Magma storage constrains by compositional zoning of plagioclase from dacites of the caldera forming eruptions of Vetrovoy Isthmus and Lvinaya Past’ Bay (Iturup Island, Kurile Islands)

I A Maksimovich\textsuperscript{1,2}, S Z Smirnov\textsuperscript{2,3}, A A Kotov\textsuperscript{1,2}, T Yu Timina\textsuperscript{2}, A V Shevko\textsuperscript{2}

\textsuperscript{1}Novosibirsk State University, Pirogova, 1/2, 630090, Novosibirsk, Russia
\textsuperscript{2}V S Sobolev Institute of Geology and Mineralogy SB RAS, pr. ak. Koptyuga, 3, 630090, Novosibirsk, Russia
\textsuperscript{3}Tomsk State University, pr. Lenina, 36, 634050, Tomsk, Russia

Abstract. The Vetrovoy Isthmus and the Lvinaya Past’ Bay on the Iturup island (Kuril island arc) are the results of large Plinian eruptions of compositionally similar dacitic magmas. This study is devoted to a comparative analysis of the storage and crystallization conditions for magma reservoirs, which were a source of large-scale explosive eruptions. The plagioclase is most informative mineral in studying of the melt evolution. The studied plagioclases possess a complex zoning patterns, which are not typical for silicic rocks in island-arc systems. It was shown that increase of Ca in the plagioclase up to unusually high An\textsuperscript{95} is related to increase of H\textsubscript{2}O pressure in both volcanic magma chambers. The study revealed that minerals of the Vetrovoy Isthmus and Lvinaya Past’ crystallized from compositionally similar melts. Despite the compositional similarity of the melts, the phenocryst assemblage of the Lvinaya Past’ differs from the Vetrovoy Isthmus by the presence of the amphibole, which indicates that the pressure in the magmatic chamber exceeded 1-2 kbar at a 4-6 wt. % of H\textsubscript{2}O in the melt. The rocks of the Vetrovoy Isthmus do not contain amphibole phenocrysts, but melt and fluid inclusions assemblages in plagioclase demonstrate that the magma degassed in the course of evolution. This is an indication that the pressure did not exceed significantly 1-2 kbar.

1. Introduction

The Kurile-Kamchatka island-arc system stretching from the Kamchatka peninsula to the Hokkaido Island is an area of modern active island-arc volcanism. A wide spectrum of volcanic rocks: from basalts to rhyolites is represented on the islands of the Great Kurile island chain. The most common rocks are andesites. Silicic rocks are subordinate to the mafic and intermediate rocks. Their proportion increases southward. Nevertheless, the silicic rocks of the Kurile Islands are poorly studied and are of great importance for understanding the evolution of island-arc magmas and the formation of the Kurile island-arc crust.

Lvinaya Past’ (LP) caldera is located in the southern part of Iturup Island. The northwestern part of the caldera ridge is absent. Caldera’s interior is filled with the waters of the Sea of Okhotsk. The caldera has the shape of an ellipse. Different erupted volume estimates vary from 20 to 170 km\textsuperscript{3} [1-2]. The maximum diameter of the caldera is 8 km. Fragments of the somma form the Bezvodynyi (Waterless) Ridge, which raises up to 350-400 meters above the sea level. The inner walls of the caldera are composed of alternating lava and pyroclastic material of the pre-caldera stratovolcano [3].
Dacitic pumaceous tuffs are developed on a periphery of the broken stratovolcano and cover a wide area between Breutarube volcano on the south and the Golubka Mountain on the north. The size of Lvinaya Past’ caldera is comparable to the caldera of Kurilskoe Lake, which is associated with the most powerful explosive eruption in the Holocene on the Kamchatka peninsula [4].

The Vetrovoy Isthmus (VI) is located in the northern part of the island and separates the Medvezhiy Peninsula from the rest of the island. The entire area of the VI is covered by pumice deposits with a thickness more than 264 meters. Formation of these rocks is associated with a caldera eruption that occurred in the Late Pleistocene. According to the state geological mapping [5], the pyroclastic rocks extend for 10 km to the Sea of Okhotsk bottom in the north-west direction. Remnants of large caldera have a more than 7 km in diameter, with a maximum height of 264 m. The erupted material volume was estimated by I.V. Melekestsev [6] at about 100 km$^3$.

The aim of this article is to determine the magma storage conditions that preceded catastrophic eruptions of VI and LP on the basis of comparative analysis of chemical zoning and inclusions of fluids and melts in the plagioclase phenocrysts.

2. Research methods

The bulk composition of the rocks was determined by X-ray fluorescence (XRF) and ICP-MS analyzes at the Center for Collective Use of Scientific Equipment for Multielement and Isotopic Studies in IGM SB RAS (Novosibirsk).

2.1. X-Ray spectral analysis.

Energy-dispersive electron-microprobe analysis (EDS) on TESCAN MIRA-3 LMU SEM equipped with a microanalysis system, including the INCA Energy 450+ software and X-Max 80 analyzer, was used for determination of the compositions of minerals and melt inclusion glasses in phenocrysts of pumices. The accelerating voltage was 20 kV, probe current 1.4 - 1.6 nA, the diameter of the focused electron beam was 10 nm. The counting time was 60 seconds. With these parameters, the detection limits of different elements vary within 0.1-0.3 wt. %. The analysis of the melt inclusion glass was carried out by scanning the 10x10 $\mu$m area in order to reduce the effect of sodium loss [7-9]. For each inclusion, three glass analyzes and one analysis of the host mineral near the inclusion were performed. The analysis of the host mineral was carried out to verify the correctness. If necessary, a correction was applied.

3. Mineralogy and petrography

The rocks of the LP and VI are presented by white or light gray strongly porous pumice chunks and volcanic sands. The pumices contain about 25-30% phenocrysts. Porphyritic phenocrysts are immersed in the vitreous silicic (SiO$_2$ 73-76 wt.%) groundmass with a fibrous texture. The phenocrysts are presented by plagioclase, quartz, augite (Wol 0.43-0.44, Mg # 0.73-0.74), hypersthene (Mg # 0.62-0.64) and Fe-Ti oxides [10]. Major feature that differs LP phenocryst assemblage from that of VI is a presence of amphibole. Apatite does not occur as phenocrysts, but is abundant in as mineral inclusions in all minerals. Sulfides of Fe and Cu were found also as mineral inclusions in mafic minerals and Fe-Ti oxides.

The composition of the plagioclase is sensitive to changes in the PTX conditions. This is manifested in compositional zoning. The phenocrysts of the plagioclase of both volcanic centers usually form well-shaped transparent crystals with abundant inclusions. Plagioclase dominates the both phenocryst assemblages (more than 50-60 % of all phenocrysts). The K$_2$O content does not exceed 0.17 wt. %. Compositions of phenocrysts vary from andesine to labrador and, less often, to anorthite (An$_{41.95}$) in VI rocks and from andesine to labrador (An$_{40.85}$) in the LP rocks.

The plagioclases possess complex patchy and concentrically zoned patterns [11-12] (figure1). Patchy plagioclase consists of domains with contrast compositions. In VI plagioclase they belong to An$_{41}$-An$_{95}$ and An$_{41}$-An$_{85}$ (figure 1 b). In the LP plagioclases – to An$_{75}$-An$_{85}$ and An$_{40}$-An$_{55}$ (figure 1 a). There is a gap between An$_{70}$-80 and An$_{90}$ in the domain compositions. There are no obvious signs of skeletal growth in the both LP and VI patchy plagioclase.
Oppositely to patchy plagioclase compositions gradually change in the concentrically zoned one from An$_{95}$ to An$_{41}$ on VI plagioclase and from An$_{85}$ to An$_{41}$ in the LP plagioclase. When both patterns are presented in the same crystal the patchy one composes the core and the concentrically zoned form a periphery. The highest Ca contents are confined to the boundary separating the patchy and concentric-zoned parts (figure 1 a, b).

Figure 1. BSE-images and EDS profiles of plagioclase phenocrysts from LP (a) and VI (b).

4. Mineral-forming media
In the phenocrysts of plagioclase, a large number of melt inclusions (MI) were found. They are mostly distributed along the growth zones or form irregular “clouds”. By the phase compositions at room temperature, MI in VI plagioclases can be divided into several groups: single-phase, containing only glass (figure 2 a); two-phase, containing glass and shrinkage or gas bubbles (figure 2 b); multiphase, containing glass, crystals and a gas bubble (figure 2 c). Mineral phases in the multiphase inclusions are represented by apatite, magnetite, ilmenite, pyrrhotite, hypersthene and augite. All these minerals occur as crystalline inclusions and are not daughter phases of MIs. Apatite, magnetite, ilmenite and augite are found in patchy parts of the VI plagioclase as crystalline inclusions. In the vast majority of cases, the inclusion of hypersthene occurs only in the concentrically-zoned parts of the plagioclase.

Figure 2. Melt inclusions in transmitted light at room temperature; a-c - MI in plagioclases of the Vetrovoy Isthmus; d-f - MI in plagioclases of Lvinaya Past'; a, d - single-phase vitreous MIs, b, c - two-phase MIs, e, f - devitrified.
The LP plagioclases contain all the types of MIs (figure 2 d, e) reported above along with finely crystallized inclusions (figure 2 f), in which the crystalline phases appear as a result of the devitrification of glass. Crystalline inclusions in the LP plagioclases are represented byapatite, magnetite, ilmenite, pyrrhotine, hypersthene, augite, amphibole and quartz. Unlike VI, hypersthene occurs in association with augite in patchy cores of the LP plagioclase. Inclusions of the amphibole are extremely rare. Amphibole in an intergrowths with pyroxenes was found on the boundary between the patchy core and the concentrically zoned periphery of one of the phenocrysts of plagioclase with An$_{70}$. Inclusions of quartz were found only in the low-calcium outer zones of phenocrysts.

Fluid inclusions (FI) are found only in the VI plagioclases only in areas with a high Ca contents. At room temperature, FIs contain two phases: low-density CO$_2$ with a thin rim of liquid water (figure 3 a). FIs always appear in the association with MIs (figure 3 b).

Figure 3. Fluid inclusions in plagioclase phenocrysts from the pumice of the Vetrovoy Isthmus at room temperature (a, b); fluid and melt inclusion assemblage (b).

4.1. Melt inclusions composition

The rocks of both eruptions correspond to dacites with normal alkalinity (figure 4). The MIs compositions in the LP and VI plagioclases are similar to groundmass glass and correspond to the high-alumina (A / CNK 1.0-1.2 mol.%) rhyolite (SiO$_2$ - 74-75 wt.%) with normal alkalinity, low potassium (K$_2$O 1.6-2.0 wt.%) (figure 4) and high Cl content (0.2-0.4 wt. %).

Figure 4. Bulk composition of LP and VI pumices and composition of melt inclusions from plagioclase phenocrysts.

Compositions of the plagioclase MIs shown in (figure 5) demonstrate positive correlation between CaO and Al$_2$O$_3$ within narrow concentration range and slight positive or no correlation between FeO and Al$_2$O$_3$ contents. These regularities are similar to MIs in other minerals of phenocryst assemblages both from LP and VI [10]. This means that the trapped melts changed their compositions due to
crystallization of Ca-Al rich mineral, e.g. plagioclase, and were only slightly or not affected by crystallization of mafic minerals. Compositional similarity with MIs in other minerals allows conclusion that this regularity reflects plagioclase fractionation in the reservoir rather than crystallization of plagioclase on inclusion walls after entrapment. Thus MI glass compositions could be considered as compositions of the parent melt.

![Figure 5. Composition variations of the melt inclusions glasses in plagioclases for the Lvinaya Past’ caldera and Vetrovoy Isthmus. Dotted line - compositions of glasses of melt inclusions from other minerals according to Smirnov et al. (2017).](image)

The water content in the VI and LP melts was estimated by secondary-ion mass-spectrometry (SIMS). The water content of MIs in the VI plagioclase varies from 2.3 to 5.3 wt. %, while for MIs in the LP plagioclase – within 4.5 – 4.9 wt. %. Raman spectroscopy demonstrated that water contents of MIs in the VI plagioclase varies from 3.5 to 6.0 wt.%, which agrees well with the data of SIMS.

5. Mineral thermometry
Crystallization temperatures were estimated using plagioclase-liquid [13-14] and two-pyroxene geothermometers [15]. In order to estimate the temperature by the plagioclase-liquid geothermometer, the compositions of melt inclusion and plagioclase from the zone containing the inclusion were taken into account. The calculated temperatures for both LP and VI plagioclases at 1 kbar and 4 wt.% H₂O were 843 to 868°C. For 5 wt.% H₂O – 825 - 845°C, and for 6 wt.% H₂O – 800-823°C.

Two-pyroxene temperatures at 1 kbar were 832 - 848°C for VI and 845-860°C for LP, which agrees well with data obtained from the plagioclase-liquid geothermometer.

6. Discussion
The earliest mineral paragenesis of VI is represented by the assemblage of the intermediate plagioclase (An$_{41-55}$) with augite and Fe-Ti oxides. The patchy zones occur due to the replacement of the intermediate plagioclase by the Ca-rich one (An$_{41-95}$). This process coincides with the beginning of the melt degassing and release of water-carbon dioxide fluid that was trapped by plagioclase as fluid inclusions [10]. The domains and zones of Ca-rich plagioclase contain less augite inclusions, while inclusions of hypersthene and apatite appear. An increase in the calcium content is also associated with a change of the pattern of zoning in plagioclase. It becomes concentrically zoned and demonstrates gradual outward decrease in Ca-content.

Variations in the melt compositions during the evolution of both magma chambers were insignificant and were related to plagioclase crystallization. The absence of compositionally contrasting MIs implies that no mixing or mingling with andesitic or basaltic magmas took place.

The beginning of relatively monotonous outward decrease in the calcium content in the VI plagioclase from An$_{95}$ to An$_{41}$ coincides with the disappearance of fluid inclusions, i.e. with the end of the degassing process. The outer zones contain less crystalline inclusions. The latter are mainly represented by rare apatite needles. The quartz joins the plagioclase at the final stages immediately
before the catastrophic eruption, as is evidenced by the absence of quartz in the form of inclusions in plagioclase and the presence of rare intergrowths of quartz and plagioclase. The nature of the zoning of plagioclases in the pumice of the LP (figure 1) allows us to conclude that the crystallization process was similar in general to the VI. The earliest plagioclase had an intermediate composition ($\text{An}_{40-55}$) and was associated with hypersthene, augite, and Fe–Ti oxides. The patchy structure of cores of some phenocrysts resembles the substitution of the low-Ca plagioclase by the high-Ca one, similarly to VI. This similarity along with similarity in mineral and bulk rock compositions implies that this process also was controlled by increase in $\text{H}_2\text{O}$ pressure. However, unlike VI, pressure increase did not trigger the degassing. Oppositely it favored crystallization of of magnesian hornblende amphibole phenocrysts. Apparently, this it could be a reason why Ca contents in the Ca-rich zones of LP plagioclases are lower (less than $\text{An}_{85}$) than in those of VI plagioclases. A monotonic decrease in the Ca contents towards the outermost zones suggests a decrease in fluid pressure, the cause of which remains to be established. Quartz begins to crystallize at later stages, but unlike VI, it occurs as inclusions in concentrically zoned plagioclase. The above analysis indicates that VI magma storage developed at pressure less than 1 - 2 kbar. Low total pressure impeded the formation of phenocrysts of amphibole but favored fluid degassing. The presence of amphibole in assemblage with plagioclase and two pyroxenes in LP rocks indicated that pressures were more than 1 – 2 kbar as confirmed by experiments on the dehydration melting of andesibasaltic metabasites [16]. According to experimental data on the melting and crystallization of the Mt. St. Helens rhyodacites (USA) amphibole becomes stable at 885 °C [17] and pressures that exceed 1.5-2.5 kbar, at the water contents similar to the melts of the LP and VI.

7. Conclusion
The appearance of high-calcium zones in plagioclase crystallizing from rhyolitic melts of VI and LP is explained by an increase in the partial pressure of $\text{H}_2\text{O}$ [18], [12], and not by the influence of more mafic melts intruding the dacite magma [19], [12]. At 5 kbar, the liquidus and solidus temperatures in the binary albite-anorthite system decrease by ~ 300°C and plagioclase with higher Ca contents become more stable [20]. The results of melting experiments on mafic and intermediate rocks in water-saturated systems [24-26] showed that the addition of water to the melt of the basaltic and andesitic composition can increase the anorthite content in plagioclase by 10 mol.%, and when the melt is saturated with $\text{H}_2\text{O}$ - by more than 20 mol.%. The authors of [21], [24] emphasize that for island arc magmas $\text{H}_2\text{O}$ affects composition of plagioclase during magmatic crystallization more than the bulk magma composition.

On the basis of the data obtained, it can be concluded that the rocks of the Lvinaya Past’ caldera and the Vetrovoy Isthmus were formed as a result of crystallization of low-potassium plagiortholite-rhyodacite melts with a high water content at temperatures close to 850°C. Despite the same magma chemistry and similar crystallization temperatures, the assemblages of porphyritic phenocrysts are different because the evolution of magma reservoirs occurred at different pressures.

Acknowledgements
The work was carried out within the framework of projects 0330-2016-0005 and 0330-2016-0001 of the state assignment of the IGM SB RAS and with the support of the RFBR grant 16-05-00894. Analytical studies were carried out in the Center for Multielement and Isotope Studies of the SB RAS.

References
[1] Degterev A V Rybin A V Arslanov H A 2014 Calderaforming eruption of Lvinaya Past’ (Iturup island, Kurile Islands): stratigraphy and age VII Siberian scientific and practical conference materials of young scientists of Earth sciences VS Sobolev IGM SB RAS p. 14-15 (In Russian).
[2] Laverov N P 2005 Modern and holocene volcanism in Russia (Moscow: Nauka) 604 p.
[3] Lomtev V L 2008 Extrusion of the south of the Okhotsk outskirts of the Kuril arch near the Lvinaya Past’ caldera (Iturup Island) *Geologiya i razvedka* (short articles) 4 pp 72-74 (in Russian)

[4] Bazanova L I Melekescev I V Ponomareva V V Dirksen O V Dirksen V G 2016 Late Pleistocene and Holocene volcanic catastrophies in Kamchatka and in the Kuril islands. Part 1. Types and classes of catastrophic eruptions as the leading components of volcanic catastrophism *Journal of volcanology and seismology* 10(3) pp 151-169

[5] Kovtunovich P Yu Safonov A D Udodov V V Raschepkina E V 2002 State geological map of Russian Federation, 2nd edition Page L-55-XXXIII Explanatory letter Saint-Petersburg: VSEGEI, 269 p. (in Russian)

[6] Melekescev I V Braitseva O A Sulerzhitsky L D 1988 Catastrophic explosive eruptions of volcanoes of the Kurile-Kamchatka region at the end of the Pleistocene-Early Holocene DAS USSR, 300(1) pp 175-181 (in Russian)

[7] Lineweaver, J L 1963 Oxygen outgasing caused by the electron bombardment of glass *Journal of Applied Physics* 34 pp 1796-1791

[8] Morgan G B London D 1996 Optimizing the electron microprobe analysis of hydrous alkali aluminosilicate glasses *American Mineralogist* 8(9-10) pp 1176-1185

[9] Morgan G B London D 2005 Effect of current density on the electron microprobe analysis of alkali aluminosilicate glasses *American Mineralogist* 90(7) pp 1131-1138

[10] Smirnov S Z Rybin A V Sokolova E N Kuzmin D V Degtere A V Timina T Yu 2017 Felsic magmas of the caldera-forming eruptions on the Iturup Island: the first results of studies of melt inclusions in phenocrysts from pumices of the Lvinaya Past and Vetrovoy Isthmus calderas *Russian Journal of Pacific Geology* 11(1) pp 46-63

[11] Kawamoto T 1992 Dusty and honeycomb plagioclase – indicators of processes in the Uchino stratified magma chamber, Izu Peninsula, Japan *Journal of Volcanology and Geothermal Research* 49(3-4) pp 191-208

[12] Shcherbakov V D Plechov P Y Izbekov P E Shipman J S 2011 Plagioclase zoning as an indicator of magma processes at Bezymianny Volcano, Kamchatka *Contributions to Mineralogy and Petrology* 162(1) pp 83-99

[13] Putirka K A 2005 Igneous thermometers and barometers based on plagioclase plus liquid equilibria: Tests of some existing models and new calibrations *American Mineralogist* 90(2-3) pp 336-346

[14] Laura E Waters Rebecca A Lange 2015 An updated calibration of the plagioclase-liquid hygrometer-thermometer applicable to basalts through rhyolites *American mineralogist* 100 pp 2172–2184

[15] Putirka K D 2008 Thermometers and Barometers for Volcanic Systems *Minerals, Inclusions and Volcanic Processes* 69 pp 61-120

[16] Beard J S Lofgren G E 1991 Dehydration melting and water-saturated melting of basaltic and andesitic greenstones and amphibolites at 1.3 and 6.9 *Journal of Petrology* 32(2) pp 365-401

[17] Riker J M Blundy J D Rust A C Botcharnikov R E Humphreys M C S 2015 Experimental phase equilibria of a Mount St. Helens rhyodacite: A framework for interpreting crystallization paths in degassing silicic magmas *Contributions to Mineralogy and Petrology* 170(6) p 22

[18] Hattori K Sato H 1996 Magma evolution recorded in plagioclase zoning in 1991 Pinatubo eruption products *American Mineralogist* 81(7-8) pp 982-994

[19] Snyder D Tait S 1996 Magma mixing by convective entrainment *Nature* 379(6565) pp 529-531

[20] Yoder H S Stewart D B Smith J R 1957 Ternary feldspars *Carnegie Institution of Washington Year Book* 56 pp 206-214

[21] Plechov P Y Gerya T V 1998 Effect of H2O on plagioclase-melt equilibrium *Experiment in Geosciences* pp 7-9

[22] Housh T B Luhr J F 1994 Plagioclase-melt equilibria in hydrous systems *American Mineralogist* 79(3-4) pp 352-352
[23] Sisson T W Grove T L 1993 Experimental investigations of the role of H2O in calc-alkaline differentiation and subduction zone magmatism *Contributions to Mineralogy and Petrology* **113**(2) pp 143-166

[24] Panjasawatwong Y Danyushevsky L V Crawford A J Harris K L 1995 An experimental-study of the effects of the effects of melt composition on plagioclase-melt equilibria at 5-kbar and 10-kbar – implications for the origin of magmatic high-An plagioclase *Contributions to Mineralogy and Petrology* **118**(4) pp 420-432

[25] Almeev R R Ariskin A A 1996 Mineral-melt equilibria in a hydrous basaltic system: Computer modeling *Geochemistry International* **7** pp 624-636

[26] Bachmann O Bergantz G W 2003 Rejuvenation of the Fish Canyon magma body: A window into the evolution of large-volume silicic magma systems *Geology* **31**(9) pp 789-792