GOLD- AND COPPER-BEARING SALT CRUSTS IN LAVA TUBES OF TOLBACHIK VOLCANO (KAMCHATKA ARC)

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The 2012-2013 flank fissure eruption of Tolbachik volcano in Kamchatka Peninsula (Far East Russia) lasted 9 months and produced 0.54 km^3 of basaltic trachyandesite lava that covered the total area of 36 km^2 with maximum thickness of 70 m (Belousov, 2015). This eruption is considered as one of the most voluminous historical outpouring of basic lava in the subduction-related environment. During the eruption the lava gradually changed from ´a´a flows to tube-fed pahoehoe flows (Belousov, 2018). When the magma discharged declined from the initial 440 m^3/s to several tens of m^3/s in January 2013, lave tubes started forming by surface solidification ("roofing") of the open lava channels (Fig. 1A, B). The tube system extended downslope by complex branching to reach a total length of ~ 4 km and include multiple interlacing tubes with average diameters between 1 and 10 m.

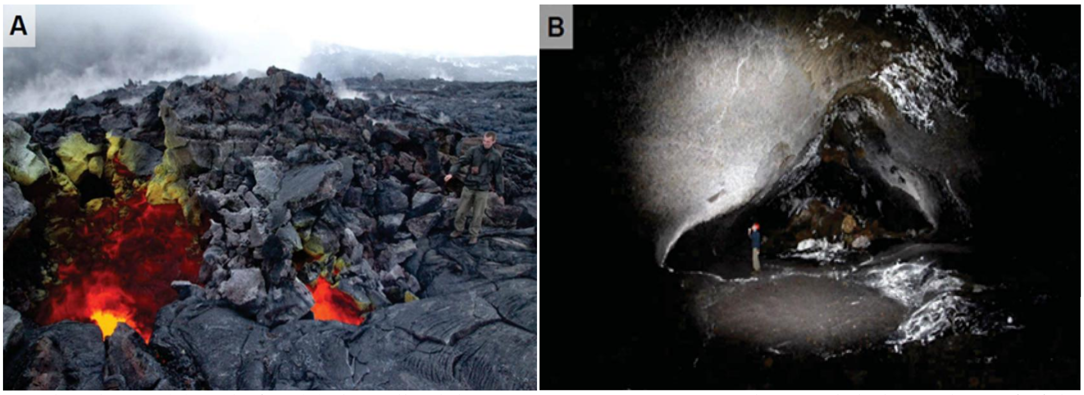

Fig. 1. Lava tubes during (A) and after (B) the Tolbachik eruption in 2012-2013. A: Glowing skylights in the roof of the lava tube, emitting a mixture of volcanic gas and hot air, and surrounded by colorful fumarolic incrustations; B: Walls and roof of the "Duplex" lava tube segment near the entrance covered by white chlorides

Lava flowing through the tube system had temperature and viscosity close to those at the start of eruption (1082 ^oC and (1-3)×10^3 Pa s; (Belousov, 2018), but experienced notable degassing, frequently visible as bursting bubbles at the surface. Fluids released from the magma leaked upward through the fractured roof of the tubes and vigorously vented out through "skylights". The temperature of venting gases, measured directly at the skylights (Zelenski, 2014; Chaplygin, 2016), was as high as the temperature of the lava (1025-1065 ^oC). Such high temperatures of the volcanic gas, possibly caused by air admixture through skylights and related oxidation, triggered partial melting of the roof's rocks and formation of multiple lava stalactites. Rocks in the areas of gas venting (skylights and open cracks) were covered by colorful crusts composed of various minerals emplaced from the venting gas.

Towards the eruption cessation the tube system became separated by plugs of solidified lava into numerous isolated segments that started to cool from ~1000 ^oC independently from each other. The studied cave "Dvoinaya" (means "Duplex"), represented by two galleries located one above the other), 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: ~ 50 °C in the entrance area, while the walls inside the cave had strong temperature gradients from 100 °C to up to 540 °C in some wall fractures. Entrance to the lower inaccessible gallery of this tube segment had air temperature around 200 °C. Noteworthy, at the same time the incandescent cracks at the surface of the lava field ~ 100 m from the cave entrance were as hot as 660 °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 fine-grained, 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). Sylvite forms the majority of cubic crystals that are sprinkled with round and rod- and lens-shaped halite with different sizes and orientation (Fig. 2C). 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. 2C-D). Small octahedral crystals (< 3 mm) of pure gold occasionally present among salt (Fig. 3B).

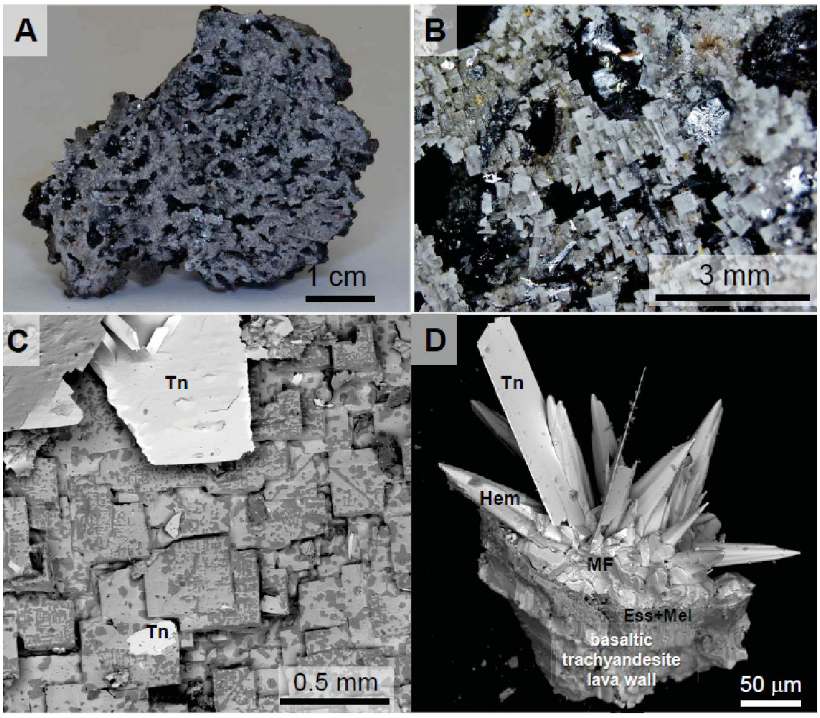

Fig. 2. Optical photographs (A, B) and backscattered electron images (C-D) showing mineral assemblage on the lava walls in the "Duplex" lava tube segment. The main minerals are halite (Ha), sylvite (Sy), tenorite (Tn), hematite (Hem), Cu-bearing magnesioferrite (MF). Note micro-emulsion textures on (C) represented by halite blebs (dark grey) in sylvite cubes (light-grey).

A thin rim (~ 100 mm) of the basalt lava is distinctively altered at the contact with the chloride crust (Fig. 2D, 3A). The outer rim of this reaction zone is represented by octahedral Cu-bearing magnesioferrite ($(Mg,Cu)(Fe^{3+})_2O_4$ with 5.8-17.3 wt% CuO and up to 0.9 wt% TiO_2, 2.4 wt% Al_2O_3, 3.0 wt% MnO and 0.8 wt% ZnO) that is followed by intergrown hematite and high-Ca silicates towards and inside the basalt. The high-Ca silicate minerals, represented by esseneite $(Ca_{0.98}Na_{0.02})$ $(Fe^{3+}_{0.48}Mg_{0.26}Al_{0.19}Fe^{2+}_{0.03}Ti_{0.03}Mn_{0.01})$ $(Si_{1.28}Al_{0.72})O_6$, Na-melilite/Al-akermanite $(Ca_{1.40}Na_{0.59}K_{0.01})(Al_{0.85}Mg_{0.08}Fe_{0.07})(Si_{1.68}Al_{0.32})O_7$, wollastonite, monticellite, titanite and grossular garnet. We found that hematite, magnesioferrite and Cu-rich spinel can form as a replacement of magmatic oxides in the basalt (magnetite and ilmenite) and by direct crystallization on the vesicular walls.

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. 2D, 3A) resembles cuprospinel ($CuFe_2O_4$; note "tenorite" CuO and "hematite" Fe_2O_3 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 (Fig. 3A), 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.

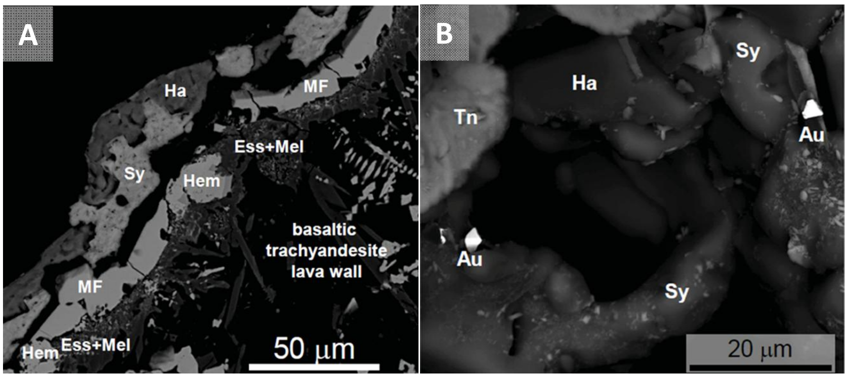

Fig. 3. Backscattered electron images showing mineral assemblage on the lava walls in the "Duplex" lava tube segment. The main minerals are halite (Ha), sylvite (Sy), tenorite (Tn), hematite (Hem), Cu-bearing magnesioferrite (MF), high-Ca silicates (e.g., esseneite, melilite – Ess+Mel).

Our hypothesis envisages 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 fluids and metals. In contrast to existing views on a prerequisite metal-concentrating sulfide melt in volcanic arcs, we argue that metal buildups, although initially sub-economic, accompany and postdate every stage of magma injection and eruption. Metal accumulations scattered vertically and laterally in shallow magmatic conduit can be upgraded by coupled dissolution and re-deposition in successive volcanic cycles. It is also anticipated that long-lived volcanic systems, processing tens to hundreds of cubic km of common magmas to the surface, are capable of attaining high gold endowment by consuming precursor accumulations.

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