MINERALOGY OF SALTY CRUSTS COVERING BASALT WALLS IN THE "DUPLEX" LAVA TUBE OF TOLBACHIK VOLCANO (KAMCHATKA ARC)

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The 2012-2013 flank fissure eruption of Tolbachik volcano in Kamchatka Peninsula (Far East Russia) is considered as one of the most voluminous historical outpouring of basic lava in the subduction-related environment (Belousov, 2015). The Tolbachik eruptive system is characterized by an extensive system of lava tubes with diameters varying between 1 and 10 meters. Towards the eruption cessation the tube system became separated by plugs of solidified lava into numerous isolated segments that started to cool from ~ 1000 °C independently from each other.

The studied cave "Dvoinaya" (means "Duplex"), represented by two galleries located one above the other (Fig. 1), is a 150 m segment of the lava tube system that was cut-off from lava supply in May 2013. Since then the tube (that originally had air outflow from its entrance) started to cool and became accessible in 2017. We recorded very complex distribution of temperatures in the upper gallery: $\sim 50~^{\circ}\text{C}$ in the entrance area, while the walls inside the cave had strong temperature gradients from 100 $^{\circ}\text{C}$ to up to 540 $^{\circ}\text{C}$ in some wall fractures. Entrance to the lower inaccessible gallery of this tube segment had air temperature around 200 $^{\circ}\text{C}$. Noteworthy, at the same time the incandescent cracks at the surface of the lava field $\sim 100~\text{m}$ from the cave entrance were as hot as $660~^{\circ}\text{C}$.



Fig. 1. Entrance into the "Duplex" lava tube of the 2012-2013 eruption of Tolbachik volcano; June 2017. Temperatures of the tube walls and inside the wall fracture are $\sim 60^{\circ}$ C.

Various, dominantly Na-, K- and Cu-bearing chloride and sulfate minerals (Vergasova, 2012; Chaplygin, 2015) are present at the surface as colorful incrustations around skylights and cracks in lava. In contrast, the interior of the dry parts of cooled lava tubes, especially around wall fractures, is coated by finegrained, grayish-white material. The studied mineral assemblage, covering the vesicular lava in the "Duplex" cave, consists of intergrown Na-K chlorides and tenorite (CuO). The dominant chloride on the rock surfaces and within the vesicles is represented by halite and sylvite in roughly equal proportions (Fig. 2A-C, 3A-D). Sylvite forms the majority of cubic crystals that are sprinkled with round and rod- and lens-shaped halite with different sizes and orientation (Fig. 3A-C). The overall emulsion-

like texture of chlorides is reminiscent of immiscibility, most likely in the form of solid solution breakdown. Platy tenorite is scattered among the chloride masses and crystals and commonly grows into the open space (Fig. 3C-D). Small octahedral crystals (< 3 mm) of pure gold occasionally present among salt (Fig. 4A-B).

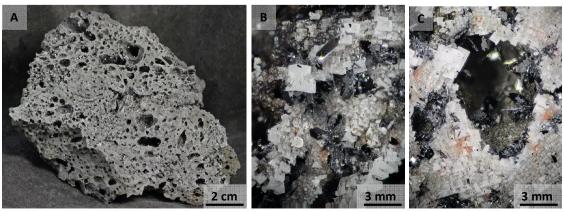


Fig. 2. Optical photographs (A-C) showing mineral assemblage on the lava walls in the "Duplex" cave. The main minerals are halite, sylvite, tenorite, hematite.

A thin rim (~ 100 mm) of the basalt lava is distinctively altered at the contact with the chloride crust (Fig. 3E-F). The outer rim of this reaction zone is represented by octahedral Cu-bearing magnesioferrite ((Mg,Cu)(Fe³⁺)₂O₄ with 5.8-17.3 wt% CuO and up to 0.9 wt% TiO₂, 2.4 wt% Al₂O₃, 3.0 wt% MnO and 0.8 wt% ZnO) that is followed by intergrown hematite and high-Ca silicates towards and inside the basalt.

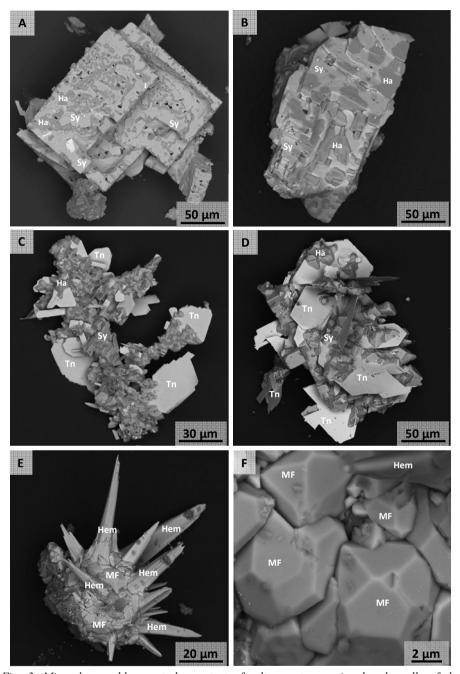


Fig. 3. Mineral assemblages at the contact of salty crusts covering basalt walls of the "Duplex" lava tube segment. The main minerals are halite (Ha), sylvite (Sy), tenorite (Tn), hematite (Hem), Cu-bearing magnesioferrite (MF). Note micro-emulsion textures on (A-B) represented by halite blebs (dark grey) in sylvite cubes (light-grey).

Gold- and copper-bearing salt crusts covering walls and fractures in the lava tube and associated mineral assemblage of unusual Cu-bearing spinel, hematite and high-Ca silicates in the outer rim of the lava may help to decipher compositions and processes in the shallow volcanic plumbing system. The recorded Cu-bearing magnesioferrite in a close association with tenorite and hematite (Fig. 3E-F) resembles cuprospinel (CuFe₂O₄; note "tenorite" CuO and "hematite" Fe₂O₃ components) and other Cu-Mg spinel from the ignited Cu-Zn ore dump in Newfoundland, where high-temperature roasting was caused by oxidation and involved Mg-silicates. Similarly, the high-Ca silicate assemblage, especially esseneite, melilite and spinel, is suggestive of pyrometamorphic transformations in the solid lava. We imply that such "chemical" roasting at low pressure and high oxygen fugacity was caused by periodic bursts of high-temperature gas through the

lava tubes. High, nearly magmatic temperature of the gaseous media in this case is independently confirmed by direct measurements of venting gases in skylights and lava fractures (Zelenski, 2014; Chaplygin, 2016) and lava melting in the tube roof.

We believe that gold accumulations in shallow volcanic environment are supplied by metals that are extracted from solid rocks by hot Cl-rich gases and salt melts. Near-magmatic temperature and efficiency of metal smelting in the post-eruptive environment are facilitated by elevated oxygen fugacity, which is caused by ingress of air into episodically emptied plumbing magmatic system and related oxidation of

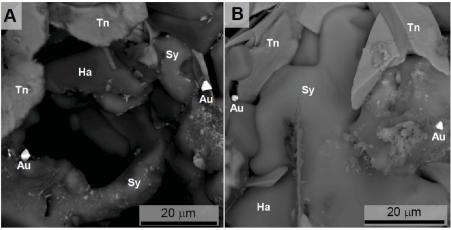


Fig. 4. Backscattered electron images showing octahedral crystals (< 3 mm) of pure gold in salt crusts covering basalt walls of the "Duplex" lava tube segment. Tn – tenorite, Ha – halite, Sy – sylvite.

fluids and metals. By analogy with experimental studies and metallurgical practices we propose that this naturally occurring smelting process in the presence of the chloride melt flux was responsible for extraction of metals from the basaltic wall rocks and deposition of Cu-, Fe- and Cu-Fe-oxides and native gold.

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