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# Textural, morphological and compositional varieties of modern arc sulfides: A case study of the Tolbachik volcano, Kamchatka

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# ABSTRACT

Magma unmixing into separate sulfide and silicate melts is a key process in the formation of magmatic sulfide ore deposits. Sulfide inclusions in olivine preserve the original chemical composition of the segregated sulfide melt, whereas the phase compositions of the solidified sulfide droplets and their textures record the final stages of sulfide evolution. Sulfide globules hosted in olivine phenocrysts of magnesian basalts from the Tolbachik volcano (Kamchatka) display a variety of textures ranging from homogeneous to fine-grained to coarse-grained and lamellar. Porous textures and textures associated with the oxidation and dissolution of sulfides were identified as separate categories. The outer surfaces of sulfides vary significantly in shape, which includes normal spherical or elliptical globules, gravitationally layered inclusions, thin sulfide foils and concave deformed sulfides in contact with fluid bubbles. The estimated cooling rate of olivine phenocrysts responsible for observed crystallization textures varies by five orders of magnitude. The Fe:Ni:Cu ratio also exerts an influence on the resulting texture, whereas the size of the globules does not have any significant effect. The morphology and textural patterns of individual grains indicates that fine-grained textures resulted from the rapid breakdown of a homogeneous solid phase, which the sulfide melt solidified into during extremely rapid quenching. The presence of large or abundant small pores in sulfides, along with channels at the globule periphery indicates the separation of an appreciable amount of dissolved fluid from the sulfide melt during crystallization. Sulfides in the form of thin foils and planar swarms in healed cracks indicate cyclic pressure changes in the olivine environment, which resulted in phenocrysts rupturing and healing. The sulfide mineralogy is represented by high-temperature sulfides MSS (monosulfide solid solution) and ISS (intermediate solid solution), as well as pyrrhotite-pentlandite-chalcopyrite-cubanite-bornite-magnetite assemblages, which formed at lower temperatures.

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## 1. Introduction

Phenocrysts of early magmatic minerals (e.g., olivine, spinel), which formed in a magma chamber and were ejected to the surface during a volcanic eruptions possess a wealth of information about crystal nucleation and growth, the chemical composition and physical parameters of non-erupted and non-degassed silicate melts and fluids, and sulfide liquid immiscibility in the magma reservoirs. This information is ascertained from the study of preserved fluid bubbles, non-silicate liquids (e.g., sulfide melt) and other small crystals hosted within the magma and silicate melt itself, which have been entrapped by growing phenocrysts that were transported unaltered to the surface in during volcanic eruption. Among the various inclusions hosted in magmatic

\* Corresponding author. *E-mail address:* volcangas@gmail.com (M. Zelenski). phenocrysts, sulfide globules are of particular interest. These globules preserve the original characteristics of sulfide melts at the time of their separation from the silicate melt and are instrumental in the study of silicate-sulfide liquid unmixing, which plays a key role in the formation of magmatic sulfide ore deposits.

Most of the data on natural sulfide globules has been obtained from quenched basaltic glasses formed during underwater eruptions and olivine phenocrysts from mid-oceanic ridge basalts (MORB; e.g., Czamanske and Moore, 1977; Francis, 1990; Gurenko et al., 1987; Kamenetsky et al., 2013; Mathez, 1976; Patten et al., 2012; Savelyev et al., 2018). Sulfide globules have also been described in ocean island basalts (OIB; e.g., Desborough et al., 1968; Stone and Fleet, 1991).

Unlike fresh glasses, mafic continental rocks and sulfide ores rarely preserve unmodified sulfides. Deuteric/hydrothermal activity and recrystallization partially-to-completely erases the original textures and compositions of such sulfides. One of the rare exceptions is sulfide





melt inclusions hosted in chromite crystals, which permits the study of early-stage sulfide melts in layered intrusions (e.g., Platreef, Bushveld Complex; Holwell et al., 2011). However, as chromitites in the Bushveld Complex are thought to have formed due to mixing between crustal siliceous melts and primitive basaltic melts, the sulfide parental media in intrusive complexes may not necessarily be mantle-derived.

Cu-rich sulfide globules occur in intermediate to felsic island arc magmas (Humphreys et al., 2015; Keith et al., 1997; Parat et al., 2011), some of which could have been reduced by the extensive crystallization of magnetite (Jenner et al., 2010). However, these rocks are not primitive and do not fully reflect the characteristic conditions for the formation of magmatic sulfide ores. Common arc basalts ( $fO_2 \sim QFM + 1.5... + 3$ ) are more oxidized than MORB and OIB ( $fO_2 \sim QFM + 1;$  e.g., Evans et al., 2012; Matjuschkin et al., 2016; Richards, 2015), which means that sulfur in such magmas is dissolved mainly in the form of sulfate (Jugo et al., 2010) and sulfide segregation is unlikely. Only if the basaltic arc magma is reduced by the assimilation of carbon, then silicate-sulfide unmixing is possible (Tomkins et al., 2012).

Recent studies of Ni- and Cu-rich sulfides in unaltered olivine phenocrysts from primitive high-Mg arc basalt (Tolbachik volcano, Kamchatka; Zelenski et al., 2017, 2018) present a unique opportunity to study primitive sulfide melts from a continental arc location in an unaltered state. These sulfides are characterized by a diversity of textures, which provide information about various events during their solidification history. Magma ascent ensured the rapid transport of entrapped sulfide globules from a deep chamber to the surface. When phenocrysts of olivine were ejected at the surface, the included sulfide melt underwent cooling, decompression, crystallization and fluid separation. The transition from high- to low-temperature phases and the breakdown of solid solutions occurred in the last stages of sulfide evolution. A combination of these processes was imprinted in the form of a specific sulfide texture. The goal of this article is to describe the textures of the Tolbachik sulfides and to establish links between the observed textural variability of the globules and the evolutionary history of the sulfide melt.

#### 2. Geology of the Tolbachik area

The Tolbachik volcanic massif (Central Kamchatka, Klyuchevskoy group of volcanoes, Russia) is a complex stratovolcano composed of two cones, Ostry ("Sharp") Tolbachik and Plosky ("Flat") Tolbachik, where the latter is active. Two adjacent rift zones comprised of >170 monogenetic scoria cones stretch in NE and SSW directions from the main volcano (Fig. 1, Supplementary Fig. S1). The volcano lavas possess a compositional range from high-magnesian basalts (49–51 wt% SiO<sub>2</sub>, 8–12 wt% MgO, 10–14 wt% Al<sub>2</sub>O<sub>3</sub>) to high-alumina basalts (50–52 wt% SiO<sub>2</sub>, 4–5 wt% MgO, 17–18 wt% Al<sub>2</sub>O<sub>3</sub>) and basaltic trachyandesites (52–55 wt% SiO<sub>2</sub>, 3–4 wt% MgO, and up to 7 wt% Na<sub>2</sub>O + K<sub>2</sub>O) (Fig. 1, Supplementary Fig. S2a). In terms of K<sub>2</sub>O contents, medium-K and high-K lava series can be easily distinguished (Supplementary Fig. S2b). Detailed descriptions of Tolbachik geology and recent eruptive history are provided in Belousov et al. (2015) and Churikova et al. (2015 and references therein).

All studied sulfide globules were observed in olivine phenocrysts from the 1941 eruptive cone (55.79494°N, 160.33199°E, 2105 m asl; Supplementary Figs. S1, S3a), and from the pre-historic Mt. 1004 cone (55,67,538° N, 160,23,663° E, 1025 m asl). These cones are composed of high-Mg, high-K basalts, which contain 2–3 vol% olivine phenocrysts (the 1941 eruption cone) or 10–12 vol% olivine + clinopyroxene phenocrysts (Mt. 1004 cone). The difference in phenocryst abundance is reflected in the bulk-rock composition, where the Mt. 1004 basalt is more Mg-rich (11.5 wt% MgO, compared to 8.9 wt% MgO in the 1941 basalt; Supplementary Table S2). The groundmass of both rocks is composed of olivine, clinopyroxene, plagioclase, Ti-magnetite and interstitial glass. Samples from the 1941 cone and from Mt. 1004 are enriched by a factor of two in lithophile trace elements relative to N-MORB (Churikova et al., 2015; Portnyagin et al., 2015). Olivine phenocrysts have high magnesian numbers ( $Fo_{80-92}$ ) and contain abundant melt inclusions and lesser amounts of sulfide globules.

The Tolbachik basalt shows no evidence of assimilated carbon or massive magnetite crystallization (Kamenetsky et al., 2017). Sulfide segregation was likely caused by slightly more reduced silicate melt (QFM = +1 - +1.5) and anomalously high sulfur contents in some batches of Tolbachik magma (4000–11,500 ppm was measured in some olivine-hosted melt inclusions; Kamenetsky et al., 2017; Zelenski et al., 2018). Sulfide droplets segregated from the silicate melt under P-T conditions characteristic middle crust conditions (1200 °C and 5–6 kbar; Kamenetsky et al., 2017). The formation of sulfides occurred locally and did not affect the bulk of the magmatic reservoir.

#### 3. Sampling and analytical methods

Individual olivine grains, bulk scoria samples (~30 kg) and bulk lava samples (~60 kg) were collected within the vicinity of the 1941 cone. A bulk sample of basaltic spatter (~20 kg) served as a source for olivine grains from the prehistoric Mt. 1004 cone (Supplementary Table S1). Under laboratory conditions, bulk samples were crushed to <3 mm and sieved, and a fraction containing mostly olivine, pyroxene and spinel phenocrysts was gravitationally separated by heavy liquid (tetrabromoethane,  $\rho = 2.97$ ). Olivine grains immersed in isopropanol were examined under binocular microscope. >300 olivine grains with sulfide globules were handpicked and mounted in 6-mm-diameter epoxy resin mounts. Each grain was placed on a separate mount and polished to a level slightly above the midsection of a sulfide globule, thereby allowing maximum exposure of sulfide globules. Each mount was studied under optical and electron microscope (see below).

An additional 60 olivine grains with sulfide globules were homogenized by heating at 1200 °C at 1 bar for 5 min in an open platinum ampoule (3 mm OD) filled with silicon carbide + diamond powder (i.e. to ensure reduced conditions) to determine unbiased compositions of sulfide melts and exclude random variability caused by exposure of different phases. The ampoule was quenched in water at 615 °C/s and the cooling rate was controlled by a thermocouple type K inserted into the Pt ampoule. A sketch of the heating and quenching apparatus is shown in Supplementary Fig. S4. Reheated and quenched (homogenized) olivine grains were mounted and polished as described above. Homogenized globules were studied similarly to natural samples. Some olivine grains were heated and quenched in a 5-mm-OD platinum ampoule that provided a cooling rate 220 °C/s. One experiment was done using a piston cylinder apparatus at 1400°C and 7 kbar with a maximum cooling rate of ~80 °C/s.

All sulfide globules were first examined and photographed in reflected light (Nikon Eclipse LV100N-POL Trinocular Microscope) and then carbon-coated and examined under an electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS; Vega Tescan II XMU, Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Russia; Hitachi SU-70, Central Scientific Laboratory, University of Tasmania, Hobart). An accelerating voltage of 15–20 kV, a probe current of 300–400 pA, a beam diameter of 100– 200 nm (spot analyses) or a rasterized beam (the whole area of a globule) were applied. The compositions of naturally quenched sulfides (visually homogeneous or fine-grained) from individual olivine grains were measured by a rastered beam spanning the entire exposed area. Given the fine-grained texture of most globules, the rasterized beam provided values close to the average volume composition, even for multiphase globules (Czamanske and Moore, 1977; Francis, 1990; Zelenski et al., 2018). If a globule had a clearly visible coarse texture, no area measurements were performed since the average measured composition depends on the random ratios of different phases on the exposed surface. Instead, the compositions of individual phases were measured. The following standards were used for calibration (Vega Tescan only):



Fig. 1. Simplified geological map of Tolbachik volcanic massif showing monogenetic cones, lava fields and rock compositions. Modified after Churikova et al. (2015).

Na – albite, Mg – MgO, Al – Al<sub>2</sub>O<sub>3</sub>, Si – SiO<sub>2</sub>, S – FeS<sub>2</sub>, K – orthoclase, Ca – wollastonite, Fe – Fe metal, Ni – Ni metal, and Cu – Cu metal.

Optical microscopy can provide distinguish natural colors with a resolution equal to or exceeding the resolution of the corresponding SEM-BSE image (Supplementary Materials: "Comparison of SEM and optical imaging of sulfides"). In addition, some base metal sulfides (BMS) have indistinguishable colors in BSE but are clearly distinguished in reflected light. The best approach for studying BMS was a preliminary study and photography using an optical microscope, followed by investigation using electron microscope. Spot beam analyses do not guarantee an accurate analysis of a sulfide grain enclosed in another sulfide due to X-ray fluorescence of the neighboring phase (Friel, 1994), even if the beam diameter is comparatively smaller than the observed grain sizes. Increases in the size of the X-ray excitation region is coupled with accelerating voltage and decreases with an increase in the atomic number of the analyzed element and/or the specimen density (Anderson and Hasler, 1966; Duncumb and Shields, 1963); the two latter parameters are obviously interconnected. Anderson and Hasler (1966) published a formula for estimating the spatial resolution in EDS analysis, which is convenient from a practical point of view:  $R = 0.064 \cdot (Ea^{1.68} - Ec^{1.68})/\rho$ , where R = spatial resolution in µm, Ea = accelerating voltage in keV, Ec = critical excitation energy in keV and  $\rho =$  specimen density in g/cm<sup>3</sup>. In the case of sulfides containing both light and heavy elements, the X-ray excitation region is on the order of 1.5 µm for Fe, Ni and Cu and reaches 3 µm for sulfur. For optimal results, an individual sulfide phase should be larger than 5 µm, which is comparable with small sulfide globules.

Several dozen sulfide globules were extracted from olivine crystals by complete dissolution of the host grain in warm (~60 °C) 48% HF. In such an environment, sulfide experiences moderate surficial etching from fractions of a µm to several µm, while a 1-mm olivine crystal dissolves within 15 min and produces MgF<sub>2</sub>. After the extraction, the phase compositions of the sulfide globules were studied by X-ray diffraction using a 57.3 mm Debue-Scherrer camera. The following conditions were applied: Fe K-alpha radiation, an acceleration voltage of 50 kV, a cathode current of 14 mA, a rotating sample around a single axis, and an exposure time of 12 h. An entire sulfide globule was mounted on the tip of a glass needle, but not pulverized. This technique allowed us to estimate the degree of crystallinity of the globules relative to their phase compositions. The developed X-ray film was scanned and processed using specially designed software. To compare phase and chemical compositions, the X-ray-studied globules were placed in epoxy resin mounts, polished, and analyzed by SEM-EDS.

#### 4. Results

Sulfide melt inclusions are hosted in primitive olivine phenocrysts (80-92 mol% Fo for the 1941 eruptive cone and 80-90 mol% Fo for Mt. 1004 basalts). Sulfide globules occur individually or form clusters or even swarms composed of hundreds and thousands of individual sulfide globules. However, phenocrysts with sulfides are rare and their frequency does not exceed 0.6% in the 1941 basalt and <0.2% of the olivine grains from the Mt. 1004 cone (Zelenski et al., 2018). The globules are enclosed in olivine phenocrysts and sometimes in larger silicate melt inclusions (Fig. 2). Sulfide globules in silicate melt inclusions usually have perfectly spherical shapes, unless they are in contact with an inclusion boundary or a gas (contraction) bubble (Fig. 2b). Individual sulfide globules enclosed in olivine often have elliptical shape with a long axis parallel to the crystallographic axis of the host crystal (Fig. 2a). The size of the globules ranges from submicron to 250  $\mu m$  , with the majority of sizes ranging between 10 and 100 µm. Sulfide globules from Tolbachik are characterized by chemical, phase and textural diversity.

## 4.1. Sulfide globules: chemical composition

Bulk compositions of naturally quenched and reheated/quenched sulfides and point analyses of individual phases of Tolbachik sulfides in terms of Fe-Ni-Cu, Fe-Cu-S and Fe-Ni-S are plotted in Fig. 3a(a complete list of analytical data points are displayed in Supplementary Tables S3–S6). The minimum, average and maximum atomic concentrations of elements and metal to sulfur (Me:S) ratios in sulfide globules normalized to 100% sulfide are given in Table 1. For comparison, the same characteristics for MORB sulfides are also shown (Czamanske and Moore, 1977; Francis, 1990; Patten et al., 2012).

The compositional diversity of the Tolbachik sulfides was previously discussed in Zelenski et al. (2017, 2018) and Kamenetsky et al. (2017). Sulfides show significant variability in bulk metal contents (globules measured as a whole) as well as in Me:S and S:O ratios. Zelenski et al. (2018) and Kamenetsky et al. (2017) attributed this variability to different Ni:Cu:Fe ratios in the magma as well as to variable  $fO_2$ , which in turn affects Ni partitioning in olivine (Barnes et al., 2013; Brenan, 2003; Doyle and Naldrett, 1987).

The variations in element contents in the Tolbachik sulfides are similar to those in MORB sulfides, both in terms of segregated mineral phases and bulk sulfide globules (Czamanske and Moore (1977), although variations of the Tolbachik sulfides are somewhat higher in absolute values. Chalcophile metals (Ni and Cu) show the greatest variability. In particular, the bulk-copper content in sulfides varies from 0 to 36 at.%. The least variability is observed for sulfur content ( $50.6 \pm 2.8$  at.%,  $1\sigma$ ). The variabilities of naturally quenched sulfide globules and reheated and quenched sulfide globules are similar; where the compositions plot along the whole Fe–0.5 Ni–0.5 Cu triangle (Fig. 3a). The Cu/Ni ratio varies widely, but is on average close to unity for the Tolbachik sulfides.





Fig. 2. Optical (a) reflected light and (b) oblique light microscope images of sulfide globules in Tolbachik olivine grains. (a) Olivine crystal with sulfide globules. A large melt inclusion in the center contains two spherical globules surrounded by silicate glass. These two globules, as well as two yellow globules in the upper left corner of the crystal, are exposed on the polished surface. Other gray globules are located inside the crystal and enclosed directly in olivine. Small crystals of chromite are present on the periphery of the crystal as well as some amount of groundmass. (b) A large silicate melt inclusion with a fluid bubble and four entrapped sulfide globules. Three of them are exposed at the polished surface and have almost pure pyrrhotite composition ( $\Sigma$  [CuS + NiS] < 4%). The surfaces of sulfide globules divide they are in contact with olivine or a bubble. Other sulfide globules included in olivine outside this melt inclusion are also visible.

#### 4.2. Sulfide globules: mineralogy

Arc-related sulfides from the Tolbachik volcano have diverse phase compositions, which is common for continental sulfide ores. Point analyses (Supplementary Table S7) of individual sulfide phases are scattered, but also form dense clusters that can be tentatively assigned to ideal mineral compositions CuFeS<sub>2</sub> and CuFe<sub>2</sub>S<sub>3</sub> or represent almost the whole FeS–NiS side of the FeS–NiS–CuS ternary diagram (Fig. 3b). A limited number of analyses correspond to copper-rich bornite (Cu<sub>5</sub>FeS<sub>4</sub>) and chalcocite (Cu<sub>2</sub>S).

On the ternary plot Fe–Cu–S (Fig. 4a; only sulfides with <3 at.% Ni are shown), the majority of analyses fall within the field of ISS (intermediate solid solution, high-temperature Cu-rich sulfide). The ISS field also encompasses the compositions of several of the most common low-temperature copper sulfides – chalcopyrite (CuFeS<sub>2</sub>), cubanite CuFe<sub>2</sub>S<sub>3</sub>, talnakhite (Cu<sub>9</sub>Fe<sub>8</sub>S<sub>16</sub>), haycockite (Cu<sub>4</sub>Fe<sub>5</sub>S<sub>8</sub>) and mooihoekite (Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub>). There is also a visible trend from ISS compositions to more copper-rich bornite. ISS cannot be distinguished from the low-temperature copper sulfides based only on element contents



**Fig. 3.** Compositions of Tolbachik sulfides in terms of Fe-Ni-Cu contents. (a) Bulk compositions of naturally quenched sulfide globules and reheated and quenched sulfide globules (Tables S3–S6) show significant variability in the Fe–0.5Ni–0.5Cu triangle. (b) Point analyses of individual phases (Table S7). The ideal compositions of sulfide minerals and compositions of solid solutions MSS, high-temperature pentlandite and low-temperature pentlandite are shown for comparison. MSS – monosulfide solid solution, ISS – intermediate solid solution, bnSS – bornite solid solution, bn – bornite, cb – cubanite, cc – chalcocite, pn – pentlandite, hpn – high pentlandite, mil – millerite, po – pyrrhotite. Compare with Fig. 5a and b in Czamanske and Moore (1977).

(Cabri, 1973). Instead, other criteria such as X-ray diffraction (XRD) data and morphology should be considered. Based on chemical composition, XRD analyses and individual phase morphology and color, we regard large isotropic yellow grains as ISS while lamellar textures (see below) are interpreted as alternate lamellae of cubanite (beige) and chalcopyrite (yellow).

Cu-poor compositions (<3 at.% Cu) likely correspond to pyrrhotite, high-temperature Ni-rich sulfide MSS (monosulfide solid solution) and pentlandite. Unlike ISS, monosulfide solid solution can be distinguished from pentlandite due to its noticeably higher sulfur content (Fig. 4b). It appears that all Ni-rich phases with <50 mol% NiS are MSS, whereas Ni-rich phases with >50 mol% NiS belong to low pentlandite or high pentlandite (e.g., Kitakaze et al., 2011). The most Ni-rich phases (up to 80 mol% NiS) formed as a result of exsolution in the solid state (Kelly and Vaughan, 1983), as shown by their "flame-shaped" morphology, which is interpreted as low-temperature pentlandite. No millerite (pure NiS) was observed. The presence of >3–4 wt% Ni in copper-rich phases and >2–3 wt% of Cu in nickel-rich phases was detected in a number of analyses, which most likely arose from analyses of micron-sized grains smaller than the X-ray excitation volume.

## Table 1

Summary of concentrations of elements (at. %) in sulfide globules from Tolbachik. Statistics for MORB sulfides presented according to Czamanske and Moore (1977) and Patten et al. (2012).

	S	Fe	Ni	Cu	Cu:Ni	Me:S
Tolbachik Average Min Max	50.56 20.87 55.83	35.06 19.42 67.77	9.77 0.37 22.54	4.61 0.00 35.76	1.17 0.00 17.00	0.99 0.79 3.79
MORB Average Min Max	50.45 47.40 64.11	37.45 24.71 46.66	5.49 0.00 13.36	6.61 0.00 25.11	2.74 0.01 46.50	1.00 0.56 1.10

X-ray diffraction analyses of the Tolbachik sulfides has confirmed the presence of low-temperature sulfide phases pyrrhotite  $Fe_{(1-x)}S$ , pentlandite (Fe,Ni)<sub>9</sub>S<sub>8</sub>, chalcopyrite CuFeS<sub>2</sub> and cubanite CuFe<sub>2</sub>S<sub>3</sub>. Low-temperature phases in sulfide globules that experienced very rapid cooling indicate that the kinetics of phase transformations in natural micron-sized Fe-Ni-Cu sulfide globules may differ from those in coarse-grained natural sulfides or in laboratory experiments (e.g., Kelly and Vaughan, 1983).

# 4.3. Sulfide globules: The variety of textures

Textures of the Tolbachik sulfides have been classified according to their inferred origin. We distinguished textures according to styles of crystallization, dissolution and oxidation. Deformed and porous textures were classified separately. Each class of textures contains subdivisions. A summary of textural diversity is displayed in Table 2 and examples of each textural class are shown in Figs. 5–12 and referred to in Table 2.

#### 4.3.1. Textures related to crystallization

**Homogeneous textures** have no visible features under optical or electron microscope (Figs. 2b, 5). These textures are characteristic of globules where the Ni:Cu ratio significantly deviates from unity (Ni: Cu >> 1 or Ni:Cu << 1). Globules composed mainly of pyrrhotite (Fig. 2b) also form homogeneous textures. XRD reveals that visually homogeneous globules are composed of a few randomly oriented crystals with identical compositions and indistinguishable boundaries. The homogeneity of such globules is determined by the fact that the sulfide melt crystallized into a single phase (pyrrhotite, chalcopyrite, MSS or pentlandite) and no further changes (decomposition of solid solution) occurred.

**Fine-grained textures** are composed of small (1–10 µm) Ni-rich grains, which are dispersed throughout a Cu-rich matrix (Fig. 6; Supplementary Fig. S5). Most of Ni-rich grains have Me:S ratio characteristic of



**Fig. 4.** Compositions of Tolbachik sulfides in terms of Fe-Cu-S and Fe-Ni-S contents measured from point analyses of individual phases. The ideal compositions of sulfide minerals and compositions of solid solutions MSS, ISS, bnSS, Ni<sub>3</sub>S<sub>2</sub>-SS, high pentlandite and low pentlandite are shown for comparison. (a) Cu-rich phases with low-Ni content of  $\leq 3$  wt% (Table S7). (b) Ni-rich phases with low-Cu content of  $\leq 3$  wt% (Table S7). hay – haycockite, moo – mooihoekite, tal – talnakhite; for other abbreviations, see Fig. 3.

MSS (see Section 4.2.) and homogeneous Cu-rich matrix, which is interpreted as quenched ISS. Ni-rich grains can be distributed randomly, but often they form clearly visible arrays (Fig. 6a–b; Supplementary Fig. S5), vermiculate textures (Fig. 6c–d) or rarely parallel lamellae (Fig. 6e– f). Fine-grained textures supposedly appear due to high rates of cooling. Such textures have been recorded at cooling rates of >600 °C/s in experimentally reheated and quenched sulfides and similar fine-grained globules occur inside loose ablated olivine grains. Our observations show that fine-grained textures are found in sulfide globules with bulk Ni:Cu ratios ranging from ~1:3 to ~3:1. At higher or lower nickelcopper ratios, globules with homogeneous or coarse-grained textures are observed.

**Coarse-grained textures** include "patchy", "zoned" and "halved" varieties, according to their appearance. Patchy textures consist of a few relatively large grains of Ni-rich sulfide within a Cu-rich matrix (Fig. 7a). In the rare case that only one grain of MSS is present, this texture degenerates into zoned (Fig. 7c) or halved (Fig. 7d) textures, depending only on the shape of the Ni-rich grains (which solidifies first as a high-temperature phase). Zoned textures were previously described earlier

#### Table 2

Textural classification of sulfide globules.

Texture types	Sub-texture type	Reference figure
Textures related to the crystallization of sulfide melts	Homogeneous textures Fine-grained textures: crystallization or decomposition?	Figs. 5, 2b Fig. 6
	Coarse-grained patched textures Coarse-grained zoned textures Coarse-grained halved textures	Fig. 7a Fig. 7c Fig. 7d
Lamellar textures: breakdown of ISS	C	Fig. 7a, b, e, f
Crystallization of early magnetite		Fig. 7b, e
Porous textures: exsolution of fluid from sulfide melt?		Figs. 8, S6
Geopetal (gravitationally oriented) structures		Figs. 5a, 7b. 8a
Thin sulfide foils: decompression or thermal shock fracturing		Fig. 9
Sulfides deformed by growing crystals		Fig. 10
Sulfides deformed by fluid bubbles		Figs. 11, 2b
Textures related to oxidation and		Fig. 12,
dissolution		Fig. 7f

for MORB sulfides (Patten et al., 2012). Halved textures were not observed in MORB, and only several globules with this texture were found in Tolbachik. Similar textures are known for large layered sulfide droplets and are believed to form due to gravitational differentiation (Barnes et al., 2017; Prichard et al., 2004). However, such layered droplets have an approximately flat boundary between the Ni-rich and Curich phases (horizontal at the time of solidification), whereas all halved globules from Tolbachik exhibit irregular boundaries.

**Lamellar textures: breakdown of ISS?** Lamellar textures (Fig. 7ab, e–f) are present where a Cu-rich sulfide melt underwent relatively slow cooling. In this case, ISS crystallizes from the sulfide melt (Barton, 1973; Cabri, 1973; Ebel and Naldrett, 1996; Fleet and Pan, 1994) and subsequently decomposes into chalcopyrite and cubanite (e.g., Schwartz, 1942, and references therein). The presence of both minerals is confirmed by X-ray phase analysis. A small amount of nickel contained in ISS is released during the ISS breakdown, which is evidenced by the presence of small rounded grains of pentlandite scattered within the lamellar matrix (Fig. 7e). The nickel-rich hightemperature phase (MSS) decomposes under slow cooling into low pentlandite and Ni-poor MSS. These two phases have almost the same color in reflected light, but can be distinguished in a BSE image (Supplementary Fig. S8). No regular exsolution textures for Ni-rich MSS were observed.

**Crystallization of early magnetite** Small grains of primary low-Ti magnetite are common in Tolbachik sulfides. They are scattered on the surface of polished sulfide globules or confined to the globule edges (Fig. 7b, e). Magnetite occurs in globules with patchy, zoned or lamellar textures (i.e. slowly cooled), which were not observed in homogeneous or fine-grained (rapidly quenched) globules. However, some sulfide globules without visible magnetite (mainly with fine-grained textures) have high contents of oxygen, thus suggesting that magnetite was not exsolved because of kinetic reasons. Magnetite grains are typically associated with minerals of later crystallization, such as ICC matrix or lamellar chalcopyrite-cubanite intergrowths, which appear to be the result of ICC breakdown. Magnetite inclusions in early MSS are rare. Most magnetite crystals have roundish or irregular shapes with common sizes of  $1-2 \mu$ m, and rarely exceeding 5  $\mu$ m. The modal abundance of low-Ti magnetite can be up to 2-3 vol%.

MORB sulfides show similar appearance of magnetite in only coarsegrained sulfides (Czamanske and Moore, 1977; Patten et al., 2012). Low-Ti magnetite in sulfides is explained by the presence of dissolved oxygen in the sulfide melt, or a (Fe,Ni,Cu)-S-O melt (Naldrett, 1969). Early (syngenetic) magnetite crystallizing from Fe-S-O melt should be distinguished from magnetite in oxidized sulfide globules.



Fig. 5. Reflected light microscope images of sulfide globules with homogeneous texture. (a) Visually homogeneous sulfide globule composed of MSS (84% FeS, 16% NiS) sitting inside a cavity formed by a large fluid bubble. (b) Ni-rich MSS (64% FeS, 36% NiS) included in olivine.

## 4.3.2. Textures related to exsolution of fluid from sulfide melt

Porous sulfides Many globules contain one or more large pores (Fig. 8a) or numerous smaller pores (Fig. 8b, e). Porous sulfides are very common, whereas the pore-free Tolbachik sulfides are rare and only occur in globules with homogeneous crystallization textures. Pores are usually larger in the center of a porous globule than near the edges. Some pores have the shape of negative crystals (Fig. 8c). Pores are usually randomly scattered and rarely form reticulated patterns (Fig. 8e), especially in experimentally reheated and quenched globules. Similar reticulated porous patterns were observed in experimental sulfide globules equilibrated with H<sub>2</sub>O- and S-bearing fluids at 200 MPa and 1150 °C (Fig. 8f; Botcharnikov et al., 2013). If fluid escapes from a globule through tiny channels (Fig. 8b) and reaches the sulfide-silicate interface, it can form bubbles that adhere to the globule (Fig. 8d), which sometimes cover the entire surface of the latter. We suggest that the pores inside sulfide globules are bubbles of fluid exsolved during sulfide melt solidification. Small bubbles or reticular bubbles likely form during rapid quenching, while large bubbles require slower cooling.

### 4.3.3. Textures related to sulfide deformation

Geopetal (gravitationally oriented) structures The morphology of sulfide globules and their relationship with their surrounding area suggests that some of the observed structures may have formed under gravitational influence. These structures occur as flat sulfide/bubble interfaces (Fig. 5a) and sulfide/silicate interfaces (Fig. 7b). Groups of small fluid bubbles attached to sulfide globules commonly appear only from one side (Fig. 8d). The inclusion shown in Fig. 8a can also be considered as a layered structure, with increasing material density from top to bottom (silicate material - porous sulfide - massive sulfide). Large sulfide globules stratified due to gravity are a well-documented phenomenon (e.g., Barnes et al., 2017; Prichard et al., 2004, and references therein). However, in the case of small (<100 µm) globules, interfacial tension plays a much greater role because of the larger surface to volume ratio. This tension retains the round shape of the globules and prevents the appearance of flat boundaries between sulfides and silicates. Most of the Tolbachik sulfide globules surrounded by silicate melt have a round shape due to significant interfacial tension. Only some slowly cooled globules acquired a flat sulfide-silicate interface, characteristic of gravitational stratification. The cause for such selective differentiation remains unclear.

Thin sulfide foils and planar swarms Some olivine crystals contain solidified melt in the form of thin films resembling foil, which infills tiny cracks. These can be considered as a variety of deformed sulfides. Such "leaflets of foil" have micron to sub-micron thickness, but all other properties (phase and chemical compositions, patched, zoned and lamellar textures) are the same as those of massive sulfide globules (Fig. 9a, b). Some healed cracks contain planar swarms of small sulfide spherules (Fig. 9c) or form complex planar patterns of sulfide resembling hieroglyphics (Fig. 9d). The existence of healed cracks suggests that rupture of a crystal, followed by healing of cracks with sulfide melt occurred within a plumbing system.

Deformations caused by growth of surrounding crystals If a small  $(\leq 150 \,\mu\text{m})$  sulfide drop solidifies rapidly within a silicate melt, it usually retains a spherical shape (Figs. 2a, 6, 7). In the cases of direct contact of a sulfide globule and olivine, crystals inside a silicate melt inclusion or contraction bubble causes deformation of the originally spherical globule. Sulfide globules enclosed directly in olivine acquire an elongated ellipsoid shape that is orientated along the crystallographic axis of the host crystal (Fig. 2a). More significant deformation of the spherical shape occurs if a sulfide globule undergoes slow cooling inside a large silicate melt inclusion, which crystallizes into an aggregate of silicate minerals (pyroxenes and amphiboles). Here, the sulfide globule infills the interstitial space between growing silicate crystals (Fig. 10). The last portions of unsolidified Cu-rich sulfide melt are pushed out by growing pyroxene and amphibole crystals into the remaining space between the crystals. Fig. 10 also illustrates that some pyroxene crystals grew simultaneously with or after the solidification of MSS.

**Deformations caused by adjacent fluid bubbles** Sulfide droplets can be also deformed along the contacts with fluid bubbles. In this case, the surface of the sulfide-fluid interface concaves into the sulfide (Fig. 11, see also Fig. 2b). This relationship indicates a higher surface energy for the high-density fluid in comparison to the sulfide melt. Fluid bubbles can be in direct contact with sulfide (Fig. 11a, c, d), or can be separated by a thin silicate layer (Fig. 11b). Some small bubbles (Fig. 11c) do not form concave interfaces, thereby suggesting that they formed after the sulfide globule solidified. There are also examples where the sulfide is sandwiched between two bubbles and has a biconcave surface (Fig. 11d). Implications for such fluid-sulfide interaction are detailed below.

### 4.3.4. Textures related to late modifications of sulfides

**Textures related to dissolution** The majority of Tolbachik sulfide globules occur as inclusions in olivine, whereas the basaltic groundmass does not contain any sulfides. This suggests that the nucleation and growth of sulfides occurred at depth in the Tolbachik plumbing system (Kamenetsky et al., 2017). All sulfide melt droplets within magma were likely oxidized and dissolved during magma ascent and eruption, unless they were entrapped in phenocrysts. The presence of sulfide globules inside silicate melt embayments and within partially oxidized melt inclusions in olivine grains allow us to constrain the oxidation and dissolution of sulfide melt droplets during magma ascent to the surface and cooling under subaerial conditions.

As shown in Fig. 12a–c, sulfide globules may gradually dissolve in the magma beginning from the globule surface and become progressively replaced by a silicate melt. Dissolution occurs unevenly, where



**Fig. 6.** Back-scatter electron (BSE) images (left) of fine-grained textures of sulfides. (a–b) Parallel linear chains of MSS grains impregnated in ISS matrix. (c–d) Two sulfide globules of different sizes located close to each other inside a complex inclusion in olivine containing sulfide, silicates and a bubble. Similar fine-grained and vermiculated textures of both globules in (c–d) are visible. (e–f) Fine-grained lamellar symplectite-like texture.

it first forms crenulated boundaries (Fig. 12a) with the silicate melt embayments, before progressively extending into the internal parts of the globule (Fig. 12b; see also Supplementary Fig. S5c). No changes in the composition of partially dissolved sulfide were noted, even in the immediate vicinity of newly formed silicate embayments. This means that the sulfide undergoes congruent dissolution without significant oxidation or selective leaching of elements.

The textures related to sulfide dissolution can also occur among MORB sulfides, but were previously unrecognized. This texture is evident in Fig. 1b and c in Czamanske and Moore (1977). These authors attributed these textures to fractional crystallization of sulfide liquid in a viscous silicate melt. Although this process is not impossible, we believe that partial congruent dissolution of a globule is more feasible. In particular, such dissolution of the Tolbachik sulfide globules at the side facing the exit from the melt embayment is evident in Fig. 12a and c.

Sulfides dissolve in the magma when pressure decreases (e.g., Fortin et al., 2015; Liu et al., 2007; Mavrogenes and O'Neill, 1999). Virtually all studies of sulfide dissolution with decreasing pressure and the oxidation of sulfide to sulfate have been experimentally reproduced (e.g., Fortin et al., 2015; Liu et al., 2007; Matjuschkin et al., 2016; Mavrogenes and O'Neill, 1999, and references therein). The dissolution of sulfide at the surface results in the enrichment of the silicate melt in Cu and Ni, as well as in all minor elements present in sulfides, including Au and platinum group elements (PGEs). It is thought that the transfer of metals by flotation of sulfide at the release of chalcophile elements can



**Fig. 7.** Reflected light microscope images of coarse-grained, lamellar textures and magnetite. (a) Patched texture with lamellar matrix of chalcopyrite and cubanite; (b) Lamellar texture made of alternating lamellae of chalcopyrite and cubanite with approximately flat interface between the sulfide and silicate parts of the inclusion. (c) Zoned texture. (d) Halved texture. (e) Complex texture with lamellar matrix of chalcopyrite and cubanite and a large MSS-pentlandite grain (pentlandite can be better distinguished in SEM-BSE image, Supplementary Fig. S8). (f) Sulfide globule with lamellar texture, partially replaced by magnetite-hematite aggregate. MSS – monosulfide solid solution, ISS – intermediate solid solution, ol – olivine, mgt – magnetite, cr – chromite, hem – hematite.

play an important role in the formation of orthomagmatic ore deposits (e.g., Edmonds, 2015).

**Textures related to oxidation** Simultaneous with surface dissolution, or independently of it, the internal oxidation of sulfide can occur to form iron oxides. This can occur along with magma oxidation during evolution and degassing (Carmichael and Ghiorso, 1986; Mathez, 1984; Richards, 2015), or in subaerial conditions after the eruption. Based on the morphology of secondary magnetite (Fig. 12c), oxidation can take place along the boundaries of individual sulfide crystals. If both Ni-rich MSS and Cu-rich ISS are present, MSS is oxidized first, presumably by the reaction:  $3FeS + 5O_2 \Rightarrow Fe_3O_4 + 3SO_2$ . Under highly oxidizing conditions hematite  $Fe_2O_3$  (Figs. 7f, 12d) can appear instead of magnetite. Such hematite pseudomorphs, which can completely substitute sulfide, are observed in the basaltic spatter from Mt. 1004, especially in the oxidized basalt with red tint. No analyses of secondary magnetite and hematite revealed any significant residue of Ni and Cu. The exact

mechanism of escape of these elements from oxidized sulfide globules sealed within olivine remains unclear, but invisible fractures could be involved (Nadeau et al., 2010). Selective Ni and Cu leaching from Fe-Ni-Cu sulfide ores under oxidizing conditions is widely used in industry (e.g., Xu et al., 2017, and references therein). Some studies assert that selective leaching of sulfides can significantly enrich hydrothermal fluids in chalcophile elements, thus promoting the formation of porphyry and epithermal ore deposits (Nadeau et al., 2010).

## 5. Discussion: origin of textural diversity

The crystallization parameters and evolutionary history of the sulfide melts is preserved in the textures of sulfides (Czamanske and Moore, 1977; Patten et al., 2012). Sulfide textures have been extensively studied for >100 years in disseminated and massive sulfide ores due to their economic significance (e.g., Dresser, 1917; Howe, 1914; see also



**Fig. 8.** Secondary electron (SE) SEM images (a), SEM-BSE images (b, c, e, f), transmitted light microscope image (d) and modified image (f) from Botcharnikov et al. (2013) of porous sulfides. (a) Sulfide globule with a few large pores covering ~15% of the total sulfide surface. Note a "layered" structure of the inclusion (from top to bottom): silicate glass (gl) – porous sulfide – massive sulfide. (b) Experimentally reheated and quenched sulfide globule with numerous small pores. Sizes of pores decrease toward the edge of the globule; narrow effluent channels connecting pores and the globule surface are visible. (c) Close-up view of pores with negative crystal forms and small sulfide spherules inside. (d) Group of sulfide globules surrounded by silicate glass, included in olivine. Small fluid bubbles are attached to the upper surfaces of the globules. (e) Reticulate pattern of micron- and submicron-sized pores within sulfide matrix, naturally quenched sulfide. (f) Reticulate pattern of pores and effluent channels in an experimental sulfide globule saturated with water at 4 kbar.

an extensive literature review in Ridge, 1958). During cooling, sulfide melt solidifies into high-temperature phases, which can undergo further polymorphic modifications or solid solution breakdown, resulting in different textures (e.g., Ballhaus et al., 2001; Brenan et al., 2008; Cabri, 1973; Durazzo and Taylor, 1982; Naldrett et al., 1967). The cooling rate affects the nucleation density and therefore the crystal sizes of sulfide minerals. The quenching of high-temperature modifications of sulfides and the decomposition of solid solutions also depends on the cooling rate of the solidified sulfide. Other factors influencing the sulfide texture are the base metal contents (which produce different phases), P-T- $fO_2$  conditions, gravitationally induced orientation and the sizes of globules (Patten et al., 2012). The data presented in this work entails other genetic implications, such as fluid exsolution from the so-lidifying sulfide melt, and partial oxidation and dissolution of both liquid and solidified sulfide.

Our study demonstrates that the main factors responsible for sulfide textures is cooling rate and Fe:Ni:Cu:S composition, whereas the size of sulfide globules is of lesser importance. Some of the textures could form



Fig. 9. Transmitted light (a, c, d) and reflected light microscope images (b) of thin sulfide foils in cracked olivine (a, b) and planar sulfide swarms (c, d) in healed cracks. Small roundish and elongated silicate melt inclusions are visible (c, d), each with a tiny contraction bubble. sil – silicate melt inclusions, sul – sulfide.

due to the breakdown of solid solutions, whereas the "Swiss cheese" textures were formed due to fluid separation from the sulfide melt during solidification. Other specific forms of Tolbachik sulfides, such as healed cracks in olivine phenocrysts containing thin sulfide foils may indicate significant vertical movements of olivine crystals within the magma chamber. This was accompanied by a decrease in external pressure, the cracking of olivine crystals, and the subsequent healing of cracks. Deformation of sulfides under the influence of bubbles or growing silicate crystals and the propagation of sulfide melt trough thin cracks in olivine crystals provides new insights into the physical properties of natural sulfide melts, such as surface tension and wetting angles.

## 5.1. The cooling rate of olivine phenocrysts

In the 1941 basalt, high-Mg olivine ( $Fo_{80-92}$ ) occurs as phenocrysts up to 6 mm in size and includes three varieties: i) loose crystals in scoria (Supplementary Fig. S3a), ii) olivine crystals enclosed in lapilli, and iii) olivine from dense rocks (volcanic bombs or thick lava flows, Supplementary Fig. S3b). The three varieties have the same compositions, but very significantly differ in their cooling rates. The cooling rate of the erupted magma under subaerial conditions depends mainly on the mode of magma fragmentation (loose phenocrysts > fine ash >> lapilli > bombs > lava flows). The fastest cooling rate is experienced by loose



Fig. 10. Back-scatter electron (BSE) SEM image and X-ray element maps of a deformed sulfide globule surrounded by amphibole and pyroxene crystals inside a silicate melt inclusion. (a) On the MSS is the earliest phase followed by pyroxenes and amphiboles, the latest phase to crystallize is ISS. The latter is deformed by amphibole and pyroxene crystals. Appreciable amount of anhydrite occurs likely because of partial oxidation of sulfide in situ.



**Fig. 11.** Reflected light microscope image (a) and (b-d) Back-scatter electron (BSE) SEM images of sulfides deformed by fluid bubbles. (a) Deformed MSS globule in contact with a large fluid bubble and concave fluid-sulfide interface. Another round fluid bubble is located inside the sulfide. (b) Sulfide globule deformed under the influence of a fluid bubble; both are located inside a large silicate melt inclusion. The globule and the bubble are not in direct contact and a thin layer of silicate glass is visible between them. (c) Sulfide globule surrounded by several fluid bubbles. The bubble on the left affects the shape of the globule, whereas three small bubbles on the right presumably appeared after the globule solidification and do not deform the globule surface. (d) MSS globule sandwiched between two large fluid bubbles on the left and on the right, with concave fluid-sulfide interfaces. Another compound sulfide-fluid globule and a chain of smaller globules and bubbles are visible.

olivine crystals without attached melt, which was removed by air flow during atmospheric suspension. Due to high escape velocities during eruption (up to 700 m/s; Bombrun et al., 2015), such ablated crystals were cooled almost instantly due to air exposure.

The cooling rate can be measured experimentally and theoretically calculated. For example, Xu and Zhang (2002) experimentally estimated the cooling rate for 5 mm glass samples in air flows at ~300 °C/s. The cooling rate of particles of different sizes escaping hot lava and entering a colder environment can be roughly estimated based on the following considerations. The cooling rate of a solid particle is determined mainly by conductive heat transfer from its inner parts to the surface, which is roughly inversely proportional to the square of the linear size of a particle. Taking into account that the majority of loose ablated olivine grains have sizes <5 mm (sizes 1–2.5 mm crystals are the most common), we can conclude that their cooling rates exceeded 300 °C/s.

We compared naturally quenched olivine grains from the 1941 cone with crystals reheated and quenched at different rates in laboratory experiments. Both crystals experimentally quenched at ~615 °C/s (Supplementary Fig. S4) and loose ablated olivine grains from the 1941 Tolbachik cone contain glassy silicate melt inclusions and fine-grained sulfides. Crystals experimentally quenched at ~220 °C/s, and natural olivine crystals from small lapilli (2–5 cm in size) contained partially crystallized silicate melt inclusions, whereas crystals cooled down at ~80 °C/ s and natural olivine grains from volcanic bombs (>5 cm), basaltic spatter and lava flows contained fully crystallized silicate and sulfide melt inclusions. We conclude that loose Tolbachik olivine grains from the 1941 scoria cone cooled at a rate of several hundred degrees per second (minimum of 300 °C/s).

On the contrary, olivine grains from inner parts of volcanic bombs and thick lava flows cooled together with the bombs and lava on time scales from several minutes (i.e. bombs) to several hours (i.e. thick lava flows, Wallace et al., 2003). This relates to volcanic bombs and lavas from the 1941 cone and basaltic spatter from the Mt. 1004, as such spatter (volcanic bombs welded together) has properties intermediate between separate bombs and lava flows. Therefore, the whole range of cooling rates of the studied olivine grains from Tolbachik can exceed five orders of magnitude; (300 °C/s) / (10 °C/h) = ~10^5.

## 5.2. Origin of fine-grained textures: random nucleation, eutectic crystallization or breakdown of solid solutions?

Globules with fine-grained textures are common among the Tolbachik sulfides. Fine-grained textures were previously described by Patten et al. (2012) for MORB sulfides. Czamanske and Moore (1977) also noted fine-grained, "vermicular textures", but did not provide any details in their origin. There is a general consensus that the fine-grained sulfide textures resulted from spontaneous nucleation and growth of fine MSS grains from the melt, followed by quenching of the melt-grain suspension (Fleet and Pan, 1994; Patten et al., 2012, and references therein). Patten et al. (2012) argued that the nucleation parameters in sulfide globules of MORB depend on the globule size and degree of supercooling of the sulfide melt, whereas nucleation is weakly



**Fig. 12.** Reflected light microscope images (a, c) and Back-scatter electron (BSE) SEM images (b, d) – SEM BSE images of partially dissolved and oxidized sulfide globules. (a) Sulfide globule inside a melt embayment in olivine. Crenulated boundary with the silicate glass gradually turns into small embayments of silicate glass into sulfide, and more dissolution occurred on the right side closer to the exit from the embayment. (b) Partially dissolved sulfide globule with a large embayment of silicate glass inside a silicate melt inclusion. (c) Sulfide globule inside a melt embayment in olivine, with partially dissolved side exposed to the exit from the embayment. The development of secondary magnetite (gray grains) occurs predominantly in MSS. (d) Replacement of sulfide with secondary magnetite and hematite. ol – olivine, emb – embayment, gl-glass, mgt – magnetite, hem – hematite.

dependent on the sulfide melt composition and cooling rate. The random nucleation of MSS from the sulfide melt seems obvious for such conditions, but cannot explain arrays and patterns formed by Ni-rich grains within a Cu-rich matrix, which we observed in many fine-grained sulfide globules from Tolbachik (Fig. 6, Supplementary Fig. S5).

Such arrays and patterns appear as parallel linear chains (Fig. 6a), lamellar and reticular patterns (Fig. 6c) or vermicular textures (Fig. 6b). It is expected that random nucleation of MSS provides a random texture (unless some process causes ordering of random MSS grains within ISS melt). On the contrary, the patterns similar to those observed are characteristic for decomposition of solid solutions, e.g., symplectites (e.g., Ogasawara et al., 1998; Shelley, 1970). The main mechanism considered for the formation of such textures is cellular segregation reactions in solids (Cahn, 1959). Symplectite-like patterns were found in virtually every fine-grained globule of Tolbachik sulfide, which may indicate significant development of the solid solution decomposition process during the solidification and cooling of such globules.

Another possible explanation for the observed ordered textures could be directional solidification of the eutectic melt (e.g., Akamatsu and Plapp, 2016; Asta et al., 2009; Flemings, 1974, and references therein). Several types of crystallization that can generate regular micro-textural patterns were reviewed by Asta et al. (2009). In addition to simultaneous crystallization of two phases from the eutectic melt, peritectic crystallization, dendritic solidification, effects of convection on microstructure formation, solidification at a high volume fraction of solid and solid-state transformations have been proposed. In our opinion, none of the above listed processes, except solid-state transformations (solid solution breakdown) can explain the patterns observed in the Tolbachik sulfides. For example, convection cannot be expected for micron-sized droplets, which quenched within milliseconds. No eutectic or peritectic relationships are known for MSS and ISS crystallization. In contrast, many works describe fractional crystallization of a sulfide melt, where MSS is the first high-temperature phase to solidify between 1100 and 1000°C, concentrating a Cu-rich residual melt that later forms ISS and other Cu-rich minerals (e.g., Ebel and Naldrett, 1996, 1997).

If there is a breakdown of a solid solution, then the sulfide liquid should solidify into an homogeneous solid phase (vitreous sulfide?), which would likely be unstable and decompose immediately into Nirich and Cu-rich phases, producing the observed texture. The rapid cooling at a rate of hundreds of degrees per second promotes this process, but renders it impossible directly observe this intermediate unstable homogeneous phase, as it probably exists for only a small fraction of a second.

Our study of >300 sulfide globules shows that the presence or absence of fine-grained textures, as well as the spatial density of Ni-rich grains correlates weakly with the size of the globule. An example is shown in Fig. 6c, where two sulfide globules differing in size by approximately 5–6 times are present in the same silicate melt inclusion. Both globules have the same fine-grained texture. In contrast, textures are dependent on the globule composition (Fe:Ni:Cu ratio), where sulfide melts with pyrrhotite or pentlandite compositions solidify into homogeneous globules (Figs. 2b, 5). In contrast, melts simultaneously containing elevated Ni and Cu abundances always form fine-grained or coarse-grained textures.

## 5.3. Fluid exsolution from sulfide melt

Both large and small pores are very common in the Tolbachik sulfides. Their presence along with their association with small channels leading from the center of the globule to its surface together with fluid bubbles attached to the globule suggests fluid exsolution during crystallization of the sulfide melt. The solubility of water in sulfide melts is not fully understood, although there is some evidence to support the high solubility of water in sulfide liquids. For example, the presence of hydrothermally altered rocks, water-bearing minerals and veins with secondary sulfide and PGE mineralization around magmatic sulfide bodies and large sulfide droplets suggests an appreciable level of  $H_2O$  solubility andof other volatiles (CO<sub>2</sub> and HCl) in sulfide melts (Li et al., 1992; Li and Naldrett, 1993; Polferov, 1966). Experimental studies established that dissolved water in sulfide melts serves lower the sulfide solidus in a sulfide-water system (Konnikov, 1997; Wykes and Mavrogenes, 2005). Konnikov (1997) showed that the solidus temperature of pyrrhotite decreased by 80–90°C in the FeS-H<sub>2</sub>O system at 100 MPa and 1000–1160 °C with  $fO_2$  controlled by a NNO-buffer compared to the temperature of a pyrrhotite "dry" solidus. Wykes and Mavrogenes (2005) observed that the solidus temperature decreases from 900 to 865°C in the FeS-PbS-ZnS system at 1.5 GPa with the addition of water.

Fluid exsolved from solidifying sulfide melt may contain anions and metallic elements. For example, Mungall and Brenan (2003) experimentally showed the distribution of halogens between coexisting silicate and sulfide melts at 0.9-1.8 GPa and 1150-1450°C and at atmospheric pressure and 1000-1100°C. Upon cooling and solidification of the sulfide melt, S-rich or HCl-rich fluids can transport PGEs and gold from the sulfide to surrounding rocks (Baker et al., 2001; Li et al., 1992). The exsolved fluid forms veinlets and alteration zones enriched in Au and PGEs (Gorbachev, 2006). Exsolution of Au-PGEenriched fluids can supported by micron-sized particles of Pd, Pt, Au and their alloys attached to the outer surfaces of sulfide globules (Zelenski et al., 2017; Supplementary Fig. S6a). Almost every such particle of gold or PGE is located in or near a small cavity, which possibly represents an imprint of a bubble (Supplementary Fig. S6b). We propose that the observed porous sulfide textures provide evidence for the solubility of water and/or other volatile components in the sulfide melt.

## 5.4. Thin sulfide foils: decompression or thermal shock fracturing

The existence of sulfide foil morphologies raises two questions: (1) what is the cause of crack formation? And (2) what is the mechanism for filling cracks with sulfide melt? We suggest that cracks in olivine crystals may form in at least two ways, which include: i) decompression-induced cracks, and ii) thermal shock cracks. The first mechanism is supported by the presence of fluid bubbles entrapped simultaneously with sulfide, or exsolved from silicate or sulfide melt. In this case, cracks could form at depths under several kilobars of pressure during magma ascent and decompression. This assumption is supported by the fact that many cracks are partly (Fig. 9a, b) or completely (Fig. 9c, d) healed and contain planar sulfide swarms. Therefore, the crystal had sufficient time to heal these cracks. Decompression cracks sometimes intersect one or more sulfide globules and/or melt and fluid inclusions (Fig. 9c), with the crack passing through the maximum cross-section (the "equator") of the globules or inclusions.

Alternatively, thermal shock cracks could occur during the rapid cooling of a crystal due to interactions with the atmosphere at the moment of lava fragmentation. Based on laboratory experiments, thermal shock cracks always form 3D networks that do not necessarily transect melt/fluid bubbles or sulfide globules. However, if the crack does intersect a melt globule, the sulfide liquid can enter the crack.

The penetration of a sulfide melt through thin capillary cracks is hindered due to the poor wetting of olivine. Since the wetting angle of silicates by sulfide melt is much >90° (130° – 140° according to our data, or even up to 150° according to Mungall and Su (2005)), an excessive melt pressure is required to fill the crack with the sulfide melt. This pressure can be estimated from the curvature radius of the melt surface and the surface (interfacial) tension of the sulfide melt (in the case of a cylindrical meniscus in a crack of width *d*):  $\Delta p = \gamma \cdot \cos\theta/d$ , where  $\gamma$  is the interfacial tension of the free surface of the sulfide melt and  $\theta$  is the olivine/sulfide melt wetting angle. Such calculations show that for a 1 µm wide crack, a wetting angle of 150° and a surface tension of the sulfide melt surface in the range of 330–550 mN/m (Mungall and Su, 2005) is the required along with a minimum push pressure of 3–5 bar for the sulfide melt. Interfacial tension between sulfide and silicate melts can be even lower (240 mN/m, Mungall et al. (2015)) and thereby requiring a push pressure in the order of 2.4 bar. It is known from melt inclusion studies that olivine crystals are highly stable, even at high temperature (up to 1200 °C), to withstand internal pressures up to several kbar of expanding fluid from tiny fluid/melt inclusions. In the case of crystal rupture caused by internal overpressure, the sulfide melt can therefore be pushed into the newly formed capillary cracks. The mechanism of sulfide liquid propagation along thin cracks is fundamental to our understanding their percolation through fractured rocks during accumulation or intrusion, as well as the migration of sulfide melts through networks in a crystal mush (Barnes et al., 2017; Chung and Mungall, 2009; Holzheid et al., 2000; Roberts et al., 2007; Saumur and Cruden, 2017 and references therein).

## 5.5. Deformation of sulfide globules

In the presence of three immiscible liquids, such as a silicate melt **M**, sulfide melt **S** and aqueous fluid **V**, we have three pairs of liquids with different interfacial tensions  $\gamma_{SM}$ ,  $\gamma_{MV}$  and  $\gamma_{SV}$ . The fluid-sulfide interface in compound sulfide-fluid droplets concave toward the sulfide melt only if  $\gamma_{SM} < \gamma_{MV}$  and  $\gamma_{SV} < \gamma_{MV}$  (Guzowski et al., 2012; Mungall et al., 2015; Neeson et al., 2012). Botcharnikov et al. (2013), Mungall et al. (2015) and Mungall and Brenan (2014) observed similar topology of the sulfide-fluid interface at 1100-1200°C in water-saturated conditions ranging from 0.001-2 kbar. Mungall et al. (2015) suggested that in natural systems, the fluid-sulfide interface must also be concave toward the sulfide (e.g., Dowling et al., 2004; Métrich et al., 1999; Timina et al., 2006). Although the above studies described compound fluid-sulfide globules, they do not provide convincing examples of naturally occurring sulfide-fluid interfaces with the concavity toward the sulfide. Here, we show clear evidence demonstrating confirming this rule for natural compound sulfide-fluid droplets (Fig. 11).

One problem that arises is that for experimentally measured values of the sulfide-silicate and the fluid-silicate interfacial tensions, the exact opposite topology should be observed at the fluid-sulfide interface. Namely, the concavity should be in the direction of the fluid bubble because the previously measured sulfide-silicate interfacial tension  $\gamma_{SM}$ (400–600 mN/m, Ip and Toguri, 1993; Kucharski et al., 1994; Mungall and Su, 2005) is much higher than the fluid-silicate interfacial tension, especially at high water pressure ( $\gamma_{MV} = 65-90$  mN/m at pH<sub>2</sub>O = 4– 5 kbar; Bagdassarov et al., 2000; Khitarov, 1979). Mungall et al. (2015) noted this discrepancy, which still remains unconstrained. Recent measurements of  $\gamma_{SM}$  by Mungall et al. (2015) provided a value of ~240 mN/ m, which is still higher than  $\gamma_{MV}$  at high pH<sub>2</sub>O.

## 6. Conclusions

- Tolbachik sulfides are composed of high-temperature sulfide phases MSS and ISS as well as the low-temperature pyrrhotite-pentlanditechalcopyrite-cubanite-bornite suite. A minor amount of secondary chalcocite is also present. The mineral composition of the sulfide globules is more diverse than those in MORB sulfides and closely corresponds to the sulfide ores of continental magmatic deposits. The maximum NiS content in Ni-pentlandite reaches up to 80 mol%. Low-Ti magnetite occurs as small primary grains or replaces sulfide minerals during oxidation.
- 2. Based on their origin, the textures of sulfides can be classified in according to crystallization, fluid separation and oxidation and dissolution. Deformed sulfides were classified separately. The main factor affecting the crystallization textures is the cooling rate. At the highest cooling rates (~600 °C/s in experiments), fine-grained textures are produced. With decreasing cooling rates (tens of degrees per minute or less), the textures change to coarse-grained and lamellar. Homogeneous textures can be formed at any cooling rate. Another factor affecting the texture is the globule composition. Most of the globules having homogeneous textures composed of pyrrhotite, Ni-pyrrhotite

and occasionally chalcopyrite. The majority of "fine-grained" globules have a Cu: Ni ratio within a range of  $1 \pm 0.7$ . The size of the globules has little influence on the texture formation.

- 3. Porous textures were probably formed as a result of fluid separation from the sulfide melt during crystallization of the latter. Porous sulfides are very common, where pore-free Tolbachik sulfides are rare and only occur in globules with homogeneous crystallization textures. Precious metals could be transported out from sulfide together with the exsolved fluid.
- 4. Based on their shapes, sulfides can be described as "normal" (spheres and ellipsoids), gravity-dependent (complex inclusions containing planar sulfide-silicate or sulfide-fluid interfaces), deformed under the influence of growing silicate crystals or fluid bubbles, and sulfide foils in cracks. Ruptured and healed crystals containing sulfide liquid suggests significant vertical movements of olivine crystals within a magma chamber.
- 5. Textures formed by oxidation are characterized by the presence of secondary magnetite, which ranges from thin veinlets and networks to complete substitution of the whole sulfide globule. Dissolution, unlike oxidation, changes the morphology of the globule but does not affect its composition. Oxidation and dissolution of sulfides are likely independent processes but may occur simultaneously during the magma ascent.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.lithos.2018.07.029.

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