UDC 553

Suk N.I., Kotelnikov A.R., Polskoy P.F. Experimental study of melting of maligniite from Lovozerskiy massif (T=1250°C, P=3 kbar).

IEM RAS, Chernogolovka, sukni@iem.ac.ru

Abstract. Experimental study of melting of malignite from Lovozerskiy massif was produced at $T=1250^{\circ}$ C and 3 kbar in high gas pressure vessel with duration of 6 h in presence of 15 wt% H₂O. It was obtained the immiscible splitting into two liquids: aluminosilicate one, which formed matrix, and droplets, enriched in Ti, REE, Sr and Nb. This

fact can be explained by generation of liquid immiscibility which was obtained (Suk, 2007, 2012) in aluminosilicate alkaline magmatic systems, containing REE (La, Ce, Y), Sr and Nb.

Keywords:experiment, melt, liquid immiscibility, malignite, Lovozerskiy massif

Malignite melting (rock connected with rich loparite ore in Lovozerskiy massif) was produced at $T=1250^{\circ}C$ and 3 kbar in high gas pressure vessel in platinum capsules with duration of 6 h in presence of 15 wt% H₂O. The experimental samples were analyzed on a digital scanning electron Tescan Vega II XMU microscope.



Fig 1. Microemulsion structure obtained after malignite melting at $T=1250^{\circ}C$ and 3 kbar in presence of 15 wt% H₂O (a) and liquid immiscibility in model systems under pressure of water or alkaline fluid at $T=1250^{\circ}C$ and 2 kbar (b). BSE image.

After experiment the aluminosilicate glass has been obtained. In them it was observed the areas with microemulsion structure determined by melt layering into two liquids: aluminosilicate melt forming matrix and the melt enriched in ore components (Ti, REE, Sr, Nb) forming the droplets (fig. 1a). Droplets sizes vary from 1 up to 5 mkm. This fact can be explain by arising of liquid immiscibility which was obtained earlier (Suk, 2007, 2012) in the aluminosilicate alkaline magmatic systems containing Ti, REE (La, Ce), Y, Sr and Nb. To comparison at fig 1b it has been shown the liquid immiscibility in model systems under pressure of water or alkaline fluid at

 $T=1250^{\circ}C$ and 2 kbar. The results are in a good agreement.

So in malignite melting products the globule of ore melt with heterogeneous structure determined by presence of silicate and ore phases was obtained (fig 2a). Their forming can be explained by rising of titanate-silicate liquid immiscibility, too.

Therewith, in one of the malignite samples of Lovozerskiy massif it has been found the fragment which presents the matrix of loparite composition with crystals of rock forming minerals enclosed in it (fig. 3). Such image can be explained by crystallization from two phases melt. 1. Suk N.I. Experimental study of alkaline magmatic



a

Fig. 2. The globule of ore melt (a) and its heterogeneous structure (b) obtained after malignite melting at T=1250°C and 3 kbar: light - ore phase, dark - silicate phase. BSE image



Fig. 3. Malignite sample with crystals of rock forming minerals enclosed in matrix of loparite composition (light). BSE image. Ab – albite, Kfs – K-feldspar, Cpx – clinopyroxene, Eud – eudialyte.

RSMA Group IEM RAS Date(m/d/y): 01/13/11 Virus A.A.

So, the experimental data obtained show that due to rising of titanate-silicate liquid immiscibility the magmatic melt can become rich of ore components. This can have grate significant for explanation of genesis of REE-Nb (loparite) deposits at the magmatic stage.

References:

aluminosilicate systems with the connection of genesis of rare earth-niobium loparite deposits. Dokl. Akad. Sci. 2007. V. 414. N 2. P. 249-252.

2. Suk N.I. Liquid immiscibility in fluid-magmatic aluminosilicate systems containing Ti, Nb, Sr, REE and Zr (experiment). Petrology. 2012. V. 20. N 2. P. 156-165.

Solovova I.P., Averin A.A., Ryabchikov I.D., Shiryaev A.A. Fe-Ni-Co alloy, sulphides and graphite in equilibrium with CH_4 - dominant fluid (magnesia basalt, O. Disco, West Greenland).

IGEM RAS, Moscow (solovova@igem.ru)

Abstract. Fluid and melt inclusions in olivine and matrix glass of native iron-bearing basalt from Disko, Greenland, were investigated using heating and cooling microscopic techniques and Raman- and IR-spectroscopy. The melt inclusions in olivine are homogenized at temperatures of $1170-1200^{\circ}$ C. Fluid inclusions were investigated in olivine and the glass of the rock. Water and several crystalline phases were observed at low temperatures. Raman and IR-spectroscopic investigation showed that fluid inclusions were a complex mixture of CH₄, CO₂, N₂, H₂O, and contain graphite. Melt equilibrium with metallic iron at T = 1450°K suggests that log fO₂ =-13.95. The calculated composition of C–O–H fluid in equilibrium with Fe, Fe₃C and FeS is characterized by high CH₄ and H₂ contents. UDC 550.4



Fig. 1. Ellipsoidal sulfide with metallic Fe+Ni bleb

The studied sample contains up to 90% of greenish glass and olivine phenocrysts Fo78.8-85.9 with size up to 400 microns. Glass contains rounded aggregates of sulfides (troilite and chalcopyrite) with uniformly distributed therein grains of metal alloy Fe-Ni + (Co, Cu). Alloy composition is (at.%): 71.2-82.2 Fe, 14.6-25.4 Ni, Co, and 2.7 to 1.3 Cu. Additionally, rare grains of graphite, cohenite, chromite and magnetite were identified in these aggregates.

Olivine and glass rocks contain numerous fluid inclusions. In olivine, fluid inclusions are cognate with melt inclusions, graphite, droplets of sulfides and metallic alloy. Fluid vacuoles in the glass matrix Keywords: basalt, fluid inclusions, thermo-, cryo-, Raman- and IR spectroscopic methods

The study of fluid inclusions in minerals of mantle peridotites, kimberlites, alkaline, mafic and ultramafic igneous rocks of deep genesis shows the dominant role of CO₂. In recent decades there were reports about the presence in them of additional volatile components such as N2, H2O, H2S, SO2. These multicomponent fluid inclusions were studied in mantle peridotites from the Bakony-Balaton province, Hungary, East Antarctica and spinel lherzolite nodules from South Korea. At the study of fluid inclusions of magnesian basalts of. Disko (west Greenland) were obtained unexpected results dominant component was not carbon dioxide, but methane. Their investigation was conducted with the help of cryo- and thermometry techniques, Ramanand IR-spectroscopy.



Fig. 2. Fluid inclusions with graphite in glass of matrix

of rock contain a solid phase – graphite. Discoloration of glass was observed around some vacuoles.

The temperature of the homogenization of melt inclusions in olivine varies from 1170 to 1200°C. The temperature of solidification of matrix glass corresponds to 750 - 800°C.

Cryometric study of 23 fluid inclusions (Solovova et al., 2002) clearly indicates to multicomponent composition of fluid. Immediate crystallization of the substance in inclusion observed at a temperature of -100°C. Their rapid recrystallization results in the formation of one or more large crystal grains surrounded by the smallest ones. Start melting of the fine-grained crystals was

Abstracts

fixed at -73° C. Large crystals melted in a temperature range of $-36.6 - -26.7^{\circ}$ C.

The measured temperature of phase transition in inclusions differ from those for CO_2 , and suggest the presence of hydrocarbons. Clathrate crystals in the inclusions were grown in the process of low-



Fig. 3. Fragment of fluid inclusions. Temperature is - 75°C



Raman spectroscopic study of fluid inclusions showed that the solid phase inside the vacuoles is a graphite (peaks 1361, 1582, 2715, 3254 cm⁻¹). Gas components of the inclusions are CH₄ (2917 cm⁻¹), CO₂ (1284, 1387 cm⁻¹), N₂ (2329 cm⁻¹). Methane is characterized by maximum intensity of peak. The presence of H₂O confirmed by IR-spectroscopic method (peak 3334 cm⁻¹).

Estimation of carbon dioxide density in the fluid based on the Raman-spectroscopy data. It has been found that the distance between the major peaks of CO_2 is connected with its density. The pressure at the crystallization of olivine was 3 kbar. The pressure during the solidification of residual melt it does not exceed 500 bar.

Crystallization of the magma occurred under low redox potential, which is consistent with the presence of association Fe-Ni alloy – sulfide. The value logfO₂

temperature experiments. Their crystallization indicates the presence of H_2O in the fluid. Temperature of melting of crystals varies within 7.5 - 9°C.



Fig. 4. Fragment of fluid inclusions. Temperature is $-40^{\circ}\mathrm{C}$

Fig. 5. Raman spectra of fluid inclusions containing graphite

Fig. 6. Raman spectra of fluid inclusions containing CH_4

for melt in equilibrium with metallic iron at a temperature of 1450°K reach -13.95. Fluid in equilibrium with Fe, Fe₃C and FeS at contains a few mol percent H₂O and is dominated by H₂ + CH₄. The absence on the Raman spectra of H₂ peaks can be attributed to its loss by diffusion outside the inclusions. This assumption supported by clarification glass around vacuoles by reducing Fe⁺³ to Fe⁺² in the rocks melt.

This study was financially supported by the Russian Foundation for Basic Research

References:

 Li S., Shuguang S., Zhihai W. CH₄-rich fluid inclusions in the Yushigou mantle peridotite and their implications, north Qilian Mountains, China // Chinese Science Bull. 1999. 44 (21) 1992-1995.
 Pedersen A.K. Basaltic glass with high-tempereture

equilibrated immiscible sulphide bodies with native iron from Disko, ctntral west Greenland // Contrib. Mineral. Petrol. 1979. 69. 397-407

- Solovova I.P., Ryabchikov I.D., Girnis A.V., Pedersen A., and Hansteen T. Reduced magmatic fluids in basalt from the island of Disko, central West Greenland // Chem. Geol. 2002. 183. 365-371
- Song S., Suc L., Niu Y., Lai Y., Zhang L. CH4 inclusions in orogenic harzburgite: Evidence for reduced slab fluids and implication for redox melting in mantle wedge // Geochim. Cosmochim. Acta. 2009. 73. 1737–1754

UDC 550.4.02 Konyshev A.A^{1,2}, Zubkov E.S.² Fluorine concentration in the Li-F granite fluid, salmi pluton: an evaluation based on experimental data of melting.

¹ - GEOKHI RAS, Moscow; ² - IEM RAS, Chernogolovka (konyshev@iem.ac.ru; eszubkov@gmail.com)

Abstract. This paper presents a new data about P-T-X conditions of genesis of Li-F granite, associated with Salmi anorthosite-rapakivi granite pluton (A-type granites), South Karelia. Experimentally determined water-saturation solidus at 200 MPa is located between 550 and 575 °C, whereas "dry" solidus is located between 625 and 650 °C. HF content in the fluid based on the composition of mica (zinnwaldite) and experimentally based geofluorimeters for Li-contained mica is 0.066 mol/L.

Keywords: Li-F granite, solidus, fluorine, Precambrian, Karelia, A-type granites

Fluorine is one of major components in natural granitic fluids. It is responsible for transport of such elements as Sn, W, Mo, Ta, Nb, Li and Be. Fluorine concentrations in natural fluids involved in formation of granites allow to estimate ore-forming potential of the rock more correctly than fluorine concentrations measured in the bulk rock. Information on physical-chemical conditions of the transition from magmatic to postmagmatic stage of the rock evolution is important for modeling of ore-magmatic systems involving components such as tantalum.

Salminskiy (Salmi) pluton belongs to anorthosite-rapakivi granite association. The pluton is located in North Ladoga region, at the joint of the Karelian craton and the Svecofennian crust, and is composed of diverse rocks from gabbro and anorthosite to biotite leucogranite and topaz-bearing Li-F granite. The intrusion has age around 1.530-1.547 Ga [Neymark et al, 1994; Amelin et al, 1997], with Li-F granites being the lattermost intrusive rocks.

Another authors studied melt inclusions in quartz from core-samples of topaz-bearing granites of the Uuksu dome [Poutiainen and Scherbakova, 1998], which are considered as one of the most evolved granites in the pluton. The study has shown that the solidus temperature was 640 - 680 °C and the liquidus temperature was 770 - 830 °C at minimum pressure of 2 kbar. The crystallization started from water-undersaturated magma (3 wt% H_2O) but the final melt was water-saturated. These data were taken as the basis for experimental work.

An experiment was done in IEM RAS in an internally heated pressure vessel. Powder of Li-F granite from a satellite of Uuksu dome was used as a starting material. The experiment was conducted in platinum ampoules sealed by electric-arc welding. Some amount of distilled water together with 0.1m and 1m HF was added in each ampoule so that the amount of liquid phase did not exceed 20-30 wt% of powder weight, similarly to [Weidner, 1987]. The experiment lasted 7 days, after which ampoules were quenched isobarically.

Concentrations of major elements in nature rock sample were measured using XRF (IGEM RAS). Trace elements were analyzed by ICP-MS in FGUP IMGRE (standard decomposition and decomposition with preliminary fusion with Li metaborate). Compositions of minerals and quenched glasses in experimental samples were studied by SEM-EDS in IEM RAS. Trace elements compositions of micas were measured by LA-ICP-MS in IGEM RAS and FGUP IMGRE. Composition of Li-F granite powder used in the experiment is shown in Table 1.

 Table 1. Composition of Li-F granite of Salmi pluton (sample Sal4).

Oxide	Wt. %	Element	ppm
SiO ₂	72.91	Li	453
TiO ₂	0.02	Rb	639
Al ₂ O ₃	17.07	Sr	64
Fe ₂ O ₃	0.72	Ba	116
MnO	0.04	Та	38.6
MgO	0.05	Nb	101
CaO	0.21	Zr	56.7
Na ₂ O	6.32	Hf	10.0
K ₂ O	1.93	Y	11.3
P ₂ O ₅	<0.02	Ho	0.72
LOI	0.66		
F	1.05		
Sum. + LOI	99.93		

The experiment has shown that the solidus temperature of Li-F granites (Salmi Pluton) at water saturation and the total pressure 2 kbar is between 550 and 575 °C, which is lower than estimates of other authors. At the same pressure in "dry" conditions (the starting material powder contained 0.5-0.6 wt% of water preserved in mica and topaz) temperature of solidus was measured at 650 °C or slightly lower, but higher than 625 °C.

Mica (zinnwaldite) crystallized at the last stages of crystallization of Li-F granite; topaz and fluorite crystallized after mica in interstices.

Average composition of micas is shown in Table 2 (major elements are averages of 5 analyses, F is an

Abstracts

average of 18 analyses, and trace elements are averages of 43 analyses).

Element	Wt. %	Element.	ppm	
F	5.87	Li	13300	
CI	0	Zn	787	
Mg	0.05	Ga	110	
AI	10.47	Ge	3	
Si	19.42	Rb	7480	
K	8.49	Sn	105	
Ti	0.08	Ba	10	
Mn	0.64	Та	117	
Fe	10.95	W	35	
O (by stoichiometry)	36.81	TI	22	
Sum.	92.78			

Table 2. Elemental composition of micas

Concentrations of HF in the fluid in equilibrium with Li-bearing mica were calculated using mineral geofluorinemeter [Aksyuk, 2002], assuming the water activity equal to unity.

Estimated HF contents in the fluid were 0.066 mol/L at 575 °C and 0.096 mol/L at 650 °C. Topaz, which appeared at the latest stages of granite crystallization, also can be regarded as an indicator of fluorine concentration in fluid. Assuming that topaz grew in water-saturated conditions, application of the topaz geofluorinemeter [Aksyuk, Konyshev, 2006] provided 0.062 mol/L HF at 575 °C.

Conclusions. Assuming water-saturated conditions during the latest stages of the magma crystallization, concentration of HF in the fluid during the formation of Li-F granites of Salmi pluton fall on high-F trend, characteristic to the objects with Sn-W-Mo specialization [Aksyuk, 2002].

The work was supported by RFBR grants # 14-05-31098 mol a; 15-05-03393 A.

References:

- 1. Aksyuk A.M. Experimentally-reasonable geofluorinemeters and regime of fluorine in granite fluids// Petrology, 2002. V. 10, № 6. pp. 628-642. (in Russian)
- Aksyuk A.M., Konyshev A.A. Topaz geofluorimeter and estimations of HF and SiO2 concentrations in some geological fluids // Understanding the genesis of ore deposits: To meet the demands of the 21st century. 12th Quadrennial IAGOD Symposium – 2006. Moscow, pp. 1-4.
- 3. Amelin Yu.V., Larin A.M., Tucker R.D. Chronology of multiphase emplacement of the Salmi rapakivi granite-anorthosite complex, Baltic Shield: implications for magmatic evolution // Contrib Mineral Petrol 1997 127: 353-368.
- Neymark L.A., Amelin Yu.V., Larin A.M. Pb-Nd-Sr isotopic and geochemical constrains on origin of the 1.54-1.56 Ga Salmi Rapakivi Granite-Anorthosite

Batolith (Karelia, Russia) // Mineralogy and petrology, 1994, v. 50, p.173-193.

- Poutiainen M, Scherbakova T. F. Fluid and melt inclusion evidence for the origin of idiomorphic quarz crystal in topas-bearing granites from the Salmi batholith, Karelia, Russia // Lithos. 1998. V. 44. P. 141—151.
- Weidner J.R., Martin R.F. (1987) Phase equilibria of a fluorine-rich leucogranite from the St. Austell pluton, Cornwall // Geochimica et Cosmochimica Acta Vol. 51, pp. 1591-1597

Deviatova V.N.¹, Simakin A.G.^{1,2} Experimental study of nucliation and growth of the diopside in the AB-DI melt at P=0.2 GPa.

¹ - IEM RAS; ² - IPE RAS dev@iem.ac.ru +7-496-522-5852

Abstract. Crystallization of pyroxene from the melt in the system Ab-Di was studied at P=2kbar and initial water content C_{H20} =3.3 wt.%. An oscillatory temperature regime was used. Products of crystallization were characterized by the Crystal Size Distributions (CSD). We separate the parts of CSDs formed in the main stage of experiment and at the quenching. At the small enough period of oscillations (-10 min) crystals formed in the cold half period at the undercooling 15°C were only partially dissolve in the hot stage with temperature above liquidus. In this case corrected CSDs get quasi lognormal shape close to one predicted by the theoretical model developed by Simakin and Bindeman (2008). At the larger periods all crystals dissolve in each hot stage and grow in the cool one. Corresponding CSDs predominantly have exponential shape.

Keywords: crystal size distributions, temperature cycling, nucleation, growth

Introduction

Recrystallization is well studied phenomenon (Ostwald, 1901), especially in metallurgy (Gorelik et al, 2005). The presented investigation is devoted to the experimental verification of new theoretical model, which describes evolution of crystal size distributions of igneous phenocrysts in sequence of dissolution and crystallization events.

Effect of the reducing interfacial energy at the recrystallization was first described by Ostwald (1901) for crystals placed in the solvent. It works through the size effect of solubility when crystals with larger curvature of their shape (smaller size of isometric crystals) have larger solubility. In the systems with melt crystal size dependent solubility appears as effective superheating of small crystals (submicron size scale) by no more than $1-3^{\circ}$ C and usually much less depending on the interface energy. As shown in quantitative model by Lifshitz and Slyzov (1961) the Ostwald ripening makes CSD to be concave-downward with left side truncation.

In metallurgy systems the solid state recrystallization with miserable or no melt have place. The driving force of the primary recrystallization of the solid polycrystalline materials

(Gorelik et al, 2005) is decreasing of Gibbs energy at the constant temperature by damaged grains dissolution (in thin films) or transformation (with surface diffusion) into the crystals free of dislocations and strains. The driving force of the secondary recrystallization (Gorelik et al, 2005) is the minimization of the crystals interfacial energy, i.e. reducing of the between crystals boundaries surface, number of triple joints much like as at the Ostwald ripening. Recrystallization leads to the formation of the stable, coarse-grained textures. These models are correct for the recrystallization in the metamorphic rocks, during lithification.

The model of Simakin and Bindenman (2008) describes the dissolution-precipitation processes of crystals in the silicic or more basic systems driven by the external temperature oscillations which are inherently and inevitably present in the natural magma chambers. Any realistic magma system is characterized by temperature oscillations with amplitude larger than Ostwald's driving force. Crystal growth under oscillating temperature is used to grow large crystals (e.g., Hintzmann and Muller-Vogt 1969), for recrystallization of gypsum, concrete and other materials (Bajal and Kurilenko 1975). The simplified model, based on the size dependent dissolution rate for crystals in the melt and constant slow overgrowth rate, is proposed to describe evolution of the CSD in the series of the dissolutionprecipitation events. As shown theoretically (Simakin and Bindeman, 2008) repeated dissolution and crystallization events should preferentially dissolve smaller crystals and transform CSD to concavedownward shape with right side truncation.

Experiments

We performed experiments in Ab-Di system in order to investigate the effects of temperature cycling on crystal coarsening. We used homogeneous, and free of bubbles and crystallites glass with composition $Ab_{55}Di_{45}$, $C_{H2O}=3.3$ wt.%. This composition was used since practically only pyroxene crystalizes in the whole range of the temperatures of the experimental samples.

The experiments were conducted at the pressure of 200 MPa and the temperature $T = 1155^{\circ}C$ (+5°C above to liquidus temperature) – $1135^{\circ}C$ (-15°C below liquidus) in an internally heated gas pressure vessel (IHPV). The samples were quenched isobarically, the cooling rates were ~ $150^{\circ}C/min$ down to 600°C. A half cycle time was varied from 2 minutes to 1.5 hours. Amounts of the oscillation in experiments were changed from 1 to 8. Crystals appeared during the first half-cycle are partially or totally dissolved in the melt in the second hot halfcycle. Crystallization mode was significantly affected by the run thermal history.

Diffusion time of the total dissolution of the largest crystal t1 is an important controlling parameter. It was estimated to be 15-20 minutes. For calculations we used silica diffusion coefficient evaluated by (Chehmir et al. 1991, Mungall, 2002) and viscosity by (Hui and Zhang, 2007).



Fig. 1 Products of the runs, dark – aluminosilicate glass, light - clinopyroxene crystals. BSE images of the samples a)run 87, half-period 90 min, number of cycles 1 b) run 51 half-period 90 min, number of cycles 2; c) run 60 half-period 45 min, number of cycles 2;

Regime I

Temperature oscillations half cycle is less than t1. Ripening, or formation of the larger crystals at the expense of the smallest ones, reduces number of crystals at the increase of periods and number of the oscillation. Increasing of the number of cycles from 3 to 8 at constant oscillations period leads to the rise of maximum length of the observed grains (after quenching) from 13 to 24 mkm and transforms habitus from prismatic 1/1/3 to tabular 1/1.9/1.9 one.

Abstracts

Increasing of the half period of oscillations from 2 to 20 min at a constant number of cycles (5) induces maximum length increase from 13.5 to 15.6 mkm and habitus conversion from 1/1.3/5 to 1/1/2.2 (ratio of the axis lengths of ellipsoid approximating crystals shape).

Subcritical clusters distribution relaxation time τ is another controlling parameter. It can't be estimated theoretically now.

Regime II

All crystals dissolve in the hot half-period and homogeneous nucleation takes place at in the beginning of every half period of growth in some runs when half period is larger t1 and less than $t1+\tau$.(fig.1c). The largest crystals were grown with distinct by composition cores and quenching rimsMaximum core length is 16 mkm (full length 47 mkm) and habitus is 1/1.2/1.5.

Regime III

Half cycle is larger than $t1+\tau$. Fine-crystalline quenching clinopyroxene were obtained after 1 cycle(fig.1a) and homogeneous glass was formed after two cycles with half time> t1+t(fig.1b). In this case at the applied at the cold stage supercooling 15° C homogeneous nucleation had not occurred since this undercooling is less than homogeneous nucleation threshold for clinopyroxene.

Conclusions

Our experimental work confirms the theoretical model of Simakin and Bindeman (2008). Large crystals can be grown with temperature oscillation near liquidus technique for the observation of the equilibrium composition in the crystal rim formed at the growth rate coming to zero.

References:

- 1. Bajal I.G., Kurilenko O.D. Ostwald ripening in disperse systems: Kiev, Naukova dumka, 1975, 218(in Russian)
- Gorelik S.S., Dobatkin B.S. Kaputkina L.M. Recrystallization of the metals and alloies: Moscow, MISA, 2005, 432(in Russian)
- 3. Chekhmir A.S., Simakin A.G., and Epelbaum M.B. Dynamic phenomena in fluid-magmatic systems, Moscow: Nauka, 1991, 141(in Russian)
- 4. Hui H, Zhang Y Toward a general viscosity equation for natural anhydrous and hydrous silicate melts. Geochim Cosmochim Acta, 2007, 71, 403-416
- 5. Hintzmann W, Muller-Vogt G Crystal growth and lattice parameters of rare-earth doped yttrium phosphate, arsenate and vanadate prepared by the oscillating temperature flux technique, J Cryst Growth 1969, 5, 274–278
- 6. Mungall J.E. Empirical models relating viscosity and tracer diffusion in magmatic silicate melts, Geochim. Cosmochim. Acta, 2002, 66, 125-143
- Lifshitz I.M. and Slyzov V.V. (1961) The kinetics of precipitation from supersaturated solid solutions, J.Phys.Chem.Solids, 1961, 19, 35-50

- 8. W.Z.Ostwald Phys. Chem. 1901, 37, 385
- Simakin A.G. and Bindeman I.N. Evolution of crystal sizes in the series of dissolution and precipitation events in open magma systems, Journal of Volcanology and Geothermal Research, 2008, 177, 997-1010

UDC 550.4.08

Stepanov O.V.¹, Chertkova N.V.², Plechov P.Y.¹, Persikov P.Y.², Bukhtiyarov P.G.² Analytical methods for determination of high water concentrations in obsidian glasses.

1- Geol. Dep. MSU; 2 - IEM RAS odindva345@gmail.com, nvchertkova@gmail.com

Abstract. In order to prepare primary standards for confocal Raman spectroscopic measurements, obsidian glasses with water contents ranging from 4 to 10 wt.% H_2O were synthesized in the internally heated pressure vessel and piston-cylinder apparatus. Their water content was independently determined by attenuated total reflectance FTIR spectroscopy and Karl Fisher titration. Raman spectra of the glasses contain distinct bands in 3200-3700 cm⁻¹ and 200-1200 cm⁻¹ regions and the ratio of bands integrated intensities has a clear dependence on total water content. Therefore, synthesized glasses can be used as spectroscopic standards for Raman measurements of high water contents in the glasses of rhyolitic composition.

Keywords: Raman spectroscopy, FTIR, Karl Fisher titration, obsidian glasses, high water concentrations

Research objective

Obtainment of primary standards for routine measurement of water concentrations in the rhyolitic glasses using confocal Raman spectroscopy.

Starting material and methods

The objects for analysis were hydrous rhyolitic glasses synthesized in the internally heated pressure vessel and piston-cylinder apparatus at temperatures 1000 - 1100 °C and pressures from 4.2 to 10 kbars during 48 h. (Tables 1, 2). Starting obsidian glass from Arteni volcano (near Yerevan city) initially contained about 0.4 wt.% of water.

Table 1. Composition of starting glass (wt.%).

SiO ₂	AI_2O_3	Na ₂ O	K ₂ O	FeO*	CaO	MgO	MnO	TiO ₂
77.40	13.08	3.84	4.42	0.20	0.55	0.09	0.06	0.12

Table 2. Synthesis conditions for hydrous glasses.

Nº	Type of apparatus	T (°C)	P (Kbar)	Loaded amount of water (wt.%)
9	piston-cylinder	1000	10	10.3
2		1100	6.2	8.14
3	internally heated pressure	1100	4.2	6.62
4	VC35CI	1100	4.2	3.69

Methods of water content determination in the synthesized glasses:

• Quantitative attenuated total reflectance (ATR) IR spectroscopy using a Nicolet Nexus 670 spectrometer (University of Bristol);

 Karl Fischer titration (KFT) using an AQUA 40.00 titrator (Institute of Experimental Mineralogy);
 Confocal Raman spectroscopy using a JY Horiba XPloRA microscope (Department of Petrology, Moscow State University).

ATR-IR spectroscopy

Samples for analysis were doubly-polished thin sections (for ATR, polishing from one side is enough) with the thickness of 0.15–0.4 mm, mounted in epoxy. Analysis was done in the center of each glass sample and near the edge.

Quantitative evaluation of H_2O concentration in rhyolitic glasses was made based on formula [Lowenstern & Pitcher, 2013]:

$wt\%H_2O = 245(\pm 9)\cdot A_{3450} - 0.22(\pm 0.03),$

where A_{3450} is a peak height in the corresponding wavenumber region (Fig. 1a).



Fig. 1. (a) Wavenumber region of ATR-IR spectrum containing absorption peak of water. (b) Dependence of the H_2O content on the height of water absorption peak. a)

As shown on figure 1b, dependence of the H_2O content on the height of A_{3450} peak is linear with $R^2=0.99$.

Obtained data show a homogeneous distribution of H_2O in the synthesized glasses within each sample (Table 3).

Table 3. H_2O contents measured by ATR-IR spectroscopy

Sample No.	Water (wt.%)			
Sample Nº	center	edge		
9	9.31 ± 0.38	9.35 ± 0.37		
2	8.28 ± 0.34	8.38 ± 0.35		
3	5.88 ± 0.25	5.95 ± 0.26		
4	4.75 ± 0.21 4.88 ± 0.22			
Starting obsidian	0.47 ± 0.06			

KFT method

Glasses were heated up to 1200 °C. Measured water contents were systematically lower than the weight loss after titration, which can be related to the short duration of measurement (10 minutes). Water contents therefore were calculated based on the weight loss after heating (Table 4).

Table 4. Water contents calculated using results of KFT measurements (* - based on the weight loss after titration).

Sample №	Water (wt.%)	Water (wt.%)	Water (wt.%)	Water Average
9*	10.14	9.82	9.83	9.93
2*	8.86	8.97	8.81	8.88
3*	6.02	6.09	6.06	6.06
4*	<u>4.71</u>	<u>5.93</u>	<u>3.86</u>	<u>4.71</u>
Starting obsidian	0.25	0.12	0.52	0.3

Raman spectroscopy

Since Raman spectroscopy is a relative method of water content determination, true values of water concentration were estimated based on ATR-IR and KFT data. These methods showed good agreement with each other (Fig. 2). Water concentrations calculated using ATR-IR spectroscopic data were approximately 0.5 wt.% lower than those determined with KFT.



Fig.2. Correlation between water concentrations in rhyolitic glasses calculated using IR and KFT data.

Measured Raman spectra were used to calculate the ratio of integrated peak intensities for water (Rw, $3200-3700 \text{ cm}^{-1}$) and silicate (Rs, $200-1200 \text{ cm}^{-1}$) (Fig. 3).



Fig. 3. Raman spectrum of rhyolitic glass (run product No.9).

Rw/Rs ratios have a linear dependence on water content (Fig. 4). Run product No.4, which is heterogeneous according to KFT data, is an exception and shows large scatter on the diagram.



Fig. 4. Correlation between Rw/Rs and H_2O content (KFT)

Results

ATR-IR spectroscopy and KFT methods showed good agreement with the loaded water concentrations.

Recorded for these samples Raman spectra contain clearly defined peaks of water and silicate vibrations, and their ratio has a linear dependence on measured water contents. Obtained samples, excluding sample No.4, can be used as the primary standards for water content measurement in natural rhyolitic glasses [Mercier et al., 2010].

The reported study was funded by RFBR according to the research project No. 16-35-00433.

References:

- Lowenstern J. B., Pitcher B. W. Analysis of H2O in silicate glass using attenuated total reflectance (ATR) micro-FTIR spectroscopy // American Mineralogist. - 2013. - T. 98. - №. 10. - C. 1660-1668.
- 2. Mercier M. et al. Spectroscopic analysis (FTIR, Raman) of water in mafic and intermediate glasses and glass inclusions // Geochimica et Cosmochimica Acta. – 2010. – T. 74. – №. 19. – C. 5641-5656

Nazarova D.P., Portnyagin M.V., Krasheninnikov S.P. H₂O content in parental magmas of Kamchatka.

V.I. Vernadsky Institute RAS, Moscow (nazarovadariap@gmail.com)

Abstract. The paper presents an estimate of initial H_2O content in primitive magmas of the Eastern Volcanic Belt, Kamchatka. H_2O content is determined in the range 1.3 - 4.6 wt. %. But there is not monotonic decrease of H_2O content from the front to rear.

Keywords: Kamchatka, subduction zone magmatism, olivine, melt inclusions, H_2O content

Water plays an important role in formation and evolution of arc magmas.

To estimate H_2O content in primitive magmas of the Eastern Volcanic Belt, Kamchatka (volcanoes: Avachinsky, Gorely, Karymsky, Zavaritsky cone), we used a new calculated method [Sobolev et al, 2016.; Nazarova et al., In press], based on comparison of "real" and "dry" crystallization temperatures of olivine. The "real" crystallization temperatures were obtained using geothermometer based on Al partitioning between olivine and spinel. "Dry" crystallization temperatures were calculated using the composition of melt inclusions in olivine by model Ford et al., 1983.

We studied magmatic inclusions: melt inclusions and spinel inclusions in olivine from high-Mg basalts. These rocks have primitive composition and have direct information about conditions of parental magmas formation.

Melt inclusions in most of samples were partially re-crystallized and to eliminate effects of partial crystallization in inclusions, they were homogenized experimentally. Experiments were carried out at 1 atm in a vertical furnace at the Vernadsky Institute, Moscow. The heating was performed in the atmosphere of CO₂ and H₂ gases mixed in proportion corresponding to NNO oxygen buffer. Olivine grains with melt inclusions were loaded in unsealed Pt capsule, heated during 5 min at 1300 °C and then quenched in water.

Major elements in glassy melt inclusions were analyzed by electron microprobe at GEOMAR (Kiel, Germany). All inclusions were corrected for equilibrium with their host olivine with Fe-loss using Petrolog 3.1 software [Danyushevsky, Plechov, 2011]. Initial FeO in the inclusions was assumed to equal FeO in their host rocks.

To evaluate the initial water content, we used a model [Almeev et al., 2007] based on the significant influence of water presence in the melt on olivine liquidus temperature.

The initial H₂O content in primitive melts of Eastern Volcanic Belt of Kamchatka is determined in the range of 1.3 (\pm 0.6) wt. % for Zavaritsky cone to 4.6 (\pm 1.1) wt. % for Avachinsky volcano. In general there are decrease of H₂O content from front to rear (Fig. 1). However, there are large variations of H₂O content in a narrow range of distances from subducting slab (120-140 km).



Fig. 1. Dependence of H_2O content in Kamchatka's parental magmas from depth to slab. The dotted line shows a possible form of water output from slab.

There is variety of forms of water loss from slab [Van Keken et al., 2011]. Variations of H₂O content in Fig. 1 can be explained by output velocity changes of H₂O from slab. Probably the most of H₂O content came out at the depths of 100-120 km for the Eastern Volcanic Belt of Kamchatka. H₂O does not came out practically at depths of 120-130 km and in this area can be abnormally low concentration of H₂O at the source. This is observed for Gorely volcano. And then, at the depth of > 130 km, there is another peak of water output. The data obtained in this study confirm the theoretical model [Van Keken et al., 2011].

These estimates of H_2O content in parental magmas allow us to estimate formation conditions of parental magmas of rear volcanoes from the Eastern Volcanic Belt, Kamchatka for the first time.

The research was supported by the Russian Science Foundation, project no. 14-17-00582

References:

- 1. Nazarova et al. 2016 in press, Doklady Earth Sciences
- 2. Almeev et al. 2007. Am. Min., V. 92, p. 670-674
- 3. Danyushevsky, Plechov, 2011. G3, V. 12(7)
- 4. Ford et al., 1983. J. Petrol., V.24, p. 256–265
- 5. Sobolev et al., 2016. Nature, V. 531, p. 628–632
- Van Keken et al. 2011. J. Geophys. Res., V. 116, B01401

Krasheninnikov S.P.¹, Sobolev A.V.^{1,2}, Batanova V.G.^{1,2}, Kargaltsev A.A.¹, Borisov A.A.^{1,3} The new high-temperature apparatus for one-atmosphere gaz mixing experiments at Vernadsky institute: the first results.

¹ V.I. Vernadsky Institute RAS, Moscow, ² ISTerre, France, ³ IGEM RAS, Moscow (spkrasheninnikov@mail.ru)

Abstract. The paper presents new high-temperature vertical tube furnace for one-atmosphere oxygen fugacity controlled experiments at V.I.Vernadsky Institute (Moscow) and its application in modern petrological studies. Described are the main features of the furnace and reachable temperature and oxidation conditions. Reported are also the first results of high-temperature experiments on melt inclusions and those obtained using the "loop" technique. The differences between equilibrium temperatures, calculated by (Ford, 1983) and (Herzberg&O'Hara, 2002) equations are significant and, display strong dependence on experimental temperature and redox conditions.

Keywords: thermometry, olivine, melt, melt inclusions, equilibrium, Fe-Mg, tube furnace, 1atmosphere, loop, experiments.

The brand-new high-temperature Nabertherm vertical-tube one-atmosphere furnace (up to 1700° C) was mounted and launched at Vernadsky Institute (Moscow, Russia). The furnace designed quite

similar to that described in (Kargaltsev et al., 2009) and intended for experiments in C-O-H atmosphere. The Bronkhorst flowmeters for H₂ and CO₂ were integrated in a gas-flow line to control redox conditions during experimental run within the range of NNO \pm 3 log units. Furnace temperature profile at different T values shows 7 cm hot-spot zone ($\Delta T < 1^{\circ}$ C). Pt/PtRh10 or PtRh6/PtRh30 thermocouples in the working furnace were employed for measuring temperature during experimental runs and transmit data to the PC in real time. Stability of the temperature regime during each experimental run lies within $\pm 1^{\circ}$ C. Both thermocouples were calibrated using Au and Ni melting points.

Experiments on homogenization of melt inclusions, trapped by olivine crystals were conducted on the new furnace (Sobolev et al, 2016; Nazarova et al., in press). The compositions of experimentally heated and quenched melt inclusions in olivine from 2.7 Ga old komatiites of Abitibi greenstone belt (Canada) indicate the evidence for water enriched reservoir in Archean mantle and confirm mantle plume origin of studied komatiites (Sobolev et al., 2016).

Twenty experiments with natural mafic and ultramafic compositions were conducted at high temperatures (1297-1588° C) and NNO $\pm 2 \log$ units buffer conditions, each experimental run contains 5-6 loops with different composition (Hill & Roeder 1974, Barnes 1986, Wan et al, 2008). Samples were crushed and grinded in a mortar and pestle to fine powder and after that were mounted to Pt loops with organic glue. Loops were preliminary saturated with Fe from the sample. Fe saturated Pt loops were placed for a short time in a hot zone of the furnace at temperature above liquidus and then quenched to homogenize samples. The homogenized samples were exposed under experimental conditions for 192 hours at lowest temperature to 12 hours at highest temperatures.

Major elements in glasses and olivines from the experiment products were measured by EPMA (ISTerre, France) using precise olivine protocol (Batanova et al, 2015). Very homogeneous olivine compositions were used as a major equilibrium criteria. The average standard deviation values for Fo# do not exceed 0.02 mol.% (fig. 1). In addition, the model based on Fe-Mg partitioning between coexisting olivine and liquid (Toplis, 2005) was also used to check experiments for equilibrium.

The temperatures from coexisting olivine-liquid compositions were calculated using Petrolog3 software (Danyushevsky & Plechov, 2011) and equations (Ford et al., 1983) and (Herzberg & O'Hara, 2002), which were acknowledged as the most precise models for basaltic magmas (Falloon et al, 2007). As shown on figure 2, used models give similar results for T_{calc} at lower temperatures

 $(T < 1400^{\circ} \text{ C})$ and growing difference with the experiment temperature and $lgfO_2$ value ascent (up to 100° C at 1550° C and $lgfO_2=-2,59$). In-situ temperatures measured with the thermocouple give average values between chosen models.



Fig. 1. Diagrams illustrating homogeneous olivine compositions (Fo# vs CaO and Fo# vs NiO) in experimental products. Black dots – average olivine compositions (on 8-38 points); grey dots – individual analyses of olivine crystals.



Fig. 2. Dependence of differences between temperature values calculated using models (Ford,1983) and (Herzberg&O'Hara, 2002) with increase of experimental temperature and $lgfO_2$ values.

Reported data shows that the new updated quantitative model of olivine-liquid equilibria should be developed for high-temperature ultramafic melts and that such a study could be done using presented furnace at Vernadsky Institute.

Research made with support of the RSF grant 14-17-00491

References:

- 1. Kargaltsev A.A., Volovetskiy M.V., Kadik A.A., Lukanin O.A. // Geochimiya, 2009, № 7, p. 769-774
- Sobolev A.V, Asafov E.V., Gurenko A.A., Arndt N.T., Batanova V.G., Portnyagin M.V., Garbe-Schoenberg D., Krasheninnikov S.P. // Nature, 2016, V. 531, p. 628-632, doi:10.1038/nature17152
- Nazarova D.P., Portnyagin M.V., Krasheninnikov S.P., Mironov N.L., Sobolev A.V. // DAN, in print.
- Hill R. and Roeder P. // J. of Geology, 1974, V. 82, No. 6, p. 709-729
- Barnes S.J. // Geochem.Cosmochem.Acta, 1986, V. 50, p. 1889-1909
- Wan, Z., Coogan, L.A., Canil, D. // Am. Mineral., 2008, V. 93, p. 1142–1147.
- Batanova, V.G., Sobolev, A.V. & Kuzmin, D.V. // Chem. Geol., 2015, V. 419, p. 149–157.
- Toplis M.J. // Contrib.Mineral.Petrol., 2005, V. 149, p. 22–39, doi:10.1007/s00410-004-0629-4
- Danyushevsky L.V., Plechov P. // Geochem. Geophys. Geosyst., 2011, V. 12(7), doi:10.1029/2011GC003516
- Ford C.E., Russell D.G., Groven J.A., Fisk M.R. // J.Petrol., 1983, V. 24, p. 256–265
- Herzberg, C. and M.J. O'Hara // J. Petrol., 2002, V. 43, p. 1857–1883, doi:10.1093/petrology/43.10.1857.
- Fallon T.J., Danyushevsky L.V., Ariskin A.A., Green D.H., Ford C.E. // Chem. Geol., 2007, V. 241, p. 207-233

UDC 552.11 Kuzyura A.V.¹, Litvin Yu.A.¹, Limanov E.V.^{1,2}, Varlamov D.A.¹ Experimental modeling of physico-chemical differenciation mechanism of ultrabasic magma in the earth mantle.

¹IEM RAS, Chernogolovka, Moscow region, ²Geol. dep. MSU, Moscow (shushkanova@iem.ac.ru, litvin@iem.ac.ru)

Abstract. Garnet peridotites and eclogites are the main rocks of the Earth mantle. Petrochemical trends demonstrate continuous transitions from peridotite to eclogite rocks (Marakushev, 1984) and compositions of mineral inclusions in diamonds (Sobolev, 1977). However, direct petrogenetic relations of peridotites and eclogites are not clarified enough in relation of physico-chemistry. Experimental research of physico-chemical mechanism able to realize continuous ultrabasic to basic evolution of the mantle peridotite became sensed after experimental discovering of the reaction between olivine and jadeite that leads to olivine disappearing (Gasparik, Litvin, 1997). Experimental studies at 6.0 GPa of phase relations in multicomponent system olivine O/clinopyroxene Cpx – jadeite Jd (with boundary compositions reproducing the compositions of natural phases) were carried out. A preliminary phase diagram of the system was plotted; it reveals a peritectic physico-chemical mechanism of olivine disappearing in the 4-phase peritectics O + Cpx+Grt+L (in reaction O and L = Grt with association of Jd-component in a melt). As a result of the reaction olivine disappears, and monovariant cotectics Omph+Grt+L appears, that the bimineral eclogites form.

Keywords: ultrabasic-basic evolution, mantle peridotite, olivine – clinopyroxene – jadeite system, reaction of garnetization, physico-chemical experiment, phase diagram

Studies of xenoliths of the Earth upper mantle rocks testify to that the upper mantle is composed peridotites mainly. They dominates over eclogites in relations about 95:5 volume % [Mathias et al., 1970; Ringwood, 1975]. Herewith, diamondiferous eclogite xenoliths more than 1-2 orders of magnitude greater than peridotie ones among upper-mantle xenoliths. More likely, the process resulting in that eclogite forms (evaluates) through peridotite, take place within the upper mantle. The petrochemical trends demonstrate continuous transitions between peridotite and eclogite rocks [Marakushev, 1984, in russian] and compositions of mineral inclusions in diamonds [Sobolev, 1977]. Meanwhile, direct paragenetic relations of peridodites and eclogites are not clarified enough in physico-chemical aspect. After the experimental discovering of the reaction between olivine and jadeite, that leads to olivine disappearing [Gasparik, Litvin, 1997], experimental research of physico-chemical mechanism that is able to realize a continuous ultrabasic-basic evolution of mantle peridotite has been carried out.

The transition from primitive garnet lherzolite of the upper mantle to eclogite has to be accompanied by disappearing of two main phases – olivine and orthopyroxene. There was established in physiscochemical experimental study of peridotitic system olivine (Ol) – orthopyroxene (Opx) – clinopyroxene (Cpx) – garnet (Grt) at 4 GPa [Litvin, 1991], that orthopyroxene disappears at peritectic reaction Opx + L = Cpx. Further studies let us reveal that olivine reacts with jadeitic component with garnet formation [Gasparik, Litvin, 1997].

Experimental researches at 6.0 GPa of phase relations in multicomponent system olivine Ol clinopyroxene Cpx - jadeite Jd (with boundary compositions reproducing compositions of natural phases) are presented in the work. The experiments were carried out at apparatus of toroidal type "anvil with hole" using Pt- or Pt-Rh-ampoules. Pressure was 6 GPa, temperatures were 1200-1500°C. Formation of coexisting crystals of garnet and clinopyroxene, as well as appearing of paragenetic mineral association Ol + Grt + Cpx were found out. Preliminary projection of liquidus surface of the system (fig. 1) and its polythermal sections $Cpx_{80}Jd_{20}$ $- Ol_{80}Jd_{20}$ и $Cpx_{60}Jd_{40} - Ol_{60}Jd_{40}$ were plotted. The last disclose peritectic physico-chemical mechanism of disappearing of olivine within four-phase *Ol+Cpx+Grt*+L.

A point of melt composition moves along the cotectic curve Ol+Grt+L to nonvariant peritectic Ol+Jd-Cpx+Grt+L, where "garnetization" of olivine happens. After completing of peritectic reaction with disappearing of olivine the figurative point of melt composition comes to be on the cotectic curve Omph+Grt+L, where the crystallization completes.



Fig. 1. Scheme of liquidus surface of system Ol - Cpx - Jd.

Symbols: p – peritectic points, e – eutectic points. Red dashed lines show polythermal sections $Cpx_{80}Jd_{20} - Ol_{80}Jd_{20}$ and $Cpx_{60}Jd_{40} - Ol_{60}Jd_{40}$ studied in experiments. Red points demonstrate experimental compositions.

Principal meaning is in that fractional crystallization is necessary for accumulation of jadeitic component from peridotite Cpx in a melt. Complete "olivine garnetization" can realize in residual melt at intensive fractionation of *Ol*, *Cpx* and *Grt*.

Wherein, a content of Jd-component arises in clinopyroxenes, its compositions get an omphacitic (Omph) specialization. Finally, crystallization of a melt of peridotitic system Ol - Cpx - Jd ends with formation of association of bimineral omphacitegarnet (Omph-Grt) eclogites.

Support: RAS Program P34 "Substance at conditions of high static pressure", as well as RFBR grants 14-05-0053 and 16-05-00850

References

- 1. Mathias M., Siebert J.C., Rickwood P.C. 1970. Some aspects of the mineralogy and petrology of ultramafic xenoliths in kimberlite. Contributions to Mineralogy and Petrology, V. 26. P. 75-123.
- 2. Ringwood A.E. 1962. A model for the upper mantle. Journal of Geophysical Research 67, 857-866.
- Marakushev A.A. 1984. Peridotite nodules as indicators of deep lithosphere's structure. (*in Russian*) Reports of Soviet Union geologists at 27th session of International Geological Congress. Petrology. M.: Nauka,153-160.
- 4. Sobolev N.V. Deep-seated Inclusions in Kimberlites and the Problem of Upper Mantle Composition. Washington, D.C., AGU, 1977. 279 p.
- Gasparik T., Litvin Yu.A. 1997. Stability of Na₂Mg₂Si₂O₇ and melting relations on the forsteritejadeite join at pressures up to 22 GPa. European Journal of Mineralogy 9, 2, 311-326.