# HIGH DENSITY FLUID INCLUSIONS OF MAGMATIC WATER IN PHENOCRYSTS FROM RHYOLITE OF THE ŠTIAVNICA STRATOVOLCANO (CENTRAL SLOVAKIA)

VLADIMIR NAUMOV<sup>1</sup>, VLADIMIR KOVALENKER<sup>2</sup>, VLADIMIR RUSINOV<sup>2</sup>, IRINA SOLOVOVA<sup>2</sup> and MIROSLAV KAMEN<sup>3</sup>

<sup>1</sup>Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Acad. of Sci., Kosygin str. 19, 117975 Moscow, Russia
<sup>2</sup>Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Acad. of Sci., Staromonetny per. 35, 109017, Moscow, Russia

<sup>3</sup>Geological Survey, Truchleho-Sitnianskeho, 96901 Banská Štiavnica, Czecho-Slovakia

(Manuscript received May 14, 1991; accepted in revised form December 12, 1991)

Abstract: Optical, cryometric, thermometric and microprobe investigations of primary melt and fluid inclusions in quartz and sanidine phenocrysts of Neogene rhyolite of the Štiavnica Stratovolcano (Slovakia) have been carried out. Homogenization temperatures of melt inclusions in quartz phenocrysts are from 870 °C to 970 °C. Potassium content in the melt predominates over sodium content, chlorine concentration is 0.2 wt.%. Homogenization temperatures of water-rich fluid inclusions are 125 - 180 °C in quartz (18 inclusions), and 160 - 225 °C in sanidine (20 inclusions). Melting temperatures of ice in fluid inclusions vary in the narrow interval from -1.4 to -1.9 °C, indicating a low salinity of the water-rich fluid (2.3 - 3.1 wt.% equiv. NaCl). The high density of water-rich fluid (from 0.86 to 0.94 g/cm³) corresponds to a high pressure of magmatic water (from 570 to 870 MPa) at the time of fluid trapping. It follows that the formation and consequent crystallization of acid magmas of the Western Carpathians took place at a depth of about 30 km.

Key words: Western Carpathian, volcanism, magmatic water melt and fluid inclusions, P-T conditions.

#### Introduction

Numerous data on melt and fluid inclusions in phenocrysts from acid magmas suggest that the main volatile constituent of acid magmas is water, content of which varies from 0.1 to 14 wt.% (Naumov & Kovalenko 1981, 1986; Naumov & Ivanova 1984; Naumov et al. 1987; Reif 1990; Tsaryeva et al. 1990). An upper limit of the calculated water pressure is about 550 - 610 MPa for granites and pegmatites and 10 - 30 Mpa for rhyolites (Naumov & Kovalenko 1986; Tsaryeva et al. 1990; Naumov et al. 1984). Fluid inclusions of magmatic water of very high density were found in quartz and sanidine phenocrysts in rhyolite from the Štiavnica Caldera (Central Slovakia). The paper reports on the composition of fluids and melts, and P-T conditions of magma crystallization.

## Material for study

The Neogene magmatic activity in the Western Carpathian involved widespread andesitic volcanism and subvolcanic intrusions of quartz diorite, while acid volcanism was less common. Five stages of Neogene magmatic events were distinguished (Konečný et al. 1969). The extrusion of rhyolite of the Hlinice formation belongs to the third stage and the youngest rhyolites of the Jastrebská formation to the fifth stage.

The studied sample of rhyolite (No.6 - 90) was taken from the extrusive rhyolitic dome at the village Vyhne (the fifth magmatic stage) and represents the sanidine type of volcanics of the Jastrebská formation (Fig. 1). The K-Ar age of the rhyolite is 11.6 0.3 m.a (Bagdasaryan et al. 1970). It is a fresh biotite sanidine rhyolite with large phenocrysts of quartz (~15 vol.%), sanidine (~10 vol.%) and biotite (~5 vol.%). Sanidine in the phenocrysts is usually present in a form of intergrowths with quartz (subgraphic structure). Round-shaped quartz phenocrysts are fractured. Vesicles with walls instructed with fine grained quartz were observed. These vesicles are probably remnants of gas bubbles contained in the magma. The groundmass of the rhyolite consists of fine grained aggregates of K-feldspar with subordinate quartz.

### Melt and fluid inclusion study

Melt and fluid primary inclusions were found in the quartz and sanidine phenocrysts. The composition of crystalline phases and glasses based on electron microprobe analyses (Camebax Microbeam) is given in Tab. 1. Inclusions of biotite (Tab. 1, No. 3), plagioclase (Tab. 1, No. 4), apatite and zircon were found in sanidine (Tab. 1, No. 1 and 2) and quartz phenocrysts. Biotite has a remarkably high content of TiO<sub>2</sub> (up to 4.1 wt.%).

Melt inclusions (from 5 - 10  $\mu$ m to 200  $\mu$ m in diameter) were studied in more detail in quartz phenocrysts. The glass in most of these inclusions is devitrified (Fig. 2a), but in some smaller inclusions translucent glass with a high content of  $K_2O$  and  $Na_2O$  (Tab. 1, No. 5) was found. Decrepitation of large in-

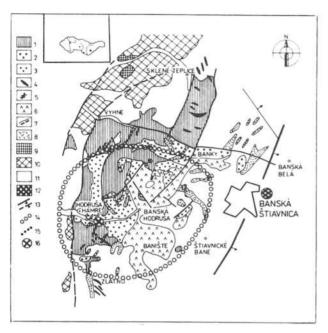


Fig. 1. Geological map of the Banská Štiavnica district according Rozložník (1988).

1 - rocks of pre-Neogene basement; 2 - diorite-gabbrodiorite; 3 - granodiorite; 4 - granodiorite porphyry; 5 - skarns, 6 - quartz-diorite-porphyry (sills, lacolites), 7 - quartz-diorite-porphyry (dikes); 8 - quartz-diorite-porphyry (thick dikes); 9 - Hliník rhyolites (Sarmatian); 10 - Kremnica rhyolites (Sarmatian); 11 - andesites undibided (Badenian - Sarmatian); 12 - basanites (Pannonian); 13 -faults; 14 - contours of Hodruša Intrusive Complex on the depth level 0 m; 15 - ore veins; 16 - locality "Kukel" - place of granodiorite sample for radiometric investigations.

clusions (30 - 40  $\,\mu\,m$  in diameter) is documented by fluid haloes and microfractures (Fig. 2b). This indicates that during the extrusion of magma the internal pressure in the inclusions significantly exceeded the external pressure. Crystallization of quartz phenocrysts thus must have occurred at conditions of high fluid pressure.

Thermometric study was performed only on melt inclusions small in size (less than 30 - 40  $\mu$ m in diameter) since the larger inclusions decrepitated. Homogenization of melt inclusions occurred at 870 - 970  $^{\circ}C$  after 0.5 - 2 hours. Inclusions held at 830 - 850  $^{\circ}C$  were still heterogeneous after 8 hours. Homogenized melt inclusions are low in Ti, Mg, Mn and P (Tab.1, No. 6 - 8), relatively high in Cl (0.14 - 0.19 wt.%) and have more K<sub>2</sub>O than Na<sub>2</sub>O. The content of water in the melt reaches 3 - 5 wt.%.

Primary water-rich fluid inclusions (Fig. 2 c-h), found in quartz and sanidine phenocrysts of rhyolite have usually negative crystal forms (9 - 95  $\mu$ m in diameter). They commonly occur in the marginal zones of phenocrysts and close to the melt inclusions. They were found in about 10 - 15% of the phenocrysts. In all, 40 inclusions were studied. As a rule each phenocryst contained one, rarely 2 - 3 fluid inclusions. The presence of opaque phase (one or several crystals) in inclusions, occupying 0.1 - 0.5 vol.%, is typical (Fig. 2 e,f). Secondary fluid inclusions were not found in any of the phenocrysts which indicates a absence of later hydrothermal events. Hence the fluid inclusions studied are considered as relics of magmatic fluid.

Results of microthermometric study of 39 fluid inclusions are presented in Tab. 2. The interval of all measured homogenization is about  $200\,^{\circ}C$  (from 125 to  $320\,^{\circ}C$ ), however for 37 inclusions it is less than 75  $^{\circ}C$  (from 125 to  $200\,^{\circ}C$ ). All fluid inclusions homogenized into liquid phase. Freezing of inclusions was observed in the temperature range from -25 to -40  $^{\circ}C$  accompanied by a decrease of the gas phase volume. This behaviour is typical of water-rich fluid inclusions. The melting temperatures of ice varied in the narrow interval from -1.0 to -1.9  $^{\circ}C$ , indicating of ice salinity (1.6 - 3.1 wt.% equiv. NaCl).

These data correspond to the fluid density at the conditions of homogenization between 0.70 - 0.96 g/cm³, with most frequent values from 0.89 to 0.96 g/cm³. For the estimation of fluid density at the time of trapping it is necessary to estimate the coefficient of volume thermal expansion and the compressibility coefficient of hosted minerals. In the temperature interval of 20 - 850 °C and for pressures from 100 to 750 MPa these two coefficients are 4.4% and 1.9% for quartz, and 1.9% and 1.7% for sanidine respectively (Clark 1969). The volume effects under heating and compression of minerals are opposite. Therefore the density of fluid inclusions in sanidine does not require any expansion/compressibility correction while that of quartz should

Table 1. Chemical analyses of sanidine, biotite, plagioclase and melt inclusions in quartz from rhyolites (weight %).

Oxides	1(1)	2(3)	3(4)	4(1)	5(1)	6(3)	7(1)	8(1)
SiO <sub>2</sub>	64.23	63.73	38.86	56.56	69.06	71.42	74.20	74.71
TiO <sub>2</sub>	0.01	0.00	4.13	0.03	0.03	0.07	0.04	0.06
Al2O <sub>3</sub>	19.35	18.09	14.55	27.44	14.14	13.17	12.12	11.77
FeO	0.06	0.07	21.86	0.18	1.14	0.67	0.57	0.71
MnO	0.00	0.02	0.30	0.00	0.10	0.05	0.02	0.04
MgO	0.02	0.00	9.22	0.00	0.08	0.07	0.05	0.02
CaO	0.17	0.18	0.01	9.70	0.97	0.98	0.95	0.80
Na <sub>2</sub> O	2.72	3.17	0.58	6.23	4.41	3.74	3.96	3.52
K <sub>2</sub> O	12.79	13.26	9.36	0.48	5.87	4.64	4.80	4.44
P <sub>2</sub> O <sub>5</sub>	0.02	0.01	0.01	0.01	0.00	0.01	0.04	0.02
CI	0.00	0.01	0.45	0.02	0.16	0.19	0.19	0.14
Total	99.37	98.54	99.06	100.65	95.96	94.83	96.94	96.23

Explanations: FeO - total iron; number of analyses is given in brackets; 1 and 2 - sanidine, 3 - biotite, 4, - inclusion of plagioclase in sanidine, 5-residual glass in melt inclusion in quartz, 6 - 8 - homogenized melt inclusions in quartz; 6 - 970 °C, 8-940 °C.

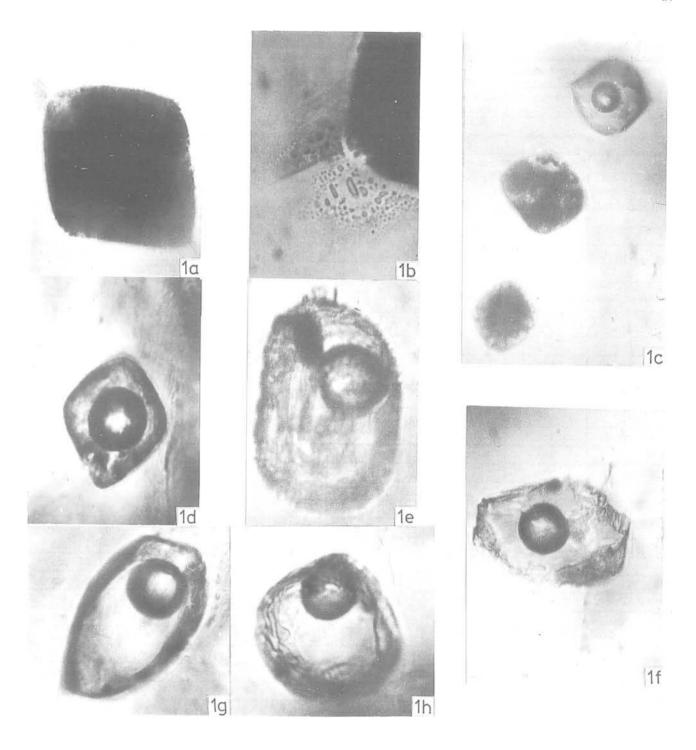


Fig. 2. Melt (a - c) and fluid (c - h) inclusions in quartz in sanidine phenocrysts from rhyolite of the Štiavnica Stratovolcano. a - d: quartz phenocrysts; c - h: sanidine.

be increased by 2%. In Tab. 2 densities of fluids at the time of trapping are given after volumometric corrections: 0.69 - 0.94  $g/cm^3$  for quartz and 0.86 - 0.93  $g/cm^3$  for sanidine.

# Geological interpretation

Fluid pressure during trapping was calculated for two temperatures:  $850\,^{\circ}C$  and  $700\,^{\circ}C$  (Tab. 2). The first temperature is close to the lowest homogenization temperature of melt inclusions in quartz whereas the second is closed to the lowest tem-

perature of acid magmas during volcanic eruptions. In virtually all cases the calculated pressures are high reaching 600 - 870 Mpa. A relatively low pressure of 330 - 470 MPa indicated only by one inclusion in quartz phenocryst. This inclusion was the largest of all the inclusions investigated (95  $\mu$ m) and leakage resulting from an abrupt change in external pressure is not unlikely.

The calculated high fluid pressure of magmatic water (water content in magma is about 3 - 5 wt.%) is possible only under conditions of superheated acid magmas under the total pressure of more than 1000 MPa (Ryabchikov 1975). These data indi-

88 NAUMOV et al.

Table 2. Results of studying of high density fluid inclusions of magmatic water in phenocrysts in rhyolites from Štiavnica Caldera (Slovakia).

Diameter of inclusion,	Temperature °C		Salinity wt. % of NaCl	Density of	fluid, g/cm <sup>3</sup>	Pressure, Mpa	
$\mu m$	1	2	equivalent	3	4	5	6
			Quar	t z			
31	125	-1.6	2.6	0.96	0.94	870	680
15	130	-1.6	2.6	0.96	0.94	870	680
45	135	-1.5	2.4	0.95	0.93	860	670
31	137	-1.5	2.4	0.95	0.93	860	670
18	143	-1.5	2.4	0.94	0.92	840	660
9	145	-	2	0.94	0.92	840	660
24	145	-1.6	2.6	0.94	0.92	840	660
20	152	-1.7	2.9	0.94	0.92	840	660
31	164	-1.5	2.4	0.93	0.91	830	650
38	170	-1.6	2.6	0.92	0.90	820	630
22	170	-1.9	3.1	0.92	0.90	820	630
15	172	-1.4	2.3	0.92	0.90	820	630
18	173	-1.4	2.3	0.92	0.90	820	630
19	174	-1.7	2.9	0.91	0.89	800	620
21	176	-1.6	2.6	0.91	0.89	800	620
22	176	-1.9	3.1	0.91	0.89	800	620
47	179	-1.9	3.1	0.90	0.89	790	600
33	180	-1.6	2.6	0.90	0.88	790	600
95	320	-1.4	2.3	0.70	0.69	470	330
			Sanid	ine			
71	160	-1.5	2.4	0.93	0.93	860	670
70	165	-1.5	2.4	0.92	0.92	850	660
88	165	-1.6	2.6	0.92	0.92	850	660
79	167	-1.5	2.4	0.92	0.92	850	660
52	169	-1.6	2.6	0.92	0.92	840	660
66	170	-1.0	1.6	0.92	0.92	840	660
70	170	-1.0	1.6	0.92	0.92	840	660
44	171	-1.0	1.6	0.92	0.92	840	660
22	173	-1.2	1.9	0.91.	0.91	830	650
50	174	-1.5	2.4	0.91	0.91	830	650
50	175	-1.5	2.4	0.91	0.91	830	650
30	176	-1.2	1.9	0.91	0.91	830	650
67	177	-1.8	3.0	0.91	0.91	820	640
94	177	-1.8	3.0	0.91	0.91	820	640
82	178	-1.4	2.3	0.91	0.91	820	640
66	180	-1.9	3.1	0.90	0.90	820	630
48	183	-1.7	2.9	0.90	0.90	810	630
62	183	-1.7	2.9	0.90	0.90	810	630
22	200	-1.4	2.3	0.89	0.89	790	600
30	225	-1.0	1.6	0.86	0.86	760	570

Explanations: 1 - homogenization temperature, 2 - melting temperature of ice, 3 - fluid density at the homogenization temperature, 4 - fluid density during the formation of the inclusion, 5 - pressure at  $850^{\circ}C$ , 6 - pressure at  $700^{\circ}C$ .

cate the existence of a deep-seated source, more than 30 km below the Earth surface. At such depth acid magmas of the Western Carpathian region were formed and their crystallization was initiated. The rapid uplift of magma to the Earth surface lead to the decompression and to the removal of magmatic water from the melt. The water formed a separate fluid phase, that was capable to take pert in ore-forming hydrothermal processes which are common within the Štiavnica Caldera.

#### References

- Bagdasaryan G.P., Konen V. & Vass D., 1970: Contribution of the absolute ages to the evolution scheme of the Central Slovakia Neogene volcanism. Geol. Práce. Spr. (Bratislava), 51, 47 - 69.
- Clark S.P. Jr. (Ed.), 1969: Handbook of physical constants. Mir, Moscow.
- Bagdasaryan G.P., Konečný V. & Vass D., 1969: Evolution Neogene volcanism in Central Slovakia and its confrontation with absolute age. Acta Geol. Acad. Sci. Hung. (Budapest), 13,1-4, 245 -258.
- Naumov V.B. & Kovalenko V.I., 1981: Water concentration and pressure in acid magmas according to the results of study of inclusions in minerals. *Dokl. Akad. Nauk SSSR* (Moscow), 261, 6, 1417 1420.

- Naumov V.B. & Ivanova G.F., 1984: Geochemical criteria for a genetic relation between rare-metal mineralization and acid magmatism. Geochemistry Internat. (Silver Spring), 21, 6, 1 - 12.
- Naumov V.B., Kovalenko V.I., Clocchiatti R. & Solovova I.P., 1984: Crystallization parameters and phase compositions for melt inclusions in ongorhyolite quartz. Geochemistry Internat. (Silver Spring), 21, 451 - 463.
- Naumov V.B. & Kovalenko V.I., 1986: Mineral-inclusion data on the principal volatile components of magmas metamorphic fluids. Geochemistry Internat. (Silver Spring), 23, 11 - 22.
- Naumov V.B., Solovova I.P., Kovalenko V.I. & Ryabchikov I.D., 1987: Composition, concentration of fluid phase and water content in pantellerite and ongonite melts on melt inclusion data. *Dokl. A-kad. Nauk SSSR* (Moscow), 295, 2, 456 - 459.
- Reif F.G., 1990: Ore-forming potential of granites and conditions of its realization. Nauka, Moscow, 1 - 181.
- Ryabchikov I.D., 1975: Fluid phase thermodynamics in granitoid magmas. Nauka, Moscow, 1 - 232.
- Tsaryeva G.M., Kovalenko V.I., Naumov V.B., Babansky A.D. & Tsepin A.I., 1990: Melt inclusions with high density water phase in quartz phenocrysts from rare-metal topaz rhyolites of Spor Mountain (USA). Dokl. Akad. Nauk SSSR (Moscow), 314, 3, 694 -697.