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P- bearing olivine from lava flow of 2012-2013 Tolbachik volcano eruption

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We discovered skeletal crystals of olivine (Figure 1) with zones containing up to 0.48% by weight of P_2O_5 in the PK-13-07 sample (Plechov et al., 2015) collected from the moving lava flow of the Tolbachik volcano. The maximum content of phosphorus in crystals is confined to the central part of skeletal crystals (their size is 200-300 μm), which contain inclusions of volcanic glass. The distribution of phosphorus in the crystals was obtained by mapping of the P K-line characteristic X-ray intensity for crystals from a sample of lava (Fig. 1). Zones with a high concentration of phosphorus (up to 15 μm wide) extend from the center of the grains along the directions of dendritic growth. The phosphorus content decrease toward the crystal border. In the outer parts of the crystals, the distribution of phosphorus exhibits an oscillatory zoning, characterized by small variations in its content. Phosphorus content obtained by electron probe analysis in different zones range from 0.04 to 0.48 wt.% of P_2O_5 (Table 1). The phosphorus content up to 0.5% is described only in certain zones of olivine crystals of the volcanic rocks Manua-Kea (Hawaii) and Gorgon (Columbia) (Welsch et al., 2014, Millman-Barris et al., 2008). The phosphorus content up to 0.15 wt.% P_2O_5) is described for many intrusive rocks (Minerals ..., 1972).

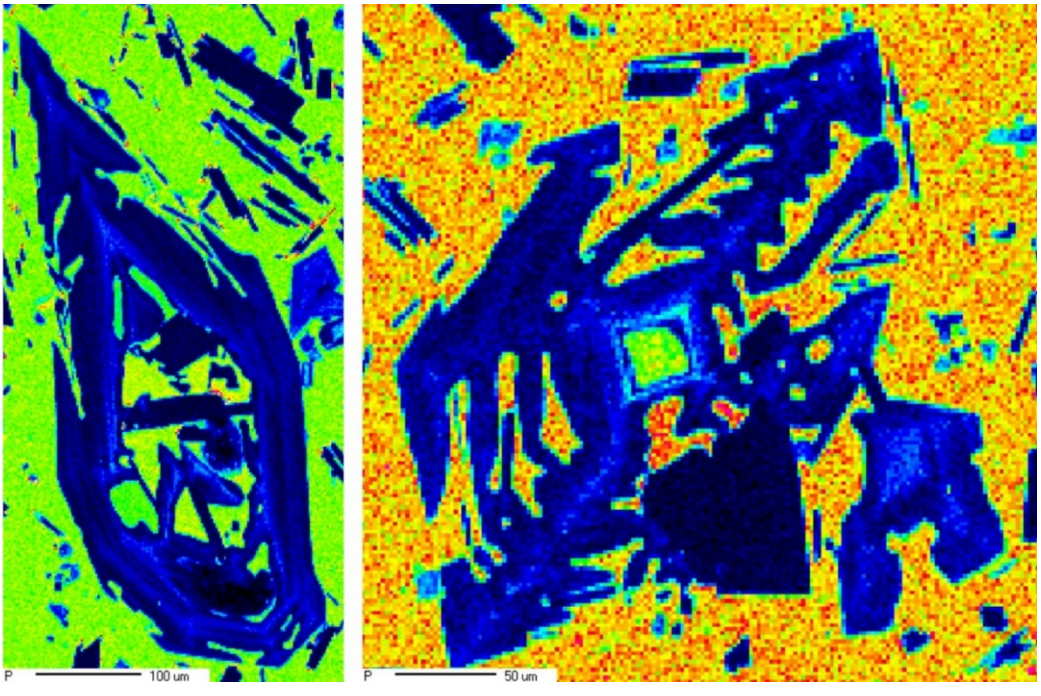

Fig. 1. Distribution of P Kα X-ray intensity over two fragments of Tolbachik lava sample containing skeletal olivine crystals.

The olivine crystals are surrounded by a glassy groundmass with a trace amount of olivine, plagioclase, and titanomagnetite microlites. Volcanic glass contains 0.63-1.2 wt. % P_2O_5 (Plechov et al., 2015).

Olivine in the lava is characterized by a range of Mg# (f.u. ratio Mg / (Mg + Fe)) from 70 to 73. The P_2O_5 content in olivine from the lava sample naturally increases from 0.06 at Mg# = 73 to 0.48% with Mg# = 70, and as the Mg # decreases, the dispersion of the phosphorus concentration increases. Ca, Al and Ti content behaves similarly: CaO increases from 0.14 to 2.63%, Al_2O_3 - from 0.01 to 0.83%, TiO_2 - from 0.01 to 0.22% as forsterite content decrease. The concentration of Ni and Cr decreases, and the Mn content increases with decreasing of olivine Mg#.

The olivine crystals from tephra (sample NK13-2) are characterized by the ratio Mg # = 71.5-75.2. The P_2O_5 content is in the narrow range 0.02-0.1, the uneven distribution of phosphorus is not observed, despite the obvious signs of skeletal growth. The Ca, Al, Ti content is also characterized by relatively small variations and a lack of correlation with the content of the olivine Mg#. The behavior of Ni, Mn and Cr in olivine from lava and tephra is not significantly different (Fig.2).

In general, olivine from lava is characterized by a lower content of forsterite minal and continues the crystallization trend in tephra. Unlike olivine in tephra, in lava, the content of trace elements varies with Mg#.

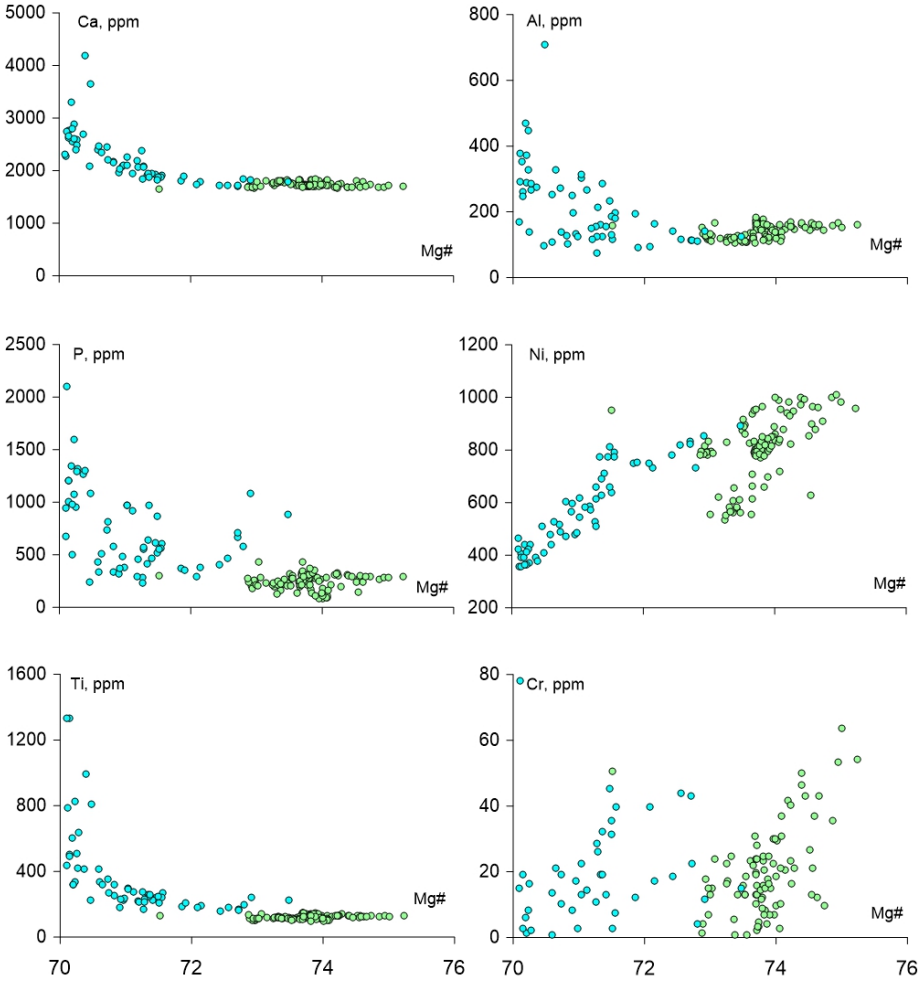

Fig. 2. Olivine crystals composition from Tolbachik volcanic products (blue symbols – olivine from lava, green – olivine from tephra).

The difference in the composition of olivine from tephra and lava allows us to state that the described skeletal crystals with an increased P content grew directly in the lava flow for two reasons: 1) the composition of olivine from the lava continues the crystallization trend of olivine from tephra and does not overlap with it, 2) the olivine from lava is significantly enriched with P, Al, Ca and Ti compared with olivine from tephra.

The majority of researchers (Millman-Barris, 2008, Bouvet de Maisonneuve et al., 2016) explain a significant amount of phosphorus in the crystal structure of olivine with rapid non-equilibrium crystal growth associated with the skeletal growth of crystals (Welsch et al, 2014).

Formation of phosphorus-enriched zones in skeletal crystals occurs during lava flowing due to rapid growth, resulting in enrichment of olivine with incompatible elements (K_D <1) due to an increase in their concentration in the boundary layer of the growing crystal. Nickel, distributed mainly in olivine, on the contrary, demonstrates the opposite behavior: a rapid decrease in concentration with the fall of Mg#.

Formation of the described zoning occurs during the flow of lava flows (from the first hours to several days according to Plechov et al., 2015), suggesting that zoning has not undergone a significant diffusion re-equilibration, and the current distribution of elements is thus a primary growth zoning.

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