

# Magmatic evolution of the Štiavnica volcano

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**Abstract:** The Štiavnica stratovolcano evolved in five stages: (1) construction of the extensive andesite strato-volcano during the interval 15.0–13.6 Ma, including diorite and diorite porphyry intrusions; (2) emplacement of subvolcanic intrusive rocks associated with a resurgent uplift, sector collapse and denudation of the volcano — with the granodiorite pluton showing the age around 13.6 Ma, quartz-diorite porphyry sills and dykes dated at 13.77–13.0 Ma and granodiorite porphyry stocks showing the age around 12.95 Ma, (3) subsidence of the caldera and its filling by differentiated andesites around 12.9 Ma, (4) renewed volcanic activity marked by post-caldera andesites between 12.8 and 12.2 Ma; (5) uplift of the resurgent horst in the central part of the caldera accompanied by rhyolite volcanic/intrusive activity between 12.2 and 11.4 Ma. Volcanic and intrusive rocks of the Štiavnica volcano were sourced from an upper crustal magmatic reservoir stored at a pressure between ~1 and ~3 kbar. The different phenocrysts (plagioclase, orthopyroxene, clinopyroxene, Mg-hornblende, and quartz) have crystallized from dacitic to rhyolitic melts at a temperature between ~960 to ~700 °C. A clear change in mineralogy from plagioclase–orthopyroxene–clinopyroxene, plagioclase–orthopyroxene, plagioclase–orthopyroxene–hornblende, plagioclase–hornblende–biotite, and then plagioclase–hornblende–biotite–quartz is observed with the decrease of temperature of the melts. Crystal mush in the upper-crustal magma chamber was repeatedly fed by magmas having an andesitic composition resulting from differentiation and crustal contamination of primitive mantle magmas in a lower and/or middle crustal reservoir. Eruption of volcanic rocks and emplacement of subvolcanic intrusions resulted from a mixing between the evolved magmas stored in the upper crustal reservoir and newly injected primitive magmas and/or due to fluid saturation and exsolution of the magmas. Late stage rhyolites represent a segregation of the interstitial silicic melt from the crystals mush in the upper crustal reservoir during its cooling at temperature <750 °C. The porphyry-skarn Cu–Au, Fe-skarn, disseminated base metal and epithermal mineralizations of the Štiavnica volcano associate genetically with those magmatic rocks that resulted from a prolonged cooling of magma in the upper crustal reservoir — cooling and perhaps magma mixing that provoked fluid exsolution from the long-lived crystal mush were the key factors in formation of ore deposits.

*We dedicate this contribution to the late RNDr. Vlastimil Konečný, CSc., who played a leading role in mapping of the Štiavnica volcano and along with J. Lexa has laid down essential aspects of its geology and evolution.*

## Introduction

Majority of the world's Cu, Au, Ag, and Mo are sourced from magmatic–hydrothermal and epithermal ore deposits. These deposits are generally formed during discrete short periods of times in long-lived magmatic systems and their formation results from an interplay between magmatic and hydrothermal factors (e.g., Sillitoe 2010; Richards 2011; Audétat & Simon 2012). The middle Miocene Štiavnica volcano provides a unique opportunity to study relationships among magmatic evolution and related metallogenetic processes. While preserved volcanic complexes allow a serious paleovolcanic reconstruction (Konečný et al. 1998; Chernyshev et al. 2013) a resurgent horst in the central part of its caldera exposes subvolcanic intrusive complexes with related ore mineralizations. Thanks to extensive past and ongoing mining works and exploration drilling as well as extensive labo-

ratory investigation of varied mineralizations, we have extensive data concerning their mineralogy and genesis. This opens a way to study one of the fundamental metallogenetic aspects — their relationship to the magmatic evolution of the volcano.

Previous studies on the magmatic evolution of the volcano (Lexa et al. 1997; Konečný P. et al. 2002; Kovalenker et al. 2006), based on petrography, major and trace elements geochemistry and a limited application of thermo-barometer, concluded that magma evolved first in a lower crustal reservoir probably up to an andesitic composition and then evolved further in an upper crustal magma chamber by assimilation–fractionation processes. Mixing due to repeated injections of andesitic magma was a common phenomenon in this shallow reservoir. Storage conditions in the upper crustal magma chamber were estimated to be 850–1050 °C, 1.7–2.5 kbar and 3–6 H<sub>2</sub>O wt. %.

Here, the magmatic evolution of the volcano is reconstructed in a greater detail by studying major and trace element compositions of minerals and silicate melt inclusions hosted in orthopyroxene, clinopyroxene, plagioclase, amphibole, and/or quartz from the pre-, syn-, and post-ore volcanic and subvolcanic rocks and using up-to-date methods of thermobarometry. This approach is coupled with U–Pb zircon dating of subvolcanic intrusive rocks that due to alterations could not be dated well enough by conventional K/Ar and Rb/Sr methods.

### Methods applied

We have selected 39 rock samples typical of different stages of the Štiavnica volcano. Textures and mutual relationships of mineral phases were documented by optical microscopy. Major and minor elements of selected samples were determined by ICP-ES and trace elements by ICP-MS in ACME laboratories. Phenocrysts and glassy silicate melt inclusions hosted in orthopyroxene, clinopyroxene, plagioclase, and quartz from samples of different stages were analyzed by EPMA for major elements, Cl and S concentrations. Using the LA-ICP-MS at the Bayerisches Geoinstitut we have analyzed in the selected rocks different silicates, oxides, rock matrixes and also un-exposed silicate melt inclusions hosted in different phenocrysts. The U–Th–Pb dating of separated accessory zircons by SHRIMP has been carried out in cooperation with Korea Basic Science Institute in its high resolution ion microprobe laboratory.

To determine oxygen fugacity, temperature and pressure at which the different minerals and matrixes were formed or at which they are in equilibrium we have variably used the opx-liquid (Putirka 2008) cpx-liquid (Neave & Putirka 2017), and amphibole thermobarometry (Ridolfi et al. 2012; Mutch et al. 2016; Putirka 2016) and Ti-in-quartz barometer (Huang & Audétat 2012; Audétat 2013), Fe–Ti oxides (Ghiorso & Evans 2008), Ti-in-zircon (Ferry & Watson 2007), and zircon saturation thermometry (Watson & Harrison 1983).

### Structure and evolution of the volcano and related mineralizations

K/Ar and Rb/Sr ages of the Štiavnica volcano rocks (Chernyshev et al. 2013) have been supplemented by new U–Th–Pb zircon dating of subvolcanic intrusions and caldera filling (Table 1).

**Table 1:** Results of new U–Th–Pb zircon dating.

Sample	Description	Age (Ma)
BLJ-1	Px andesite hosting a diorite porphyry stock	14.85±0.48
GD-1	Granodiorite bell-jar pluton, Hodruša – Mayer shaft	13.53±0.14
RB-1073	Granodiorite bell-jar pluton, Hodruša–Ravenstein	13.63±0.21
RB-1149	Granodiorite bell-jar pluton, Hodruša – All Saints mine	13.61±0.22
RB-350	Quartz-diorite porphyry sill, pre- Au mineralization	13.77±0.15
RB-349	Quartz-diorite porphyry sill, post- Au mineralization	13.46±0.19
RB-1148	Thick quartz-diorite porphyry sill above granodiorite	13.25±0.13
KDP-1	Quartz-diorite porphyry sill, Paradajz	13.73±0.20
KDP-3	Quartz-diorite porphyry ring dyke, Juraj štôľňa	12.99±0.18
R-8	Granodiorite porphyry stock; Zlatno, borehole R-8	12.92±0.11
R-12	Granodiorite porphyry stock; Zlatno, borehole R-12	12.98±0.08
ST-102	Glassy amph-bt andesite, early caldera fill, Ilija	12.85±0.15
ST-107	Amph-bt andesite; late cladera fill, south of Močiar	13.02±0.08

The scheme of the volcano evolution (Konečný et al. 1998; Chernyshev et al. 2013) has been updated as follows: (1) construction of an extensive pyroxene and amphibole–pyroxene andesite stratovolcano during the interval 15.0–13.6 Ma, including emplacement of diorite intrusion hosting a barren high sulfidation system at Šobov and a diorite porphyry stock at Beluj (1b) hosting the Au-porphyry type mineralization; (2) emplacement of subvolcanic intrusive rocks, mostly by the underground cauldron subsidence mechanism, associated with a resurgent uplift, sector collapse and denudation of the volcano following a granodiorite pluton emplacement (Kubač et al. 2018); the stage includes: (2a) emplacement of a granodiorite bell-jar pluton before the uplift in the depth 2–3 km, showing the age around 13.6 Ma; Fe-skarn and disseminated base metal mineralizations associate with the pluton; (2b) emplacement of quartz-diorite porphyry sills pre-dating the Hodruša epithermal Au mineralization related to the sector collapse (Kubač et al. 2018) around 13.75 Ma and sills that post-date the uplift and the epithermal Au mineralization in the interval 13.5–13.0 Ma; (2c) emplacement of granodiorite porphyry stocks and dyke clusters hosting the porphyry-skarn type Cu–Au mineralization around 12.95 Ma, (3) a subsidence of the caldera and its filling by evolved amphibole-biotite andesites and dacites around 12.9 Ma, including rare hot-spring siliceous deposits; (4) renewed activity of less evolved andesites during the interval 12.8–12.2 Ma, (5) an uplift of the resurgent horst in the central part of the caldera

accompanied by rhyolite volcanic/intrusive activity and an extensive system of epithermal precious and base metals veins during the interval 12.2–11.4 Ma.

### Magmatic evolution of the volcano

The Central Slovakia Volcanic Field, including the Štiavnica volcano, shows a close relationship to extension in a back-arc syn- to post-collision setting. The magmas were generated in association with tectonothermal rejuvenization related to extension induced asthenospheric upwelling. There are two concepts explaining the origin of andesitic magmas that were further subjected to evolution in the crust: (a) partial melting of metasomatized lithospheric mantle generated hydrous high-alumina basalts that evolved further at the base of the crust by a high-pressure fractionation and/or lower crustal assimilation (e.g. Harangi et al. 2007; Seghedi & Downes 2011); (b) radiogenic isotope data favor partial melting of the lower crustal metabasic source influenced by subcontinental lithospheric mantle and crustal assimilation (Kohút et al. 2019).

Essential P–T–X parameters of the investigated Štiavnica volcano rocks are summarized in Table 2. As evidenced by interpreted pressures between ~1 and ~3 kbar volcanic and intrusive rocks of the Štiavnica volcano had their source in an upper crustal magma reservoir at a depth of 4–12 km. Dominantly silicic composition of melt inclusions and thermometry indicate that the different phenocrysts (plagioclase, orthopyroxene, clinopyroxene, Mg-hornblende, and quartz) have crystallized from dacitic to rhyolitic residual melts at a temperature between ~960 and ~700 °C. A clear change of mineralogy from plagioclase–orthopyroxene–clinopyroxene, plagioclase–orthopyroxene, plagioclase–orthopyroxene–hornblende, plagioclase–hornblende–

biotite to a final plagioclase–hornblende–biotite–quartz is observed with the decrease of magma temperature. With exception of the most evolved rocks (subvolcanic intrusions 2a–2c, caldera fill (3) and late stage rhyolites (5)) matrix compositions of andesites are substantially less silicic than melt inclusions in phenocrysts. Along with the frequent presence of mafic enclaves, disequilibrium phenocrysts assemblages and resorbed cores of phenocrysts it indicates that the evolved crystal-rich magma was mixed with a more mafic magma. Apparently, the upper-crustal magma chamber was repeatedly fed by magmas having an andesitic composition. These magmas probably represent products of differentiation ( $\pm$ crustal contamination) of primitive magmas in lower and/or middle crustal reservoirs. A direct evidence for a magma evolution in the middle crustal reservoir is provided by the pressure and temperature of mafic Cr-rich clinopyroxene phenocrysts in the orthopyroxene–clinopyroxene andesites, indicating pressure and temperature conditions of 3.7–5.3 kbar and 1130 to 1170 °C, respectively. The crystal assemblage of the Beluj diorite porphyry (1b), hosting the Au-porphyry type mineralization, characterized by magmatic garnet, high-Al Mg-hornblende, Cr-rich clinopyroxene, orthopyroxene and plagioclase, suggests a mixing of magmas sourced from three levels of crystallization (lower-, middle-, and upper-crustal). Apparently, it was the extent of mafic magma input into the upper-crustal crystal mush that has governed the composition of erupting magmas — a larger input of mafic magma lead to eruptions of pyroxene and pyroxene–amphibole andesites with less silicic matrixes, while during periods of a lesser mafic magma input the erupting magmas composition was governed by magma differentiation towards more silicic and volatiles enriched composition.

Late stage rhyolites (5) show the same composition as silicate melt inclusions in phenocrysts of other rocks.

**Table 2:** Summarized P–T–X parameters of the Štiavnica volcano rocks.

Stage	SiO <sub>2</sub> (%) Whole rock Konečný et al. (1998)	SiO <sub>2</sub> (%) Dry rock ACME labs (2018)	SiO <sub>2</sub> (%) Matrix	SiO <sub>2</sub> (%) Melt inclusions	Pressure (kbar)	Temperature (°C)
5	72.2–77.7	74.30	76–77	71–80	2.9–3.2	700–760
4	56.1–63.5	–	66.5–78.1	70–78 (63–68)	1–3, ~ 4.2	770–860, ~ 910
3	58.8–64.4	61.85–66.63	74–78	70–78	1.7–2.9	730–820
2c	57.7–63.4	60.02–63.02	Eutectic Qtz–Kfs–Pl	73–79	1.5–3.0	720–810
2b	57.9–64.0	62.73–64.46	Eutectic Qtz–Kfs–Pl	73–81	~2.7	~770
2a	60.2–64.7	61.82–62.99	Eutectic Qtz–Kfs–Pl	71–81	2.0–3.3	740–820
1b	60.1–61.1	57.23–58.23	59–63	74–77	2.1–3.0, 3.7–6.1	795–880, ~1135
1	56.1–61.5	55.61–60.19	68.3–71.1	Mostly 70–80	0.7–2.2	750–860

Thus, they represent a segregation of the interstitial silicic melt from the crystal mush during its cooling at temperature  $<750$  °C, leading to the formation of erup-tible rhyolite magma pockets. Injection of mafic magma into the crystal mush and related thermal rejuvenization could be a relevant triggering mechanism. A similar conclusion has been reached by Demko in Demko et al. (2010) based on geochemical and radiogenic isotope data.

The eruption of volcanic rocks and emplacement of subvolcanic intrusions resulted from a mixing between the evolved crystal mush and injected new primitive magma and/or due to fluid saturation and exsolution of volatiles from magma. Both processes lead to a decrease in density and viscosity and thus to the magma mobiliza-tion and uprise.

Mineralizations of the Štiavnica volcano associate genetically with those magmatic rocks that resulted from a prolonged cooling of the upper crustal crystal mush and related fluid saturation (2a, 2b, 2c, 5) as well as a limited extent of magma mixing. Cooling and perhaps also magma mixing that led to the fluid saturation and exsolution from the long-lived crystal mush were the key factors in formation of the different ore deposits. In contrast, according to our observation the source magma of the Beluj Au porphyry systems resulted from a mixing between a deep and hydrous magma and an evolved, dry, upper crustal crystal mush.

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