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Platinum-group elements and gold in sulfide melts from modern arc basalt (Tolbachik volcano, Kamchatka)

M. Zelenski [a], V.S. Kamenetsky [a,b,*], J.A. Mavrogenes [c], L.V. Danyushevsky [b], D. Matveev [d], A.A. Gurenko [e]

[a] *Institute of Experimental Mineralogy RAS, Chernogolovka 142432, Russia*
[b] *Earth Sciences and CODES, University of Tasmania, Private Bag 79, Hobart, TAS 7001, Australia*
[c] *Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia*
[d] *Institute of Solid State Physics RAS, Chernogolovka 142432, Russia*
[e] *Centre de Recherches Pétrographiques et Géochimiques (CRPG), UMR 7358, Université de Lorraine, 54501 Vandoeuvre-lès-Nancy, France*

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ABSTRACT

Sulfide melt inclusions entrapped in primitive olivine phenocrysts can be used to understand the compositions of early sulfide melts that may ultimately contribute to magmatic sulfide ore deposits. Sulfide globules hosted in olivine (86–92 mol% Fo) from the Tolbachik basalt (the 1941 eruption) are characterized in terms of their major and trace element abundances using electron microscopy and LA–ICP–MS analysis. Distribution of major elements within individual sulfide globules varies from homogeneous to heterogeneous. Phases include monosulfide solid solution (MSS) and intermediate solid solution (ISS) intergrowths and exsolved low-temperature minerals such as pyrrhotite, pentlandite, chalcopyrite and cubanite. Trace elements (platinum-group elements — PGE, Ag, Te, Au, Pb and Bi) are also present in solid solution in sulfide phases and as micron-sized particles ("nuggets"). Such nuggets of dominantly Au, Pt, Au–Pd and Pd–Te are contained randomly within sulfide matrices or, more commonly, at phase boundaries. Nuggets are also attached to outer surfaces of sulfide globules. Concentrations of PGE in sulfides follow a log normal distribution over four orders of magnitude. The highest measured noble metal concentrations in the analyzed globules (436 ppm Au + PGE) are 13.3 ppm Au, 115 ppm Pt and 299 ppm Pd, whereas 40% of globules have <15 ppm of noble metals. Gold and PGE concentrations correlate, suggesting these elements were concentrated by the same process(es). We propose that a number of anomalous concentrations of one or several noble metals in the analyzed globules can be best explained by entrapment of Au–PGE-rich particles (solid or liquid) from the silicate melt. Although the individual Tolbachik sulfide globules have variable PGE abundances, their mean composition resembles those of major PGE-sulfide ore deposits (e.g., Norilsk, Sudbury, Platreef and Merensky Reef).

1. Introduction

A remarkable feature of magmatic sulfide ores is their high concentrations of platinum-group elements (PGE) and gold, which may exceed corresponding concentrations of these elements in parental silicate liquids by 3–5 orders of magnitude (Barnes and Ripley, 2016; Campbell and Barnes, 1984; Naldrett, 2004). Accumulation of PGE–Au in sulfide melts derived by liquid immiscibility relies on efficient diffusive transport of metals from cogenetic silicate melts (Barnes and Ripley, 2016; Mungall, 2002; Zhang, 2015), and is the end result of complex interactions of a number of processes. As diffusion of metals in silicate melt is relatively slow, even at magmatic temperatures (Zhang et al., 2010 and references therein), and with PGE–Au abundances at sub-ppb to ppb levels (e.g., Bezos et al., 2005; Meisel and Moser, 2004; Naldrett, 2004), noble metal enrichment of magmatic sulfide liquids requires sufficiently long interaction of the latter with large volumes of silicate melt, even with extremely high sulfide/silicate partition coefficients. Nevertheless, the modern theories of sulfide ore deposit formation consider diffusion as the main process responsible for concentration of trace elements (Au–PGE) in sulfide liquid (e.g., Campbell and Barnes, 1984; Naldrett, 2004). Concentrations of PGE in sulfide melt can be further upgraded by direct entrapment of micron- and submicron-sized PGE-containing particles (which include pure metals, PGE alloys, sulfides, bismuthinides, etc.) that may be present in primitive magmas prior to and during sulfide segregation. Although the existence of such nano- and micro-particles of PGE minerals (PGM) in silicate melts has been directly confirmed (Kamenetsky et al., 2015; Park et al., 2012) and suggested in a number of works (e.g., Andrews and Brenan, 2002; Anenburg and Mavrogenes, 2016; Tredoux et al., 1995), collection of such particles by growing sulfide droplets is yet to be recognized.

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[*] Corresponding author at: Earth Sciences and CODES, University of Tasmania, Private Bag 79, Hobart, TAS 7001, Australia.
E-mail address: Dima.Kamenetsky@utas.edu.au (V.S. Kamenetsky).

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Massive or disseminated magmatic sulfide ores cannot provide reliable evidence for physical incorporation of early particles of PGE from the silicate melt into magmatic sulfides due to their high solubility in sulfide liquids (e.g., Fonseca et al., 2009; Pruseth and Palme, 2004). Also, magmatic and post-magmatic processes erase original compositions of incipient sulfide droplets. Such processes include coalescence of sulfide droplets at the base of magma chambers (averaging compositions), recrystallization of deposited sulfides, entrainment of sulfide melts by new batches of magma and alteration caused by syn- and post-magmatic fluids. On the other hand, sulfide droplets entrapped and quenched in early magmatic minerals (e.g., olivine and Cr-spinel) represent the least modified compositions of immiscible sulfide melts. Importantly, these globules contain numerous noble-metal nuggets, which crystallized from the sulfide melt upon cooling, but also could have been trapped from magma by sulfide droplets (e.g., Holwell et al., 2011, 2015; Kamenetsky et al., 2013, 2015).

In this study, droplets of sulfide melt (sulfide globules) sealed in primitive olivine phenocrysts from island arc magma (high-Mg basalts produced by the 1941 eruption of Tolbachik volcano) reveal high concentrations of noble metals. We report the occurrence and overall abundances of noble metals and their alloys and minerals in immiscible sulfide melt. We also show that the high PGE content of sulfides could be acquired, at least partially, by direct capture of PGE-rich phases by growing sulfide droplets from the silicate magma.

2. Tolbachik volcano

The Tolbachik Volcanic Complex in the central part of the Central Kamchatka Depression is the southernmost of the Klyuchevskoy Group of volcanoes, which are located at the north termination of the Kuril–Kamchatka arc in in the northwest Pacific. Two major volcanoes, Ostry Tolbachik and Plosky Tolbachik, form a single massif with a highest point at 3680 m a.s.l. (55.8319° N, 160.3272° E). Two linear chains ("rift" zones) of more than 170 monogenetic cones extend NE and SSW from Plosky Tolbachik (Fig. 1). All recent activity was confined to the terminal caldera of Plosky Tolbachik and SSW "rift" zone, where three historic eruptions occurred with a total volume of ~2.2 km^3 of basalt (dense rock equivalent; Zelenski et al., 2016). The magmatic system of the Tolbachik volcano was reviewed by Belousov et al. (2015). Chemical compositions and petrographic features of Tolbachik rocks can be found in several publications (e.g., Churikova et al., 2015a, 2015b; Flerov et al., 1984; Portnyagin et al., 2007, 2015).

The rocks of Tolbachik belong either to medium- or high-K series, both with a relatively narrow interval of SiO_2 contents from basalts to basaltic trachyandesites (Fig. 2a). Both series have bimodal MgO distributions that range from 3 to 5.5 wt.% MgO and from 8 to 11.5 wt.% MgO (Fig. 2b). The bimodal MgO content of Tolbachik rocks was attributed to extreme fractional crystallization (Flerov et al., 1984) or the product of two different mantle sources (Churikova et al., 2015b; Dosseto et al.,

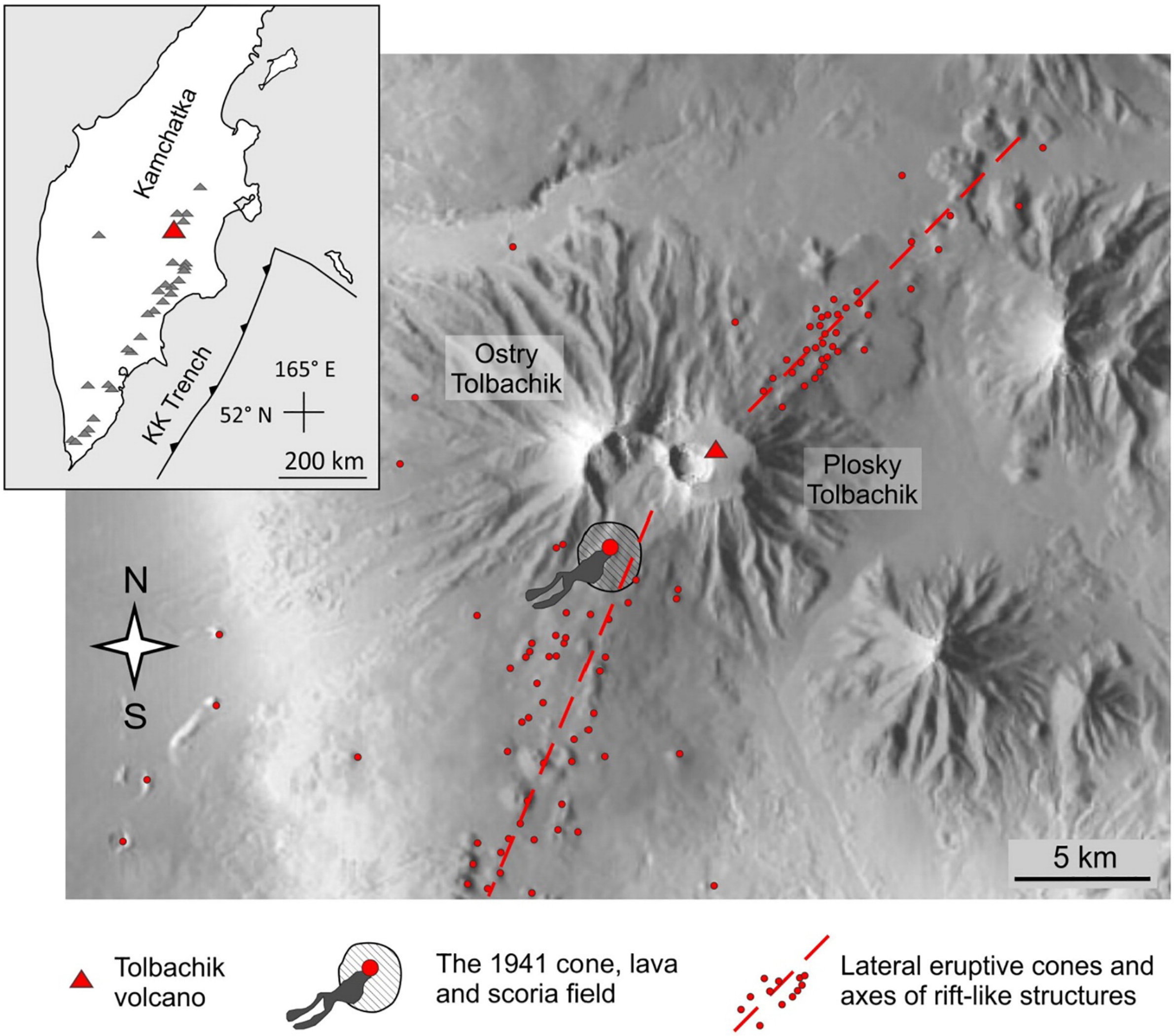

Fig. 1. Map of the Tolbachik volcano and the 1941 eruptive cone with an adjacent lava flow and scoria field.