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## Genesis of volatiles in suprasubduction basaltic melts from Tolbachik Volcano, Kamchatka

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#### Abstract

Vitreous basalts and plagioclase lapilli from Tolbachik Volcano studied by high-temperature gas chromatography reveal features of a fluid regime uncommon to suprasubduction melts. Prominent depletion in volatiles confirms the anomalous behavior of the Tolbachik fluid systems. Vitreous basalts contain minor amounts of water (0.16–0.27 wt.%) and carbon dioxide (95–440 ppm). New data on volatiles in the Tolbachik plagioclase lapilli show very low contents of CO<sub>2</sub> and total gas (exclusive of H<sub>2</sub>O) and enrichment in reduced fluids (CO and CH<sub>4</sub>) relative to the basalts. In general, analysis of basalts and plagioclase lapilli from different eruptions trace a progressive increase in reduced fluids (CO and CH<sub>4</sub>) and decrease in CO<sub>2</sub> and total gas from past to present events. The concentrations of CO<sub>2</sub> decrease, while those of CO and CH<sub>4</sub> in basalts and plagioclase lapilli increase systematically with an increase in FeO/MgO ratios and K<sub>2</sub>O contents in the lavas and in anorthite component in plagioclase.

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#### Introduction

Volatiles stored in magmas are key agents in catastrophic eruptions of volcanoes. Anomalous behavior of fluid systems in melts of individual volcanoes may be diagnostic of volcanic hazard and, in this respect, is worth special investigation. Unusual features of volatile compositions were discovered in lavas of Tolbachik Volcano in Kamchatka erupted during the latest event of 2012-2013: saturation with fluid components other than water, unlike most of suprasubduction melts. The presence of these components and the composition of hightemperature gases released from lava flows were inferred from secondary minerals (volcanic sublimates) of Na, Fe, K, and Cu chlorides and sulfates or, less often, Cu hydrochlorides (Saveliev, 2013). Thus, volcanic gases emitted from the Tolbachik magma must bear high concentrations of Cl and S. The presence of Cl and S compounds, as well as hydrogen, was confirmed by analysis of volatiles that were released from lavas and sampled during eruptions (Fedotov, 1984; Halmer et al., 2002).

Volatiles in magma reservoirs beneath Tolbachik Volcano likewise differ from those in common suprasubduction systems. Namely, glasses from melt inclusions in olivines from lavas of the 2012–2013 eruption (Plechov et al., 2015) show unusual H<sub>2</sub>O depletion of parent melts (within 1.45 wt.%) relative to island arc basalts (IAB) which commonly contain 2 to 6 wt.% H<sub>2</sub>O (Plank et al., 2013).

Generally, sampling and analysis of gases immediately during eruptions furnish useful information on the composition of volatiles in the Tolbachik basaltic melts emitted in the surface conditions, while melt inclusions can provide insights into deep fluid systems. On the other hand, volatiles preserved in glass and crystalline phases, which record the properties of fluids in magma ascending from mantle depths, remain actually beyond analysis. To bridge the gap, we have analyzed volatiles in vitreous basalts and plagioclase lapilli from the Tolbachik lavas and report the results in this paper.

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#### Tolbachik Volcano: Local geology and petrology

The Tolbachik volcanic complex belongs to the southwestern Kluchevskoi group of volcanoes in Kamchatka (Fig. 1) and consists of several edifices: Ostryi (Russian for *Sharp* or *Peak*), Ploskii (*Flat*), and the Tolbachik field in the southwestern flank of Flat Tolbachik. The Peak and Flat Tolbachik edifices began forming about 7–10 kyr ago almost coevally with Kluchevskoi volcano (Churikova et al., 2013) but Peak Tolbachik has ceased its activity while Flat Tolbachik and volcanic centers in its southwestern flank remain active.

The earliest eruptions of Tolbachik (since 7000 yr) produced mainly high-Al basaltic andesites generated in shallow reservoirs while high-Mg basalts that erupted for the past 2000 yr (Fedotov et al., 2010) come from deeper sources (Belousov et al., 2015; Volynets et al., 2013) and form a system of dikes.

Flat Tolbachik and volcanoes in its southwestern flank erupted fourteen times between 1740 and 2013, with the largest eruptions in 1941, 1975–1976, and 2012–2013. The lavas were mainly of high-Al or high-Mg basaltic compositions, while andesites exist only as bombs originated in intermediate reservoirs.

The great Tolbachik fissure eruption (GTFE) lasted 450 days in 1975 through 1976 (Northern and Southern events, respectively) and produced 0.87 km<sup>3</sup> of lavas; the duration and volume of the second largest eruption of 2012–2013 were, respectively 280 days and 0.55 km<sup>3</sup>. The products of the 1975

event (Northern eruption) were mostly Mg-rich pyroclastics while the largest Southern eruption of 1976 produced only high-Al basaltic lavas. In 2012–2013, basaltic andesites with >1.5 wt.% K<sub>2</sub>O erupted first (Menyailov cone) but mostly basaltic lavas erupted during the main phase (Krasnyi and Naboko cones) of the event (Volynets et al., 2013). Most of lavas, bombs and pyroclastics contain abundant vitreous clasts. Early during the main phase, many flat plagioclase crystals and aggregates (lapilli) covered with thin glass films were ejected. In general, the 2012–2013 event was remarkable by the highest glass contents and porosity of rocks and intense release of volcanic gases.

We studied volatiles in the Tolbachik vitreous basalts erupted during the 2012–2013, 1975–1976, and 1941 events, as well as in other events older than 1000 yr (Fig. 1). Fluids were also analyzed in plagioclase lapilli which came most likely from the shallowest part of the magma conduit rich in volatiles (Dobretsov et al., 2016) and were ejected as individual phases during the 1975–1976 and 2012–2013 events.

The features of volatiles in the Tolbachik melts were studied in samples of vitreous basalts collected during the field trip of 2015; some samples of basalts and plagioclase lapilli were courtesy of S.A. Chirkov from the Institute of Volcanology and Seismology (Petropavlovsk-Kamchatsky).

All samples (irrespective of their age) have numerous pores of different sizes in a vitreous matrix (Fig. 2). The matrix mostly consists of glass with plagioclase or less often clinopyroxene inclusions.



Fig. 1. Location of sampling sites for Tolbachik basalts. 1–4, sampling sites for vitreous basalts erupted in 2012–2013 (1), 1975–1976 (2) and 1941 (3), as well as in earlier events (4). Based on data from (Flerov et al., 1984; Fedotov et al., 2011), with reference to unpublished evidence from Khubunai, Dvigalo, and Romanova.

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