AMPHIBOLIZATION IN ULTRAMAFIC ROCKS AND BUFFERING OF OXYGEN FUGACITY OF ANDESIT

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Red-ox state of magmatic system is establishing in the fluid –rock interaction [1][2]. In such way the ultrabasites of the mantle genesis, and magmatic basic cumulates, consisting of the silicates of bivalent iron: olivine and orthopyroxene, can reduce the oxidized fluids and melts. It is widely known, that serpentinization of the ultrabasic rocks is accompanied by the generation of abiogenic hydrocarbons and hydrogen in the reducing conditions at the influx of oceanic waters containing dissolved carbon dioxide [3]. Oxidation of the ferric to ferrous iron is balanced by transformation of carbon dioxide to methane (1) and hydrogen of water to molecular hydrogen (2) [4]:

(1) $4\ Fe_2SiO_4 + 12\ Mg_2SiO_4 + 18\ H_2O + CO_2 \rightarrow 4\ Mg_6[Si_4O_{10}](OH)_8 + 4\ Fe_2O_3 + CH_4$
(2) $3\ Fe_2SiO_4 + 2\ H_2O \rightarrow 2\ Fe_3O_4 + 3\ SiO_2 + 2\ H_2$

It can be suggested, that amphibolization of the ultrabasic material both mantle, and crust origin is capable to buffer fO_2 at a low level. Iron oxidation at the replacement of the orthopyroxene and olivine with amphibole can be accompanied by reducing of S^{4+} to S^{2-} in the melt. Thus substitution of iron minal of the orthopyroxene by amphiboles can be described with reaction:

$$\{Ca,Al,H_2O,SO_2\}melt + (Mg,Fe)_8Si_8O_{24} \rightarrow Ca_2(Mg,Fe^{3+},Al)_5(Al,Si)_8O_{22}(OH)_2 + S^{2-}$$

The purpose of this work is to estimate the variations of fO_2 in the various magmatic systems containing amphibole.

Magmatic Red-Ox indicators. Currently for fO_2 estimation the titano-magnetite - ilmenite oxybarometer [5] usually is used. We suggest to use amphibole as oxybarometer, based on the experimental data obtained earlier [6].

Experimental methods. Crystallisation of amphibole from magnesium-rich andesite melts from Shiveluch volcano (Kamchatka) had been studied experimentally. Experiments were performed at P_{H2O}=2 kbar and temperatures around 950ºC. Ratio Fe^{2+}/Fe^{3+} in the started hydrous glasses had been controlled with Mossbauer spectroscopy. Used technique provided reliable estimates of oxygen fugacity in the melt during amphibole growth thus dependence of the mineral composition on the red-ox conditions had been established. Volume of the experimental data used in calibration was limited therefore other published experimental data were used for control. However, until gaining more direct experimental data on the amphibole grown at the variable oxygen fugacities estimates done with amphibole oxybarometer can be treated only as preliminary ones. Microprobe analyses (CamScan MV2300) have been recalculated to yield cation distribution by crystallographic positions and valence state of iron according to IMA-97 procedure [7]. Results were plotted in coordinates Al^{VI} - (Fe^{3+} + Ti) [6] (fig. 1).

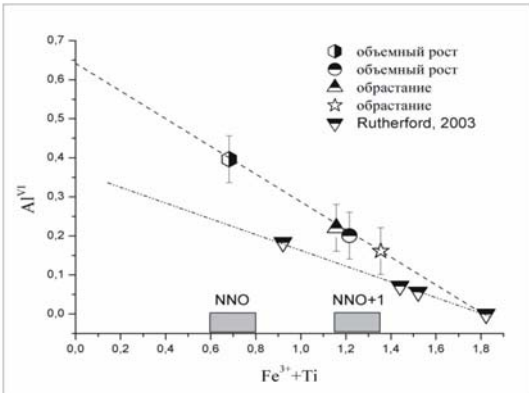

Fig.1. Composition of amphiboles experimentally grown from the Shiveluch andesite at P_{H2O} = 2 kbar and T=950°C and various f_{O2} [6]

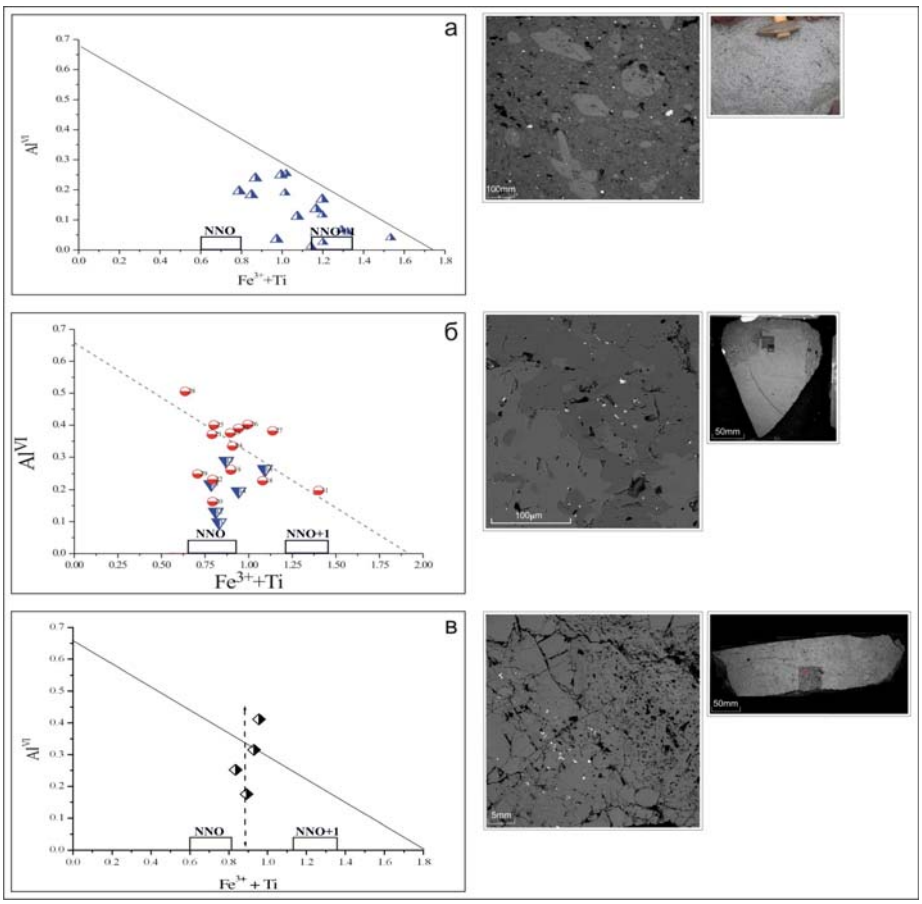

Fig.2. The diagram of the oxygen fugacity estimated using the analyses of amphiboles from ultramafic inclusions in Shiveluch andesites

Natural material. Below we present results of the study of ultrabasic xenoliths from the Shiveluch andesites. Studied samples were represented by shpinel-bearing peridotites containing olivine (~ 20-50 %), ortopyroxen (~ 30-50 %), clinopyroxen (~ 5-10 %), amphiboles (magmatic hornblende) (~10-30 %), plagioclase (~5 %), glass, also insignificant quantities of accessory minerals were present: apatite, spinel (mainly chromspinel), and occasionally sulphides (<1 %): pyrrotine, pentlandite in chromspinel, single occurrence of bornite. After studying of several samples with different amphibole content we noted following dependences

1. Composition of amphiboles from peridotite at low content corresponds to oxygen fugacity of about NNO-0.5 (fig. 2b), from regular andesites to f_{O2} » NNO+1/NNO+2 (fig. 2a), from the amphibole rim on the contact between the nodules and andesite to f_{O2} » NNO+0.5 (fig. 2c). These observations stand for the reducing of the oxidized andesitic magma (even adacites in the Shiveluch case) at the interaction with ultramafic inclusions.

2. Our estimates of f_{O2} can be correlated with practical absence of sulphides in the studied amphibolized xenoliths. Nickel sulphides were observed as inclusions in chrome-spinels from xenoliths. High nickel contents in olivine and ortopyroxene at the level up to 0.5 wt. % and 0.25 wt. % correspondingly, were found. However, sulphides out of chrome-spinel haven't been noted. It seems that in the course of reducing of andesites magmas f_{O2} level of sulphatic sulphur transformation to sulfide was not reached. According to the available experimental data this transition occurs in the narrow enough range approximately from NNO to NNO-0.5 at P=2 kbar and is shifted to more oxidized area with pressure increase [8, 9]. These data match well with our observations presented above.

Comparison with published data. We have analyzed conditions of crystallization of the various magmatic amphiboles using published data.

Analyses of amphiboles from Unsen volcano (Japan) andesites are presented in [10]. These amphiboles crystallized from andesito-dacites that were heated and melted just before eruption. Then andesitic high temperature amphibole rim was formed. Our analysis demonstrates that heating was not accompanied by magma oxidation (fig. 3). As a whole the magmatic system of Unsen volcano (Japan) is

characterized by homogeneous f_{O2} conditions opposite to the strongly variable oxidtation state of Shiveluch andesites.

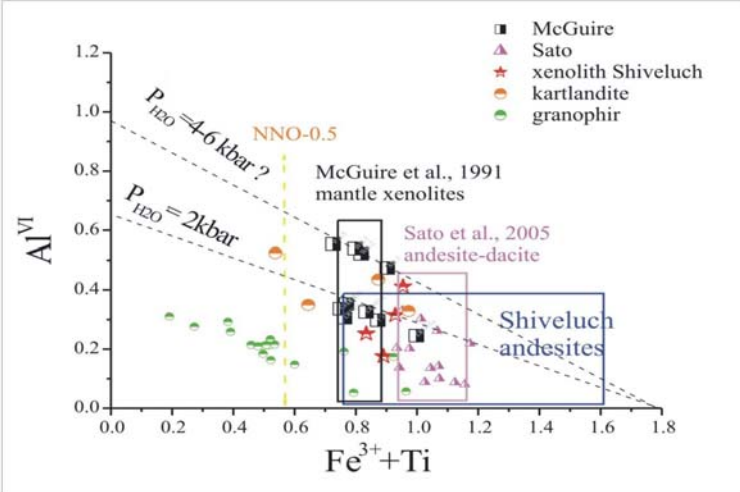

Fig.3. The results diagram of the oxygen fugacity estimated using the analyses of amphiboles from ultramafic inclusions in Shiveluch andesite and from published data

In the paper by McGuire [11] analyses of mantle (as interpreted by author) xenoliths from California are presented. Analyses of the amphiboles from two samples lay down on two trends (the Fig. see). Both linear trends are crossed with axis Fe^{3+}+ Ti in a point around 1.8 (apfe), as well as the experimental trend. One group of points is in agreement with pressure around 2 kbar. Another group corresponds to a higher pressure. Taking into account data obtained at 14 kbar [6] it can be estimated approximately in the range of 4-7 kbar. In both cases oxygen fugacity is high enough (NNO-NNO+0.5). That can testify about crustal origin of amphiboles. The ultrabasic material can be a product of the intrachamber differentiation.

Conditions of magmatic amphibole crystallization in equilibrium with sulphides can be evaluated using analyses of the cortlandites (the ultrabasic rocks containing magmatic amphibole) reported in [12]. These data relates to the magmatic sulphide ores associated with basic-ultrabasic intrusion located in Central Range of Kamchatka. The composition of amphibole from the discussed rocks reflects f_{O2}≈ NNO/NNO-1 (fig. 3).

Very reduced amphiboles are characterized in [13]. These amphiboles were found in the granophyric inclusions in basalts of the Karymsky volcano (Kamchatka). Amphibole composition corresponds to f_{O2} ≈ NNO-1/NNO-2. Probably, reduced conditions in the parent (for granophyric inclusions) dacites are caused by their close connection with basalts, instead of andesites.

Based on the considered above data, it is possible to explain practically full absence of sulphides in amphibolized nodules from Shiveluch by oxidized state of sulphur in the melt. Data of other authors [11][13] seem to reflect more reduced melt character, which can be compatible with the prevalence of sulfide sulfur in the magma. The composition of the amphiboles from cortlandite [12] corresponds to f_{O2} around NNO/NNO-1 matching well with the associated Cu-Ni ores. Then, considering the aforesaid, it is possible to make an assumption on the presence of an appreciable amount of a sulphides in the rocks described in [13].

Conclusions. On the basis of the aforesaid, we can conclude that, at the reaction of the mantle and crustal ultrabasic modules with andesites, magma is reduced, in a limiting case of the high ratio of the ultrabasic material to andesite(r>> 1), approximately to the level of NNO/NNO+0.5. This oxygen fugacity level is somewhat higher, than threshold one for the sulphate- sulfidic sulfur transition at the low pressure (up to 2-3 kbar).

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