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Geochemistry of volcanic gas at the 2012–13 New Tolbachik eruption, Kamchatka

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ABSTRACT

We report measurements of the chemical and isotopic composition of gas emitted from the lava flow at the 2012–13 New Tolbachik eruption. Gas and condensate samples were taken from two vents over a lava tube in May 2013. The 1030 °C gas sample was collected in evacuated Giggenbach bottle from a periodically pumping-to-venting outlet above active lava flow ~300 m from Naboko cone. Concentrations of major components in the 1030 °C gas sample are (mol%): 95.5 H_2O, 0.47 CO_2, 2.01 SO_2, 1.18 HCl, 0.34 HF that are within a range of gas compositions for subduction zone volcanoes. Isotopic analysis of He gives a corrected to atmosphere R/R_a ratio = 7.24 (He/Ne ratio = 1.41) that is close to MORB values. The 1030 °C condensate contained 9.7 ppm Cu, 2.5 ppm Zn, 1.5 ppm Tl, 20 ppb Re and 3 ppb Au, and can be considered as a representative sample for the metal composition of exsolved magmatic gases at the 2012–13 Tolbachik eruption. Isotopic data on the 1030 °C condensate ($\delta^{18}O = 6.4‰$, $\delta D = -32‰$) indicate a magmatic source. Another condensate sample taken at 690 °C was found to be drastically different from the magmatic 1030 °C condensate. We suggest that the disproportional enrichment in trace elements of this 690 °C condensate as compared to the 1030 °C condensate could result from evaporation at forced pumping during sampling and possible dissolution of earlier precipitated sublimates in the gas conduit. Unusual isotopic composition of the 690 °C condensate ($\delta^{18}O = 18.9‰$, $\delta D = -68.5‰$) can be explained by the isotopic exchange between volcanic vapor and atmospheric O_2 ($\delta^{18}O = 23.5‰$).

1. Introduction

High-temperature volcanic gases exsolved from magmatic melts are a source of direct information on compositions of fluid phase parental to hydrothermal and pneumatholitic mineralization (Williams-Jones and Heinrich, 2005; Pokrovski et al., 2014). Trace element chemical data allow to evaluate metal-bearing capacity of gaseous fluid whereas the isotopic composition of volcanic vapors allows to determine the origin of its components and degree of contamination. High-temperature gases on active volcanoes are difficult to sample due to evident reasons and each sample deserves detailed examination. Most of the analyses were obtained from fumaroles under stationary or post-eruptive regimes. Sampling on basaltic lava flows is rare and only few analyses of major and trace elements of uncontaminated samples are available (Taran et al., 1991, see also summary in Symonds et al., 1994; Zelenski et al., 2013; Taran and Zelenski, 2015). Hawaiian volcanoes are thought to be among the most studied although only limited data on the 1970 Kilauea and 1983 Puu Oo eruptions are published so far (Naughton et al., 1974; Gerlach, 1993). On Kamchatka, high-temperature gases have been first sampled at lava flows during the 1975–76 Large Tolbachik Fissure Eruption (LTFE) (Menyailov and Nikitina, 1980a; Menyailov et al., 1980b) and by Taran et al. (1991) during the 1988 Klyuchevskoy eruption.

The New Tolbachik fissure Eruption (NTE) lasted for more than 9 months (from November 27, 2012 to August 28, 2013) and produced flows of basaltic trachyandesite (Belousov et al., 2015). The eruption gave rare opportunity for gas sampling from lava flow at magmatic temperature. The eruption started with the opening of eruptive fissure on the southern slope of the Plosky Tolbachik volcano. At the beginning two groups of vents were fountaining lava and fire: the Menyailov vents at the center of the eruptive fissure and the Naboko vents, which later formed the complex Naboko cone. First data on NTE gas and condensate compositions collected from the lava flow have been reported by Zelenski et al. (2014). In their study, gases were sampled from February to May 2013 repeatedly from a 3 by 3 m window of a lava tube ~300 m from the Naboko cone with active lava lake inside. The condensates were collected by two methods — "standard" through a water-cooled condenser and "external" implying condensing on the outer surface of a liquid butane-charged cooler. Gas sampling was performed through pumping via three consecutive traps to reach complete condensation.

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Here we report on results of our work in late May 2013 when we applied an evacuated-bottle scheme (Giggenbach, 1975) to gas sampling and a water-filled glass cooler to collecting condensate. Our sampling was carried out from a small (~0.3 m) vent 25 m northward upstream from the large window where Zelenski et al. (2014) have taken their samples. Gas composition, major and trace elements of condensates, O and H isotopic ratios of condensed vapor and He isotopic data are given in this contribution. A comparison of the recent and previous data allows also to discuss advantages and disadvantages of different sampling methods.

Noble metal abundances in Tolbachik gases are of particular interest because of finding of exhalative gold crystallized during the eruption (Chaplygin et al., 2015a, 2015b; Zelenski et al., 2016). Abundant native gold and rich Cu mineralization have been long known to form from post-volcanic medium- to high-temperature gases at cinder cones of the previous 1975–76 LTFE (Vergasova et al., 2001). Low discharge rate gases at the 1975–76 LTFE cinder cones are not easy to condense due to a high proportion of air and a lower proportion of magmatic gas. Nevertheless, high grade of mineralization indicates an elevated capacity of halogen-rich gases with respect to Au and Cu transport.

2. Samples and analytical methods

Depressions on the lava field surface and windows in the roof of the lava tube started to occur by late February giving a first opportunity to take gas samples. Gases were sampled at two points different in gas temperature (1030 °C and 690 °C) on the lava field (Fig. 1b).

2.1. 1st sampling point TL0113

A vent ~30 cm in diameter was found on May 24 in a large depression located ~25 m upstream from the window used for sampling by Zelenski et al. (2014), which is shown as a bigger outlet in Fig. 2. Moving lava was seen ~4–5 m below the mouth of the vent. This hornito vigorously blew out gas then inhausting air. Such a periodic regime could be readily explained by changes in the lava level inside the lava tube. When the lava level went low enough for a gas gap above the lava to appear, exsolving gases escaped via the wider window. This caused air to be sucked into the small vent (Fig. 2a). Raising of the lava level closed the gap between flowing lava and the roof and made magmatic gas escape through the small vent (Fig. 2b). When the lava level got up significantly the melt overflowed from the small vent and then drained back leaving hollow eggshell-like crusts around, which eventually cracked (Fig. 3a, b). At least four such effusions have taken place judging by the number of such crusts. The periods of gas blowing out at the small vent coincided with elevated crater activity and lasted for more than 1 h. Temperature of the gas jet was measured with K type thermocouple and did not exceed 1030 °C whereas lava temperature was up to 1060 °C according to infra-red thermometer (Fig. 3a). Gas and condensate were sampled from this vent on May 26, 2013. One meter long quartz tube (dia. 25 mm) was mounted on an iron rod fixed inside the subvertical channel. A 600 ml Giggenbach quartz bottle filled with 100 ml of 4 N NH_4OH solution and evacuated was used for gas sampling (Sortino et al., 2006). Condensate was collected via a glass water-cooled condenser. Separate quartz tubes (0.5 m long, dia. 8 and 14 mm) connected by Tygon tubing to the Giggenbach bottle and the condenser were inserted in the fixed

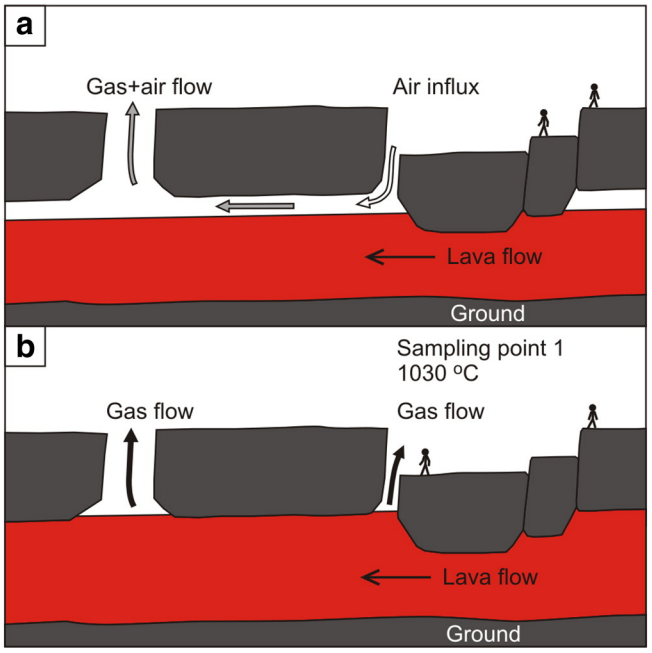

Fig. 2. Schematic cross-section along lava tube showing different gas regimes at the 1st gas sampling point (1030 °C). (a) Low lava level provides opening (gas gap) beneath the roof between two vents above degassing melt. The small 1030 °C vent inhausts air whereas the big vent, which is the sampling point of Zelenski et al. (2014), throws out gas + air mixture. (b) High lava level closes the gas gap between two vents that makes gas escape via the small vent.

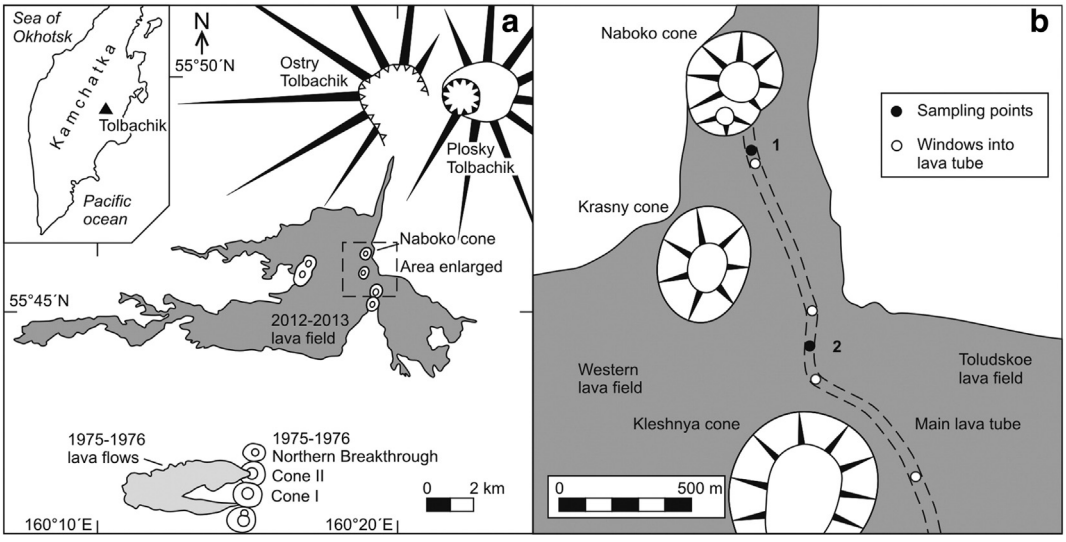

Fig. 1. Geographic scheme of Tolbachik region. (a) Location of the main eruptive center of 2012–2013 Tolbachik eruption (Naboko cone) and distribution of 2012–2013 lava flows; (b) Position of gas sampling points.