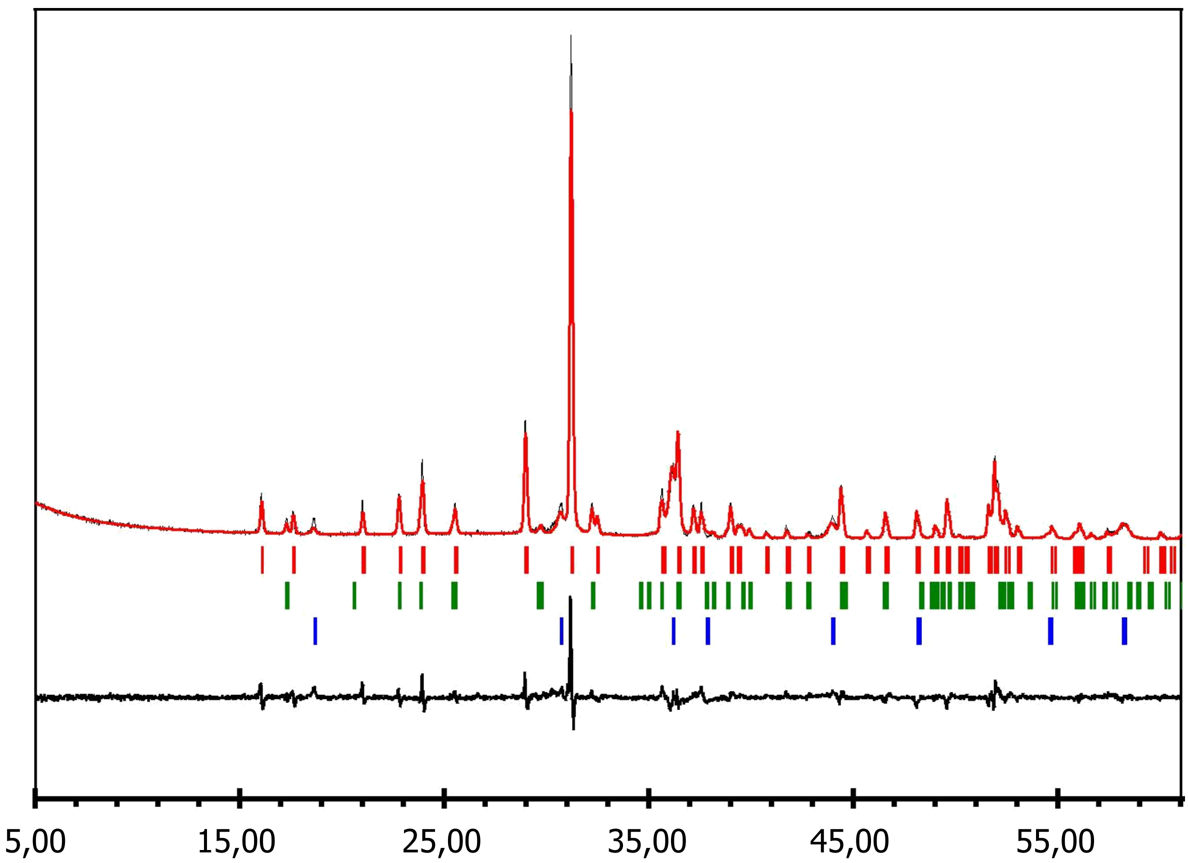
Picture 16. X-ray chart of the sample of initial basalt with 10% dolomite ($CaMg(CO_3)_2$), annealed at 1300°C for 1h, and the results of Rietveld quantitative phase analysis. Experimental (black), calculated (red) and differential (lower) charts. Vertical lines show locations of reflexes for:

1. *Augite*, $(Mg,Ca,Fe)_2(SiO_3)_2$ (red),
2. *Forsterite*, Mg_2SiO_4 (green),
3. *Kyanite*, $Al_2(SiO_4)O$ (purple),
4. *Corundum*, Al_2O_3 (blue).



Picture 17. X-ray chart of the sample of initial basalt with 10% dolomite ($CaMg(CO_3)_2$), annealed at 1300^{o}C for 1h, and the results of Rietveld quantitative phase analysis. Experimental (black), calculated (red) and differential (lower) charts. Vertical lines show locations of reflexes for:

1. *Augite*, $(Mg,Ca,Fe)_2(SiO_3)_2$) (красные),
2. *Forsterite*, Mg_2SiO_4) (зеленые),
3. *Periclase*, MgO) (фиолетовые),
4. *Ringwoodite*, Fe_2SiO_4) (синие).



Picture 18. X-ray chart of the sample of initial basalt with 35% dolomite ($CaMg(CO_3)_2$), annealed at 1300°C for 1h, and the results of Rietveld quantitative phase analysis. Experimental (black), calculated (red) and differential (lower) charts. Vertical lines show locations of reflexes for:

1. *Akermanite*, $Ca_2MgSi_2O_7$ (red),
2. *Forsterite*, Mg_2SiO_4 (green),
3. *Ringwoodite*, Fe_2SiO_4 (blue).