Water in melt inclusions from phenocrysts of dacite pumice of the Vetrovoy Isthmus (Iturup Island, Southern Kuriles)

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Abstract. This work is devoted to the study of one of the largest caldera eruptions of the Kurile-Kamchatka island-arc system that occurred on the island of Iturup. The object of investigation of this work are phenocrysts of quartz and plagioclase from dacite pumice of the Isthmus of the Isthmus, which is located on the island of Iturup. The purpose of this work is to determine the water content in the melts that participated in the caldera eruption of the Vetrovoy Isthmus and the patterns of their changes during the crystallization of magma. In the course of the work, the following were carried out: 1) adaptation and calibration of the Raman spectroscopy method for determining water in rhyolite melt's inclusions glasses in quartz and plagioclase from pumice stone; 2) determination of composition and estimation of water content in melt inclusions in quartz and plagioclase according to x-ray spectral analysis; 3) establishment of the regularities of the change in the water content during the evolution of the magmatic melt; 4) evaluation of fluid pressure by comparison with experimental data

1. Introduction

Catastrophic eruptions, such as Santorin [1], Toba [2-3], Pinatubo [4], etc., are usually associated with reservoirs of acid magmas with a high content of volatile components. Studies of volcanic emanations and melt inclusions in minerals showed that the main volatiles are water and carbon dioxide [5].

The Vetrovoy Isthmus (VI) is 12 km wide graben depression in the northern part of the Iturup Island of the Kurile island arc. Graben is filled with late Pleistocene pumice-pyroclastic deposits with a thickness of more than 260 meters and a volume of about 100 km^3 [6-7]. It is presumed that the eruptive center is located approximately in the middle of the isthmus. The pyroclastic deposits are the product of one of the largest eruptions or series of near-simultaneous eruptions in the Kurile-Kamchatka arc in the late Pleistocene and the Early Holocene.

Previous studies demonstrated that the magmatic reservoir of the Vetrovoy Isthmus in the early stages of its development was degassed, with the release of a substantially aqueous fluid. Studies of melt and fluid inclusions showed that water is the main volatile, while CO_2, F and sulfur compounds play a subordinate role [8]. This conclusion raises the question of how high pressure, which eventually led to a large-scale eruption, could develop in the early degassed reservoir. This question cannot be

answered without reconstructing the behavior of water in the magmatic reservoir and determining the change in H_2O content in the magmatic melt. This article presents the results of a detailed study of the water content in melt inclusions in quartz and plagioclase from the pumice of the Vetrovoy Isthmus at Iturup Island.

2. Mineralogy and petrography of the Vetrovoy Isthmus pumices

The rocks of the Vetrovoy Isthmus are represented by tuffs with fragments of light pumice. Pumices contain a large number of porphyritic phenocrysts (25-30%), which are found in the matrix of felsic glass (SiO_2 73-76 wt. %). The phenocrysts are represented by plagioclase, quartz, augite, hypersthene, and Fe-Ti oxides. Amphibole does not appear as phenocrysts, nevertheless it is found as crystalline inclusions in pyroxenes and has a high alumina composition (tschermakite-hornblende series).

Plagioclase, femic minerals, and Fe-Ti oxides compose the early paragenesis of the felsic pumice. Formation of femic minerals ceased immediately before the eruption, and only plagioclase and quartz crystallized then from the melt [8]. An unusual feature of plagioclase is that its crystallization begins with intermediate compositions, then Ca content increases to maximum values (An_{95}), and the latest zones again have an intermediate composition.

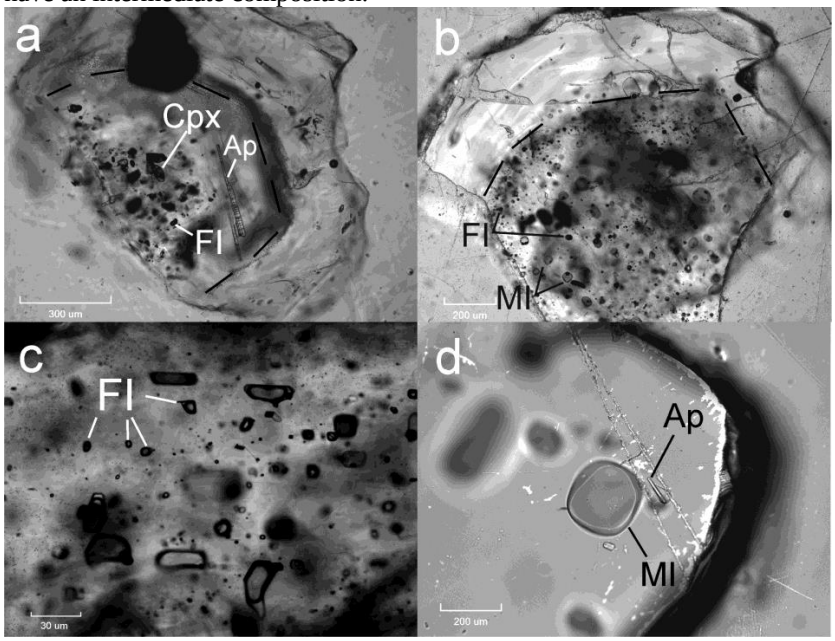

Figure 1. Zoning structure and location of fluid and melt inclusions in plagioclase and quartz: a) plagioclase with crystalline inclusions of apatite (Ap), clinopyroxene (CPx), melt (MI) and fluid inclusions (FI); b) separation of internal core with melt and fluid inclusions and concentrically zoned external parts of plagioclase; c) FI in plagioclase; d) quartz with MI and apatite with a drop of parent melt.

3. Melt and fluid inclusions

Plagioclase and quartz contain abundant melt inclusions (MI), which are located either along growth zones, form irregularly distributed groups or are trapped together with other minerals. Nonheated melt inclusions can be divided into three groups: 1) single-phase, completely vitreous (figure 1 d); 2) two-phase, containing glass and gas bubble; 3) multiphase, containing glass, crystals and / or gas bubble. Crystals in inclusions are apatite (figure 1 a, d), Fe-Ti oxide minerals, augite (figure 1 a), hypersthene and amphibole. Melt inclusions with crystals are the result of simultaneous capture of the melt and other minerals coexisting with plagioclase. Only first-type inclusions without signs of decrepitation

were selected for the study as they are naturally quenched and their composition has undergone post-entrapment transformations to the least extent.

Fluid inclusions (FI) are found only in plagioclase, located in zones and areas with the maximum Ca contents. They are represented by two-phase essentially gaseous inclusions of CO_2 with a rim of liquid at room temperature aqueous solution (figure 1 a, b, c). FI form associations with melt inclusions. In this case, some MIs contain a two-phase gas-liquid separation. These indicates the formation of high calcium zones of plagioclase under degassing conditions.

4. Analytical methods and results

4.1. Electron-microprobe analysis

The composition of MI glass was determined by the energy dispersive X-ray spectral analysis (EDS) on the TESCAN MIRA-3 LMU SEM equipped with a microanalysis system with the INCA Energy 450+ software and the X-Max 80 analyzer (IGM SB RAS, Novosibirsk). The accelerating voltage was 20 kV, the probe current was 1.4 - 1.6 nA, the diameter of the focused electron beam was 10 nm. The counting time is 60 seconds. With these parameters, the detection limits of different elements vary within 0.1-0.3 wt. %. The analysis of the MI glass was carried out by scanning the 10x10 μm site to reduce the effect of sodium loss [9-11]. For each inclusion, two glass analyzes and one analysis of the host mineral near the inclusion were carried out. The mineral analysis was carried out to verify the correctness and to account for instrument drift. If necessary, a correction was applied.

4.2. Raman spectroscopy

The study of melt inclusions by Raman spectroscopy was carried out using the LabRAM HR 800 spectrometer at IGM SB RAS. The laser beam was positioned on the analyzed inclusion using an Olympus BX-41 polarization microscope. In the course of work, a 532 nm laser beam with output power of 75 mW was used for excitation. The registration was carried out using a liquid nitrogen cooled CCD detector with an operating temperature of -120° C. The analysis was carried out in the backscattering geometry. To collect the scattered light, a 100x lens was used. The spectra were obtained in the range 100-1250 cm^{-1} and 2800-4000 cm^{-1} (figure 2). The confocal pinhole and the acquisition time were regulated depending on the size and depth of the inclusion. In the course of the work it was established that a change in the size of the confocal pinhole and the acquisition time lead to an error not exceeding ± 0.2 abs. %. The acquisition time varied from 25 sec per spectral window for large inclusions to 400 sec per spectral window for small ones.

5. Determination of the water content using Raman spectroscopy

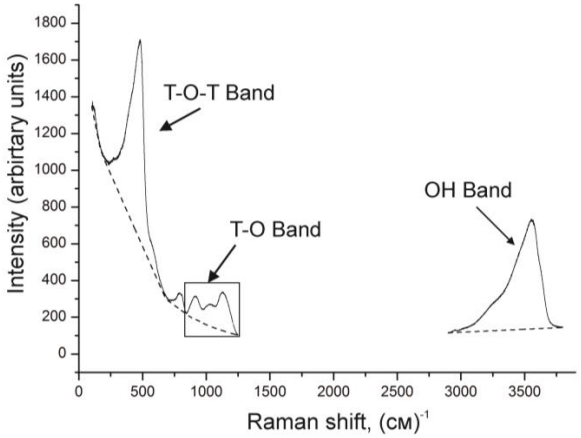

Figure 2. The Raman spectrum of the reference rhyolite glass with 6 wt. % H_2O. The dashed line is the baseline.

The method of quantitative determination of the water content is based on the calculation of the peak areas ratio in the range 2900-3800 cm^{-1} (Aw), which corresponds to vibrations of OH bonds in water molecules and hydroxyl groups in the silicate glasses [12] and the sum of peak in the range 850-1250 cm^{-1} (As) corresponding to vibrations of Si-O-Si, Al-O-Si and Si-O bonds in the structure of aluminosilicate glasses (figure 2) [13-14]. This ratio (Aw / As) directly depends on water content of the analyzed glass. In the course of this study five reference synthetic glasses of rhyolite composition with water contents from 2 to 6 wt. %, in which the water content was determined by different methods were used as calibration standards.

It is known that the spectra of silicate and aluminosilicate glasses differ significantly depending on their composition [13]. In this regard, the calibration results were checked on a series of reference felsic glasses from the Moscow State University. These glasses were obtained by remelting of natural obsidian in presence of water at specified temperatures and pressures [15]. The water contents in these glasses were measured with secondary ion mass spectrometry (figure 3 b), and Raman spectroscopy (figure 3 a) using the procedure described in [16]. In our study 16 measurements were obtained for four standard glasses by Raman spectrometry. These measurements demonstrated that the results obtained from glasses with less than 8 wt. % H_2O coincide well with the results obtained by ion probe and Raman spectrometry at Moscow State University. Significant deviation was obtained for the glass with 10 wt. % H_2O (figure 3 a, b). We believe that the reason of deviation is related to the compositional difference between the obsidian and synthetic reference glasses. In this regard, we assume that our calibration can be successfully applied to natural glasses of similar composition with a less than 8 wt. % water content.

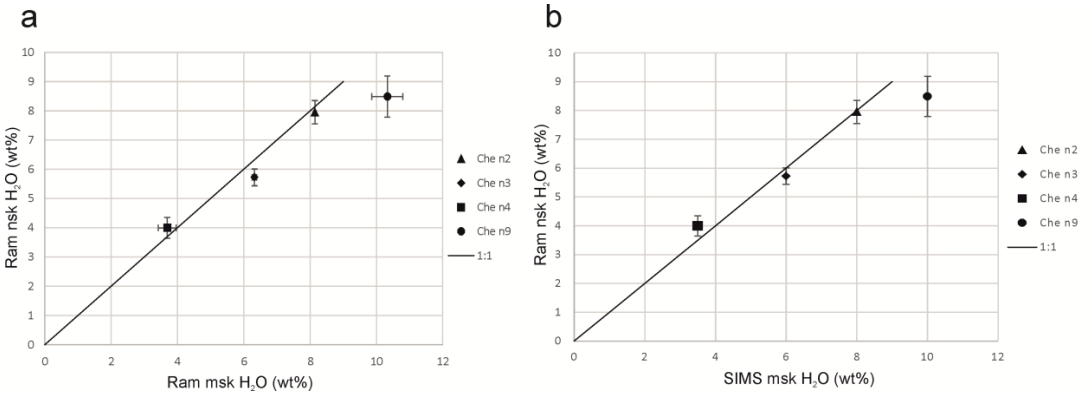

Figure 3. Comparison of water content in standard glasses from the collection of Moscow State University: a) obtained by Raman spectroscopy on the basis of IGM SB RAS (Ram nsk) and Moscow State University (Ram msk); (b) obtained by Raman spectroscopy on the basis of IGM SB RAS (Ram nsk) and secondary-ion mass spectrometry (SIMS msk).

For this study more than 50 inclusions in quartz and plagioclase from the pumices of the Vetrovoy Isthmus were measured by Raman spectroscopy. Each measured inclusion was then analyzed by the EDS method. The water content was calculated from the residual oxygen content. At first, the amount of oxygen coming from the stoichiometry to the oxides of metals and silicon was determined. It was assumed that all the iron in the melt is in a divalent form. Then this amount was subtracted from the measured amount of oxygen. The rest was recalculated to H_2O.

6. Water content in met inclusions

A comparison of the results that were obtained by SEM EDS and Raman spectroscopy is shown in the figure 4.

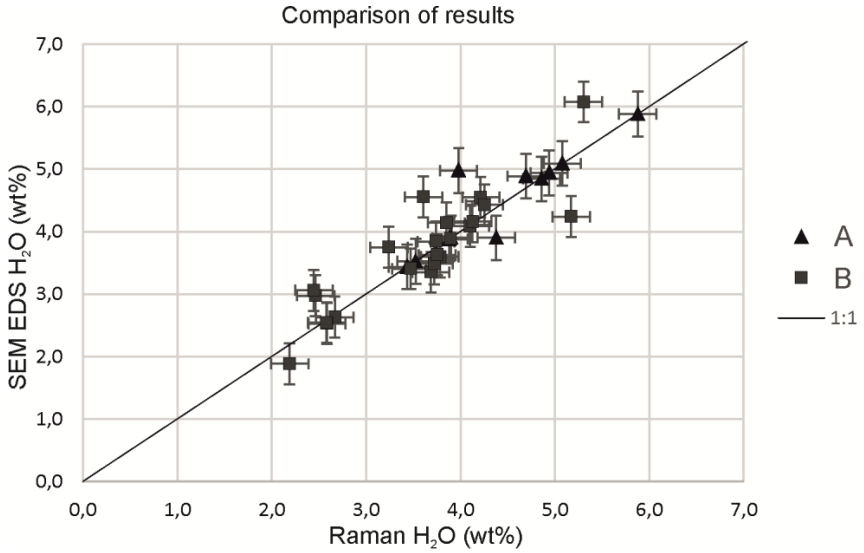

Figure 4. H_2O contents in melt inclusions in phenocrysts: (A) of plagioclase and (B) quartz, determined by Raman spectroscopy and energy dispersive X-ray spectral analysis (SEM EDS).

MI in quartz are the most suitable for analysis as there is a large number of single-phase vitreous melt inclusions, often more than 200 microns in size and the spectrum of the host mineral do not overlap those parts of the spectrum that are measured to assess the water content. Plagioclase lines overlap on the measured parts of the spectrum, and this decrease precision in processing of spectra. On the basis of the data obtained, it can be stated that the water content in quartz varies from 2.2 to 5.3 wt. %. The figure shows that most of the studied inclusions have concentrations of 3.2-2.2 wt. %. A separate group consists of inclusions with a water content of 2.2-2.7 wt. %. And only two inclusions have a concentration of more than 5 wt. % and deviate strongly from the line 1: 1. Concentrations of water in the MI belonging to one association, as a rule, have the same values.

Melt inclusions in plagioclase have water contents from 3.5 to 6.0 wt. %. Inclusions with the highest water content are few and occur in plagioclase with a highest Ca content up to An_{95}. Melt inclusions with water content of 3.5-4.5 wt. % are found only in the outer concentrically zoned plagioclase with andesine or labrador compositions.

7. Discussion

The results showed that the melts of the caldera eruption of the Vetrovoy Isthmus contained water close to saturation for magmas of dacite and rhyolite composition. The presence of amphibole in the form of inclusions in other minerals and the absence in the form of intrinsic phenocrysts suggests that the pressure in the magmatic chamber was below the stability threshold of this water-containing mineral. In these conditions, the saturation of the melt with water should lead to degassing-the separation of the aqueous fluid. Degassing of magma in the focus of the caldera eruption is fixed in the form of associations of fluid and melt inclusions in the highly calcareous zones and plagioclase phenocrysts. Formation of high-calcium plagioclase with An >> 70 mol. % of the rhyolite melt requires specific conditions. Such plagioclase is more typical for magmas of basic composition. However, in addition to the chemistry of the magma itself, the basicity of the plagioclase can also increase with an increase in the partial pressure of water, as demonstrated by experiments [17]. Investigations of fluid and melt inclusions show that the formation of high-calcium zones of plagioclase in pumice is associated with the degassing stage, which should be preceded by an increase in the partial pressure of water in the source. This stage corresponds to a water content in the melt of

not less than 6.0 wt. %, as evidenced by the maximum water concentrations in the MI from the high-calcium areas of phenocrysts. A further decrease in the calcium content indicates a re-balancing of the plagioclase with the melt at a lower pressure. The growth of the concentrically-zonal plagioclase came from a melt with a water content of 3.5-4.5 wt. %.

The absence of fluid inclusions in phenocrysts of quartz indicates that it crystallized after degassing. Probably, the lowest water concentrations (<3.5 wt %) correspond to the initial stages of the formation of this mineral. However, most of the inclusions have a water content in the range of 3.2 to 4.2 wt. %. This is close in magnitude to the water concentrations in the inclusions in the late zones of plagioclase that formed after degassing.

The rhyolite melts have a very high viscosity, which is even greater when degassed. It follows that in different parts the magma chamber degassed to different degrees, which could lead to significant differences in H_2O content. High water content can be attributed to the sections of the chamber, which retained their tightness and did not completely remove the fluid phase. In addition, a scenario is possible, suggesting an increase in the water content after degassing due to the crystallization of anhydrous minerals or the entry into its magmatic focus from the enclosing rocks due to the thermal dehydration of water-containing minerals. This enrichment could serve as a reason for re-enriching the melt with water before the final catastrophic eruption. It is suggested that melt inclusions in quartz with water contents of more than 5 wt %, were captured shortly before him.

8. Conclusion

Compositions of melt inclusions permit us to state that the crystallization of phenocrysts of dacite pumice from a catastrophic VI eruption occurred from a rhyolite melt with a water content of 2.0-6.0 wt. %. Analysis of mineral associations of pumice clearly indicates that amphibole was not stable in the magmatic focus and decomposed. In these conditions, saturation of the melt with water should lead to degassing, which occurred in the early stages of its development. This led to a significant decrease in the water content (up to 2 - 3% by weight). However, after this degassing, a new enrichment of the melt with water has probably occurred, up to saturation concentrations just before the catastrophic eruption.

Acknowledgements

The work was carried out within the framework of projects 0330-2016-0005 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.

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