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Chemical Evolution of Volcanic Rocks in the Altenberg – Teplice Caldera (Eastern Krušné Hory Mts., Czech Republic, Germany)

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ABSTRACT: The volcanic sequence of the Altenberg-Teplice caldera (ATC) in the Eastern Krušné Hory Mts./Erzgebirge, was studied at the pilot borehole of Mi-4 (Mikulov) using lithogeochemical data, petrological methods and magnetic susceptibility measurements. The dacitic and rhyolitic ignimbrites and tuffs, as well as shallow subvolcanic rhyolite and post-caldera dykes of granite porphyry are products of a fractionated, zonally arranged magma chamber. Two older units (basal rhyolite-BR and dacite-DC are calc-alkaline in character. Three younger units, traditionally termed as the Teplice rhyolite (TR1-TR3) have high-K calc-alkaline to A-type chemistry. The vertical compositional zoning and the reverse geochemical evolution within the three youngest volcanic phases (TR1-TR3) is confirmed. The successive cycles are shifted from more evolved (acid) types at the basis toward less fractionated (more basic), cumulate-rich magmas at the top of each unit. It is likely the result of a combination of the step-by-step exhausting of stratified magma reservoir.

KEY WORDS: rhyolite, dacite, magma evolution, caldera, Krušné Hory Mts.

Introduction

In 1928, Moesta first interpreted large complex of volcanic and subvolcanic rocks in the Eastern Krušné Hory Mts. (the Teplice Rhyolite -TR) as remnants of a late Variscan caldera, now termed the Altenberg-Teplice caldera (ATC).

Purpose of this contribution is to present basic data of evolution of the magma produced from the Teplice volcano obtained during new processing of the deep borehole Mi-4 (drilled in 1983–84) and of lithogeochemical data sets gathered by the Czech Geological Survey in the seventies.

Geological settings

The Altenberg–Teplice Caldera (ATC) is situated in the Eastern Krušné Hory Mts. (Osterzgebirge) between towns of Teplice (Czech Republic) in the south and Dippoldiswalde (Saxony) in the north (Hoth et al. 1995).

The ATC is 18×35 km (500 km²) in area. Country rocks of the ATC consist mainly of Proterozoic polyphase metamorphosed granitoids and paragneisses intruded by Carboniferous monzogranites of the pre-caldera Fláje pluton (G1). The crystalline footwall of the caldera dips at an angle of c. 20° east-

ZAMBOJ J., 1975. Pukanec. Osveta, Martin, 329. (in Slovak)



Fig. 1. New compiled geological section of the Mi-4 borehole.

wards (Moesta 1928; Jiránek et al. 1987). In the NW part of the ATC, the oldest remnants of the caldera fill crop out creating the volcanosedimentary Schönfeld beds complex (Westphalian B/C in age) with rhyolitic and dacitic volcanism at its base. The eastern third of the ATC is covered by the TR. The preserved volcanic rocks are supposed to represent more than 250 km³ of the erupted magma (Jiránek 1987; Benek 1991). The eastern contact of the ATC is abrupt, influenced by intrusions of granite-porphyry dykes (up to 1 km thick) and by post-caldera granites of A-type signature (Breiter et al. 1991). The western contact is flat. The S part of the ATC is hidden under Tertiary sediments of the Teplice basin (Mlčoch 1994).

Lithostratigraphy

The age of the volcanic pile in the ATC is not known very well. Some palaeontological evidence of the Westphalian B/C (c. 311 Ma) exists for the Schönfeld fossiliferous tuffite strata in the NW part of the caldera (Lobin 1983). Presence of the Westphalian C/D shale intercalation (c. 308 Ma) was redetermined by Šimůnek (in Jiránek et al. 1987) at a depth of 491–493 m in the drillhole Mi-4. The post-rhyolite Altenberg granite porphyry representing the final stage of the ATC is dated as 308 ± 1 Ma (Ar/Ar method, Seltmann and Schilka 1995).

An idealised profile through volcanic pile of the ATC has been compiled from the borehole Mi-4 situated in the western part of the TR. The declaration of the TR1, TR2 and TR3 as three independent volcanic units (events) was possible only due to evaluation of geochemical data (see below). The uppermost unit TR3, not fully drilled by the borehole Mi-4, was completed from the outcrops between villages of Mikulov and Cínovec (for details see Jiránek et al. 1987 and Breiter 1997). The individual phases are as follows:

- **1st volcanic phase**, the Basal Rhyolite (BR, borehole Mi-4 at depth 870.1–924.5 m), rhyolite tuffs of ash flows with 30% of phenocrysts (quartz, sanidine, albite, and biotite). Its equivalent was found recently in outcrops at Seyda in the NW-part of the caldera,
- sedimentary intercalations (Westphalian B/C): arcose, sandstone, shale, coal,
- 2nd volcanic phase, dacitic tuffs and ignimbrites (DC, borehole Mi-4 at depth 604.3–868.3 m) with 25% of phenocrysts (oligoclase-andesine, altered biotite) and lithic fragments. This unit is an equivalent of the Schönfeld dacite occurring in the German part of the caldera,
- **3rd volcanic phase** (TR 1, borehole Mi-4 at depth 493.4 to 601.6 m), rhyolitic tuff and/or ignimbrite with 30% of phenocrysts (quartz, sanidine, albite),
- sedimentary horizon with plant remnants dated as Westphalian C/D in coal-bearing shale (borehole Mi-4 at depth 490.6-493.4 m),
- 4th volcanic phase (TR2):
 - TR 2a tuffs (borehole Mi-4, of 412.9–490.6 m), air-fallen rhyolite tuffs with lava clots, containing 28% of phenocrysts (quartz, sanidine and albite), frequently pseudofluidal texture,
 - TR 2b ignimbrites (borehole Mi-4, 191.4–412.9 m interval), content of phenocrysts decreases from c. 50% (quartz, K-feldspar) in depth 370 m to c.30% in depth of 190 m,
- 5th volcanic phase (TR3):
- TR3a Pramenáč type, (borehole Mi-4, 0–192 m), fine-grained rhyolite ignimbrite with 35% of phenocrysts (K-feldspar, quartz, less frequently albite and biotite, up to 2 mm in size),
- TR3b Vlčí kámen type medium-grained rhyolite ignimbrite with 57% of phenocrysts (K-feldspar, quartz, plagioclase, pyroxene), not found in the borehole Mi-4,
- TR3c Přední Cínovec type, probably a subvolcanic intrusion of a crystal-rich melt into older tuffs and ignimbrites, rhyolite lava with 60% of phenocrysts, (K-feldspar, quartz, plagioclase, pyroxene), not found in the borehole Mi-4,
- the post-caldera granite porphyries (GP) build large dykes striking NW-SE to N-S. The granite- to syenite porphyries are very rich in phenocrysts of K-feldspars and chemically resemble the TR3c phase.

Methods data

From previous investigation of the borehole Mi-4 and the TR-outcrops, there are large data sets of geochemical data available: The drill core was analysed in 10 m intervals for As, Cr, Cu, Ni, Nb, Pb, Rb, Sn, Sr, U, Y, and Zr (Reichmann et al 1985). Schovánková performed c. 30 whole-rock major-element analyses (database of the CGS) and Čadková et al. (1984) made c. 50 complex whole-rock analyses from TR2 and TR3 outcrops. We made 45 new complex whole rock chemical analyses using wet chemistry for the major elements and XRF, ICP-OES, INAA, and gamma-ray spectroscopy for trace elements. Magnetic susceptibility (k) was measured using the KT-5 kappameter along the whole drill core profile (0.5 m - intervals). The measured values were corrected for the core diameter.

Results

Magnetic evidence of vertical zoning in the borehole Mi-4

Magnetic susceptibilities in rhyolitic rocks are low. Nevertheless, several slightly different layers can be recognized. The reason for the susceptibility changes remains basically unknown, perhaps they may be accounted by different degree of Ti- Fe oxide alteration and/or disintegration frequently observed in thin sections of both tuffaceous and ignimbrite rocks. Dacitic tuffs are the only anomalous member of the whole volcanic sequence. Enhanced values of k, from 1×10^{-3} up to 22×10^{-3} SI were found in the upper part and at the basis of the dacitic layer. The variations of susceptibility within the dacitic tuffs may reflect alteration effects of magnetic minerals, very likely magnetite.

Chemical evidence of vertical zoning in the borehole Mi-4

According to the contents of Rb, Sr, and Zr (Fig.2), Nb, Y, Th, and U, five effusive phases can be distinguished, corresponding to the litostratigraphic units BR, DC, TR1, TR2, and TR3 respectively.

The three uppermost units (TR1-TR3) show similar chemical trends from rocks relatively rich in Rb (Th, HREE) and poor in Sr and Zr (LREE) at the bottom of each unit to the rock depleted in Rb (Th, HREE) and enriched in Sr (LREE) in the upper part of each unit. A horizon markedly rich in Zr was found at the top of the units TR1 and TR2. Dacitic rock (DC) differs from upper rhyolitic units significantly in its chemical character. The relatively homogeneous Rb and Zr contents contrast with very variable Sr content.

The geochemical trend within the oldest rhyolite unit (BR) overlying the crystalline basement is inverse to that in the upper rhyolite units: from the bottom to the top of this unit the contents of incompatible elements (Na, Rb) increase and those of relatively compatible elements (Mg, K, P, Zr, total REE) decrease.

Geochemical evolution of the magma

Classification of the volcanic rocks of the drillhole in the TAS diagram suggests a rhyolitic composition for the BR and TR units, and dacitic to rhyo-dacitic composition for the DC-unit (Fig. 3).

Changes from primitive calc-alkaline melt (CA) to much more evolved high-K calc-alkaline melt (HKCA) during the caldera evolution are well documented chemically (Tab. 1). The older BR-DC suite represents relative primitive calc-alkaline magma with relative high contents of Fe, Mg, Ca, P, and Sr, low contents of Rb, Th and HREE, and none or small Eu-anomaly. The younger rhyolite series of the TR are relatively enriched in K, Zr, Th, Y and HREE, and depleted in Al, Ti, Mg, and Sr. The CA to HKCA change is best illustrated in the REE-patterns (Fig. 4). This trend later continued by the intrusion of highly specialised A-like type granites of the Cinovec (Zinnwald) postcaldera pluton (Breiter et al. 1991).

Discussion

Evolution of volcanic complexes with similar chemical trends to that we have found within the ATC was described from seve-



Fig. 2. Chemical (acc. to data of Reichmann et al. 1985) and magnetic (new data) vertical zonality of the Mi-4 borehole.



Fig. 3. TAS-classification of the ATC rocks.

ral places, namely in western North America. The evolution of BR-unit resemble that of the Taylor Creek rhyolite (Duffield and Ruiz 1992), the evolution of the TR-units is similar to the Bishop tuff (Hildreth 1979).

The reverse chemical zoning within the TR1-TR3 eruptions can be explained by step-by-step exhausting of stratified magma chamber according to the model of Hildreth (1979) and Fridrich and Mahood (1984): The melt produced in the deeper crust interrupted its ascent in a transitional reservoir. This gave rise to gravitational stratification – in the deeper part of the reservoir relatively heavy crystals of feldspars, dark minerals and most accessories concentrated, whereas the upper part was enriched in light melt. Chemically, the stratification is reflected by higher content of Si, Na and incompatible trace elements (Rb, Th, Y) in the melt in the upper part of the reservoir, while the deeper part is enriched in K, Fe, Mg, Sr and Zr. The subsequent eruption deposited first acid tuffs, then intermediate ignimbrites rich in phenocrysts and later, the ignimbrites rich in accessories (compare Breiter 1997). The content of fluid in the melt stepwise decreased from the TR1 to the TR3 and the explosive style of the TR1 eruption was changed to more extrusive style of TR2 and to extrusive to subvolcanic style of TR3.

The polarity of the melt reservoir of the lowermost unit (BR) was inverse to that in reservoir for TR units. This can be explained by contamination of the cap of the reservoir by a roof rock rich in Fe, Ti, Mg etc. (compare Duffield and Ruiz 1992).

The BR and DC units with relatively high contents of Fe, Mg, Ca, P, and Sr, low contents of Rb, Th and HREE, and none or small Eu-anomaly represent probably a product of the highdegree melting of immature material of the lower crust. Three younger TR units with high contents of Rb, Th, HREE and strong Eu-anomaly should be interpreted as a product of low-degree high-temperature melting of much more evolved material of the crust. The Altenberg-Teplice caldera represents a rare example of volcano, where rapid changes of CA to HKCA and later to A-type magma (during c. 5 Ma) exist in combination

	BR	DC	TR1	TR2		TR3	GP	
	early→late	early→late	early→late	early \rightarrow late TR2a \rightarrow	Pramenáč	Vlčí Kámen	Přední Cínovec	
				\rightarrow TR2b	TR3a	TR3b	TR3c	
n	9	13	6	16	7	8	8	4
SiO_2	$71 \rightarrow 73$	$67.1 \rightarrow 64.5$	76	$77.0 \rightarrow 76.4$	75.9	75.6	72.1	70.1
${\rm TiO}_2$	$0.33 \rightarrow 0.25$	$0.64\!\rightarrow\!0.65$	$0.07 \rightarrow 0.12$	$0.06 \rightarrow 0.13$	0.1	0.15	0.28	0.51
Al_2O_3	$15.2 \rightarrow 14.0$	15.0 - 16.0	$12.2 \rightarrow 11.8$	$11.5 \rightarrow 12.4$	12.3	12.2	13.4	14.1
Fe ₂ O ₃ tot	$2.1 \rightarrow 1.5$	3.1 - 3.8	$0.8 \rightarrow 1.4$	0.5 - 1.5	1.65	1.63	2.47	3.65
MgO	$0.8 \rightarrow 0.7$	1.5 - 1.9	$0.08 \rightarrow 0.14$	0.1	0.1	0.14	0.31	0.54
CaO	0.7 - 1.1	1.0 - 2.0	$0.8 \rightarrow 0.4$	0.1 - 1.1	0.57	0.56	0.70	0.62
Na ₂ O	$1.9 \rightarrow 2.5$	2.3 - 4.2	$2.4 \rightarrow 1.2$	1.6 - 2.6	3.34	2.98	3.32	3.3
K2O	$5.0 \rightarrow 4.7$	3.6 - 4.8	$5.0 \rightarrow 6.3$	$5 \rightarrow 6$	5.18	5.57	5.94	5.9
P_2O_5	0.09 - 0.07	0.23 - 0.25	$0.011\!\rightarrow\!0.017$	0.01 - 0.03	0.03	0.05	0.09	0.17
Rb	240	175	$350 \rightarrow 250$	$330 \rightarrow 265$	296	285	229	210
Sr	150 - 225	325	$25 \rightarrow 50$	$17 \rightarrow 30$	49	48	84	91
Zr	100	75	$100 \rightarrow 200$	$95 \rightarrow 145$	168	152	244	319
U	8 - 10	6 - 8	$10 \rightarrow 5$	$5 \rightarrow 30$	20	12	10	7
Th	15	17	$60 \rightarrow 30$	$43 \rightarrow 33$	75	45	38	30
Y	24 - 18	$16 \rightarrow 18$	$46 \rightarrow 24$	$72 \rightarrow 42$	75	45	38	55
Ce	77 - 54	$88 \rightarrow 92$	$84 \rightarrow 128$	$59 \rightarrow 113$	106	135	140	160
Yb	2.3 - 1.7	$1.55 \rightarrow 1.60$	$4.3 \rightarrow 2.7$	$7.4 \rightarrow 4.25$	6.2	4	3	4

Remarks: 24 – 18 variation of the element content (elements without distinct vertical evolution).

 $84 \rightarrow 128$ changes in the element content from the early to the late rocks within the individual unit (elements with distinct vertical evolution).

Tab. 1. Characteristic contents of major (in wt.%) and trace (ppm) elements in rocks of the Altenberg-Teplice Caldera (acc. to data of Schovánková (not published), Čadková et al. (1984) and new data of the authors). All major element analyses were done by wet chemistry, trace elements by XRF, INAA and ICP-OES. U and Th by laboratory gamma-ray spectroscopy.



Fig. 4. Chondrite normalised REE-patterns of the ATC rocks (normalised according to Henderson et al. 1984). The change from the CA to HKCA magma between the DC and TR1 unit and internal evolution of each of the TR1-TR3 units are well visible.

with a triple repetition of the reversal style of magma zonality produced from the same magma chamber.

Conclusion

Within the volcanic fill of the Altenberg-Teplice caldera, five subsequent volcanic phases, all Westphalian in age, were distinguished:

The two oldest units, the basal rhyolites (BR) with overlying dacites (DC) are calc alkaline in character and may probably represent a product of high-degree melting of immature material of the lower crust.

Three younger units (TR1, TR2, TR3) are high-K calc-alkaline in character, significantly enriched in Rb, Th, and HREE. The TR-units should be interpreted as a product of low-degree high-temperature melting of much more evolved crustal material.

All the three TR-units show similar chemical trends from rocks relatively more evolved (rich in Rb, Th, HREE) at the bottom of each unit to less evolved rocks (rich in Zr, Sr, and LREE) in the upper part of each unit. This can be explained by threetimes repeated exhausting of the stratified magma chamber.

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Copper mineralization in the Permian basalts of the Hronicum Unit, Slovakia

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ABSTRACT: Two types of copper mineralization occur in volcanic rocks of the Malu•iná Formation in the Kozie Chrbty Mts, and the Malé Karpaty Mts. Disseminated copper mineralization is related to carbonate-chlorite-quartz amygdales and veinlets. The younger vein type mineralization is bound to barite, barite-carbonate and quartz-carbonate veins. Both types of mineralization are hosted in basalts and andesites. The disseminated copper mineralization was formed due to the Permian post-volcanic hydrothermal activity. The vein type of mineralization is bound to faults formed during the Alpine overthrust of the Hronicum Unit. The mineral association represent chalcopyrite and bornite, accompanied by chalcocite, pyrite, covellite, digenite, tetrahedrite, tennantite, galena, sphalerite, arsenopyrite, gersdorffite, siegenite, carrollite, calcite, quartz, opal and chlorite.

KEY WORDS: basalt, copper minerals, barite, Slovakia, disseminated and vein mineralization.

Introduction

The Permian basic volcanism of the Hronicum Unit is characterized by barite and copper mineralization. The chemical composition of basic volcanic rocks corresponds to tholeiite and partly to calc-alkaline trend of volcanism (Vozár 1977). They underwent of the low grade regional metamorphism indicated by the presence of pumpellyite (Vrána 1965).

A disseminated copper mineralization hosted in basalts and andesites occurs in the uppermost part of the Malu•iná Formation at Kvetnica (Kantor 1951; Antaš 1963; Rojkovič 1990), Sološnica, Lošonec (Varček and Regásek 1962; Rojkovič 1990) and Malu•iná (Turan 1962; Petro 1974; Friedl 1985). Antaš (1963) distinguished at Kvetnica the older chalcopyrite mineralization within amygdales of the basalt and the younger vein quartz-chalcopyrite mineralization. Chalcopyrite is accompanied by chalcocite, bravoite, chalcedony and carbonate in amygdales and by calcite, pyrite, bornite, galena, sphalerite and gold in veinlets.

Methods

The optic and chemical characteristics of minerals were studied under the microscope in transmitted and reflected light, by scanning electron microscope (SEM), by wave-dispersion X-ray microanalysis (WDX), energy-dispersion X-ray microanalysis (EDX) and by X-ray diffraction analysis (XRD). Carbonates were analysed by volumetric and thermal analysis. The studies of fluid inclusions in barite provided homogenization temperatures. The rock analyses were carried out by X-ray fluorescence analysis (XFA), optical emission spectroscopy (OES) and instrumental neutron activation analysis (INAA).

Copper mineralization in the Malé Karpaty Mts.

The green amygdaloidal basalts is composed predominantly by plagioclases and chlorite. They are accompanied by relics of chloritized augite, epidote and apatite. Mineralized amygdales (up to 6 mm in size) are filled by calcite and chlorite, less by quartz. Magmatic ore minerals, as magnetite, ilmenite, are often altered to hematite, rutile and leucoxene. The copper mineralization is formed by bornite, chalcocite and pyrite. They are accompanied by chalcopyrite, digenite, covellite, idaite, sphalerite and galena.

Euhedral grains and aggregates of pyrite (up to several mm in size) are often cataclased. Chalcopyrite aggregates occur within amygdales or they are disseminated in quartz veinlets. Chalcopyrite is replaced by bornite aggregates of several mm in size. Bornite forms graphic intergrowths with chalcocite (Fig. 1) and veinlets in pyrite. The graphic intergrowths of bornite and chalcocite might document a disintegration of solid solution (Kostov et al. 1984). Bornite is close to stoichiometric composition with Cu/Fe atomic ratio 5.796. It does not correspond to a wide