Journal of Volcanology and Geothermal Research 285 (2014) 136–149

Contents lists available at ScienceDirect

Journal of Volcanology and Geothermal Research

journal homepage: www.elsevier.com/locate/jvolgeores

Emissions of trace elements during the 2012–2013 effusive eruption of Tolbachik volcano, Kamchatka: enrichment factors, partition coefficients and aerosol contribution

M. Zelenski [a,*], N. Malik [b], Yu. Taran [c]

[a] Institute of Experimental Mineralogy RAS, Chernogolovka 142432, Moscow Region, Russia
[b] Institute of Volcanology and Seismology FEB RAS, Petropavlovsk-Kamchatsky 683006, Russia
[c] Institute of Geophysics, Universidad Nacional Autonoma de Mexico, Mexico D.F. 04510, Mexico

ARTICLE INFO

Article history:
Received 3 April 2014
Accepted 2 August 2014
Available online 17 August 2014

Keywords:
Tolbachik volcano
Kamchatka
Eruption
Gas emissions
Trace elements
Aerosol
Partition coefficients

ABSTRACT

Gases and aerosols from the 2012–13 effusive eruption of Tolbachik basaltic volcano, Kamchatka, were sampled in February and May, 2013, from a lava tube window located 300 m from the eruptive crater; temperature at the sampling point was 1060–1070 °C. The chemical and isotopic compositions of the sampled gases (92.4% H_2O, 3.5% CO_2, 2.3% SO_2 on average; δD from −25.0 to −38.6‰) correspond to a typical volcanic arc gas without dilution by meteoric or hydrothermal water. Halogen contents in the gases (1.37% HCl, 0.5% HF) were higher than average arc values. The total amount of analyzed metallic and metalloid (trace) elements in the gas exceeded 665 ppm. Six most abundant trace elements, K (250 ppm), Na (220 ppm), Si (74 ppm), Br (48 ppm), Cu (21 ppm) and Fe (12 ppm), accounted for 95% of the total content of trace elements in the gas. The gases contained 24 ppb Re, 12 ppb Ag, 4.9 ppb Au and 0.45 ppb Pt. Refractory rock-forming elements (Mg, Al, Ca) and some other elements such as Ba and Th were transported mainly in the form of silicate microspheres and altered rock particles. The concentrations of metals in the eruptive Tolbachik gases are higher than the corresponding concentrations in high-temperature fumaroles worldwide, although the mutual ratios of the elements are approximately the same. The gas/magma partition coefficients of eleven elements exceed unity, including the non-metals F, S, Cl, Br, As, Se and Te and the rare metals Cd, Re, Tl and Bi. Despite the relatively low concentrations of trace elements in the volcanic gases at the highest temperatures, superficial magma degassing provides information on the sources and sinks of metals.

1. Introduction

Emissions of metals by volcanic gases have been studied for almost a century since John Shipley collected condensates and fumarolic incrustations in the Valley of Ten Thousand Smokes in 1917 (Shipley, 1920). Two years later, Allen and Zies observed in the same place the deposition of galena and sphalerite from fumarolic gases (Allen and Zies, 1923). Early studies of volcanic gases and related fumarolic deposits performed before 1959 were reviewed by White and Waring (1963). More recently, several papers have described the trace element compositions of fumarolic condensates collected around the world (e.g., Birnie and Hall, 1974; Menyailov and Nikitina, 1980; Gemmell, 1987). A subsequent period in the study of gaseous transport of trace elements began with the development of new methods to collect volcanic sublimates (Bernard and Le Guern, 1982) and thermodynamic simulations of gaseous transport and deposition of elements (e.g., Symonds et al., 1987; Quisefit et al., 1989; Symonds and Reed, 1993; Taran et al., 2001). In addition to the collection of condensates, which can be dangerous or even impossible on active volcanoes, emissions of trace elements into the atmosphere have been studied extensively using filter packs (e.g., Zoller et al., 1974; Aiuppa et al., 2003; Calabrese et al., 2011; Martin et al., 2012). The relationship between the metal content in volcanic fluids and ore deposits has also been discussed (Hedenquist and Lowenstern, 1994; Kavalieris, 1994; Williams-Jones and Heinrich, 2005). Volcanic gases transport almost the complete Periodic Table; however, most elements have extremely low concentrations (ppb-to-ppm level). The geological effects of such emissions are usually confined to the formation of fumarolic incrustations and the dissipation of element-containing aerosols in the environment. On the other hand, gas transport and deposition of elements in volcanic processes provide the opportunity to make direct observations. Therefore, despite their negligible potential for the formation of economic deposits, volcanic gases are scientifically significant as proxies for dense subterranean magmatic-hydrothermal vapors and hydrothermal fluids (Pokrovski et al., 2013).

* Corresponding author. Tel.: +7 926 255 5948.
E-mail address: volcangas@gmail.com (M. Zelenski).

http://dx.doi.org/10.1016/j.jvolgeores.2014.08.007
0377-0273/

Almost all direct sampling of volcanic gases, including those of the highest temperature gases (Taran et al., 1995; Chaplygin et al., 2012; Zelenski et al., 2013), has been performed from fumaroles. Even high-temperature fumarolic gases of 900–1000 °C can be diluted by meteoric water (Taran et al., 1995; Botcharnikov et al., 2003; Chaplygin, 2009; Chaplygin et al., 2012) or can show signatures of interaction between the gas and the conduit walls (Quisefit et al., 1988; Symonds and Reed, 1993; Aiuppa et al., 2003). Undiluted and unchanged magmatic gases are rarely accessible for sampling. However, such gases are of interest in terms of their trace element compositions because they fix the gas–magma partition coefficients for different elements. Direct sampling of gases just after exsolution from a degassing magma is possible in rare cases during effusive basaltic eruptions with smooth degassing and negligible explosive activity. Only a few papers have dealt with such samples (e.g., the 1970 eruption of Kilauea; Naughton et al., 1974).

A large-scale effusive eruption from the Tolbachik volcano in Kamchatka occurred in 2012–2013 (Edwards et al., 2013; Volynets et al., 2013). The eruption provided opportunities to study the volatile emission of elements through repeated direct sampling of high-temperature (1060–1070 °C) gas in the close proximity (2–3 m) to the degassing basaltic lava. In this paper, we present the results of direct gas sampling and filter pack sampling during the Tolbachik eruption in 2013. First, we introduce a new method for sampling volcanic gas condensates. We then characterize the major gas species and rock composition of the eruption. Then, the trace element concentrations in the gas condensates are examined, and the role of the Tolbachik aerosol in the total emissions of elements is discussed. The obtained set of gas samples contained the full spectrum of exsolved elements without losses caused by decreased temperature or dilution by meteoric water. Moderate contamination by fine fragments of magma and wall rocks was observed but was corrected for to separate the volatile emissions from the silicate and non-silicate aerosols. In the last section of the paper, we calculate the gas/magma partition coefficients.

2. Geological background

2.1. An overview of the region

Plosky (flat) Tolbachik (55°49.5′ N, 160°23.5′ E, 3080 m asl) and the extinct Ostry (sharp) Tolbachik (55°50.0′ N, 160°19.5′ E, 3682 m asl) form a predominantly basaltic volcanic complex in the central part of the Central Kamchatka depression, and belong to Klyuchevskoy volcanic group. This group comprises a cluster of ten extinct and five active volcanoes, at least two of which, Klyuchevskoy and Shiveluch, are among the most productive arc volcanoes on Earth (Portnyagin et al., 2005; Auer et al., 2008). Detailed geological descriptions of the region can be found in Portnyagin et al. (2007), Ponomareva et al. (2007) and Auer et al. (2008).

The Plosky Tolbachik volcano has a massive edifice with steep slopes and a flat summit that is formed by a caldera 3 km in diameter. An inner crater-caldera of 1.7 km diameter and 600 m deep is located in the southern part of the Plosky Tolbachik summit. This inner collapse crater was formed during the 1975–76 eruption of Tolbachik as a result of the emptying of the magmatic plumbing system.

Before the collapse of the caldera, a small pit crater ca. 300 m in diameter and containing an intermittent lava lake was present on the flat summit of Plosky Tolbachik. Several weak eruptions occurred from the terminal crater in the form of gas jets from the lava lake surface and sporadic explosions (Dvigalo et al., 1991). Two NE- and SSW-trending extension (rift) zones with linear chains of cinder cones cross the Plosky Tolbachik edifice. Polyak and Melekestsev (1981) estimated that the average effusion rate of Tolbachik during the Holocene was 0.2 m^3/s. The last three major Tolbachik eruptions occurred in 1941, 1975–76 and 2012–13, and were located in the SSW 'rift' zone. The total volume of ejected lava and tephra during these three eruptions was approximately 2.0 km^3 of compact material, which corresponds to an average rate of lava production of 0.86 m^3/s for the last 72 years.

Although it is located in a subduction zone, Plosky Tolbachik exhibits several features that are characteristic of intraplate volcanoes: (1) fluid basaltic or basaltic andesite lavas with high alkali contents of up to 7% $Na_2O + K_2O$; (2) a summit caldera with a pit-crater and an intermittent lava lake (before the 1975–76 eruption); (3) rift-like lateral extension zones with numerous monogenetic cones and (4) voluminous effusive eruptions with minor explosive activity. The great depth of the upper surface of the subducting slab under the volcano (180–190 km; Gorbatov et al., 1997) also differentiates Tolbachik from most arc volcanoes. Several hypotheses have been proposed to explain the petrologic features and high effusion rates of Tolbachik and other volcanoes in the Central Kamchatka depression (Ponomareva et al., 2007; Auer et al., 2008; Nikulin et al., 2012, and references therein).

2.2. The 2012–13 Tolbachik eruption

The last Tolbachik eruption began on 27 November 2012 and lasted 270 days until 24 August 2013, but some residual activity lasted until the middle of September. The initial lava and tephra ejections occurred from several eruptive centers along a 5-km-long fissure zone on the southern flank of the Plosky Tolbachik volcano, between 55°48.1′ N, 160°20.5′ E at 2240 asl and 55°45.6′ N, 160°18.8′ E at 1500 m asl. After three days of the eruption, the activity of all but the lowermost eruptive centers ceased. The initial effusion rate was estimated to be as high as 465 m^3/s of lava during the first two days of the eruption and 140 m^3/s of lava during the next 14 days (Dvigalo et al., 2014), with simultaneous moderate tephra emissions. Later, a 120-m-high pyroclastic cone formed at the main eruptive center (Fig. 1). The average effusion rate decreased to 19 m^3/s in the middle of January 2013 and continued at this rate until early June; then the effusion rate gradually decreased until the eruption stopped. Repeated intensifications of both the strombolian activity and the effusion rate occurred during the eruption. The effusion rates and the total volume of erupted lava were calculated from direct measurements of lava volumes through photogrammetric processing of orthogonal and oblique photographs of the eruption zone (Dvigalo et al., 2014). The total volume of erupted lava and tephra was estimated at 0.60 ± 0.05 km^3.

From February through May 2013, moderate strombolian activity was ongoing at the eruptive cone (Figs. 1, 2). A lava lake approximately 20 × 30 m in size inside the cone was constantly agitated by gas-driven explosions, which occurred 2–10 times per minute. Lava was drained from the cone through a 1-km-long lava tube (Fig. 2) and appeared from the opening of the lava tube as surface flows. Several windows over the lava tube emitted a mixture of volcanic gases and heated atmospheric air; the latter was drawn inside the tube through several holes along the lava stream.

3. Methods

3.1. Gas sampling methods

Because of the high air content, Giggenbach bottles could not be used for the gas sampling. Instead, we pumped gas through three consecutive traps, each of which was partially filled with 30 ml of 4 N KOH solution (Taran et al., 2001; Fig. 3a). The set of traps was cooled by an ice–water mixture.

A 2–3-m-long silica tube was inserted into a small hole adjacent to the side of the large window at an angle of 45° to position the tube inlet as close as possible to the lava flow. The tube inlet was located only 2–3 m above the flowing lava during the sampling session in February. The other end of the silica tube was connected through a