

Microscopic examination of alkali-reactive volcanic rocks from the Bohemian Massif (Czech Republic)

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ABSTRACT

Volcanic rocks represent 34% of the crushed aggregates produced in the Czech Republic. This study focused on the quantification of the ASR of volcanic rocks under laboratory conditions. The accelerated mortar bar test and chemical test were combined with microscopic techniques (polarizing, electron, and cathodoluminescence microscopy); the aim being to quantify the ASR potential of volcanic rocks, and to identify alkali-reactive phases. Four groups of samples were distinguished, based on the expansion values of mortar bars: (I) samples showing a very low ASR potential; (II) samples showing a low-to-medium ASR potential; (III) samples showing a medium ASR potential; and (IV) samples showing a high ASR potential. The majority of samples were characterized by an ultrabasic to basic composition (Group I-III), intermediate (Group III), and acid (Group II-IV) composition (also present). The main factor found influencing ASR potential was the presence of SiO₂-rich phases and their association with feldspars.

Keywords: alkali-silica reaction, volcanic rocks, mortar bar test, alkaline leaching, microscopy

INTRODUCTION

High alkaline conditions, sufficient humidity, and the presence of reactive SiO₂-rich phases are the main factors causing an alkali-silica reaction (ASR) (e.g. St John et al., 1998). Formation of expansive alkali-silica gels leads to the formation of cracks, and decreases the durability of concrete and mortar constructions (e.g. Carse and Dux., 1990). In the last few decades, many methods have been proposed to assess whether the components of aggregates and concrete mixtures are prone to the formation of ASR. The most effective seems to be a combination of microscopic methods (polarizing and electron microscopy) and expansion tests (mortar-bar test) (e.g. Curtil and Habita, 1984; Haha et al., 2007). Chemical testing represents another approach of how to quantify the ASR potential of aggregates under laboratory conditions (e.g. Korkanc and Tugrul, 2005; Min et al., 2008).

Within the last two decades in the Czech Republic, several concrete structures were found to have deteriorated due to ASR (Šachlová et al., 2011; Šťastná et al., 2012). ASR has mainly

been attributed to the presence of volcanic and volcano-sedimentary rocks in concrete forming approximately 34% of the crushed aggregates produced in the Czech Republic (ČGS, 2012). Until 2012, there no experimental characterisations found of the ASR potential of these rocks. The current study aims include: (1) to quantify ASR potential of selected rocks under laboratory conditions; and (2) to identify alkali-reactive phases. The experimental methods consisted of the standard accelerated mortar bar test (AMBT), accompanied with microscopic techniques (polarizing, electron, and cathodoluminescence microscopy). Additionally, the ASR potential of the aggregates were tested, based on the leaching of aggregates in alkaline solution.

EXPERIMENTAL METHODS

Samples

Samples were selected based on the following criteria: (1) the rocks are of volcanic origin, located in the Bohemian Massif (Czech Republic, Tab. 1); and (2) rocks are quarried and used in the construction industry at present. The 0/4 mm (resp. 0/5 mm) fraction was sampled in the quarries (each sample of at least 15 kg). The samples were washed and sieved into the following narrow fractions (0/0.125, 0.125/0.25, 0.25/0.5, 0.5/1, 1/2, 2/4, 4/5).

Accelerated mortar bar test (AMBT) and chemical test

AMBT (following the ASTM C1260 standard) was used with the aim to quantify the ASR potential of studied aggregates. Three different mortar bar specimens were prepared from each sample using the 0.125/4, mm fraction, and tested in 1M NaOH solution at 80°C. Expansion of the mortar bar specimens was measured during a fourteen days test period. The testing was performed in cooperation with ZKK, Ltd.

Aggregate leaching in high alkaline solutions is the main principle of the chemical test (following the ASTM C289 standard). The 0.125/0.250 fraction (each sample 25 grams) was used, and put into Teflon bottles. A solution of 1 M NaOH (25 ml) was added into the bottles and mixed with the aggregates. The mixture was tempered at 80°C for 24 hours. After rapid cooling, the mixture was filtered and 20 ml of the solution was kept apart. The solution was diluted with distilled water at a ratio of 1:10. Part of the diluted solution was analysed using ICP OES, with the aim to detect Si content (performed in the Laboratories of the Geological Institutes, Faculty of Science, Charles University in Prague). Another solution was titrated using 0.05 M HCl and phenolphthalein, and the reduction of alkalinity was measured in the Laboratory of geochemistry (Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague).

Microscopic and geochemical techniques

Polarizing microscopy was performed in the Laboratory of microscopic techniques (Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague) using thin sections prepared from crushed aggregates of the 2/4 mm fraction. A LEICA DMLP polarizing microscope was employed and combined with an Olympus digital

camera. Cathodoluminescence (CL) was determined by using CCI 8200 Mk4 cold cathodoluminescence equipment coupled with a LEICA DMLP optical microscope. The electron energy applied to the thin sections was 15 - 18 kV, and the beam current was operated at 300 μ A. The cross polarized images (XPL) as well as luminescence colours of each lithotype were photographed with an Olympus digital camera.

The uncovered polished thin sections were coated in a carbon atmosphere. Scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS) was conducted at the Laboratory of Electron Microscopy and Microanalysis (Institute of Petrology and Structural Geology, Faculty of Science, Charles University in Prague; Dr. M. Racek operator). The microscopic images were taken using a backscattered electron detector (SEM-BSE). The measurements were performed on a Tescan Vega instrument, with an energy-dispersive analytical system (Oxford Instruments LINK ISIS 300) under the following conditions: 0.8 nA (for BSE, EDS); 120 s counting time; and a 15 kV accelerating voltage. A 53 Minerals Standard Set #02753-AB (SPI Supplies) was used for the standard quantitative calibration.

The chemical composition of whole rocks were determined by means of the standard wet silicate analysis performed in the Laboratories of the Geological Institutes, Faculty of Science, Charles University in Prague.

RESULTS

ASR according to the AMBT and chemical test

The samples studied indicate expansion (Δ) of the mortar bars, ranging from 0.001 to 0.282% (Tab. 1). Standard AMBT classification distinguishes two types of aggregates: non-reactive aggregates ($\Delta < 0.100\%$); and reactive aggregates ($\Delta > 0.100\%$). Most of the samples belong to the non-reactive aggregates type. Four groups were suggested with the aim to distinguish between the high variation of ASR potentials within the investigated samples:

- I. Samples indicating a very low ASR potential - $\Delta = 0.000 - 0.050\%$ (samples Nos. CZ12, CZ14, CZ20, CZ22, CZ23, CZ29, CZ31, CZ33, CZ34, CZ43);
- II. Samples indicating a low-to-medium ASR potential - $\Delta = 0.051 - 0.100\%$ (samples Nos. CZ18, CZ30);
- III. Samples indicating a medium ASR potential - $\Delta = 0.101 - 0.200\%$ (samples Nos. CZ17, CZ21, CZ45, CZ46);
- IV. Samples indicating a high ASR potential - $\Delta = > 0.200\%$ (sample No. CZ25).

Two different values were measured according to the chemical test: Si dissolved into solution (S_C) and reduction of alkalinity (R_C). S_C values varied between 4.66 and 247.70 mmol/l. R_C values varied between 163 - 673 mmol/l (Tab. 1). Both values indicate no potential to ASR, according to the ASTM C289 classification.

A detailed examination of the values showed small differences between samples of Group I and the other samples. Samples of Group I mostly indicate lower values of the reduction of alkalinity ($R_C = 163 - 628$ mmol/l), and lower values of Si content ($S_C = 4.7 - 61.9$ mmol/l) compared to the other samples ($R_C = 220 - 673$ mmol/l, $S_C = 7.7 - 247.7$ mmol/l).

Table 1. Expansion values of mortar bars (Exp), reduction of alkalinity (R_C), and Si dissolved into the solution (S_C), measured according to the chemical test. Experience with aggregate ASR potential in concrete (EC, after Šachlová et al., 2011): 0 no experience, - non-reactive, + reactive.

Sample No.	Quarry	Geologic Age	EC	Exp (%)	R_C (mmol/l)	S_C (mmol/l)
CZ 12	Košťálov	Permian-Carboniferous	0	0.023	163.00	61.89
CZ 14	Čísařský	Tertiary	0	0.004	266.67	27.80
CZ 17	Babí	Carboniferous	0	0.125	350.83	21.77
CZ 18	Doubravice	Permian-Carboniferous	0	0.071	310.00	247.70
CZ 20	Trnčí	Neoproterozoic	-	0.028	166.67	4.66
CZ 21	Těškov	Neoproterozoic	-	0.145	220.00	136.54
CZ 22	Čenkov	Neoproterozoic	0	0.001	628.00	5.37
CZ 23	Chrtníky	Palaeozoic	0	0.043	210.00	6.58
CZ 25	Zbraslav	Neoproterozoic	+	0.282	538.00	21.49
CZ 29	Libochovany	Tertiary	-	0.050	568.00	8.12
CZ 30	Královec	Permian	0	0.051	673.00	7.71
CZ 31	Všechlapy	Tertiary	0	0.014	255.00	16.98
CZ 33	Chaberce	Tertiary	0	0.024	338.33	12.50
CZ 34	Smrčí	Permian-Carboniferous	-	0.002	241.67	45.86
CZ 43	Litice	Neoproterozoic	-	0.046	348.00	5.90
CZ 45	Třebnuška	Neoproterozoic	0	0.172	320.00	32.80
CZ 46	Pňovany	Neoproterozoic	0	0.101	270.00	39.16

Mineralogical-petrographic and geochemical characterization

The studied samples exhibited a heterogeneous rock fabric within the selected groups. The intersertal texture was typical for fine- to medium-grained samples of Group I-IV (e.g. sample Nos. CZ22, CZ17, CZ25; Fig. 1A; 2D, G). The ophitic to porphyric texture with phenocrysts of plagioclase and pyroxene, as well as cryptocrystalline to fine-grained matrix, were identified in samples of Group I-III (e.g. sample Nos. CZ29, CZ18; Fig. 1D, G).

High variability was found in the mineral composition of the investigated samples. Group I consisted of ultrabasic (nephelinite-melilitite, tephrite-basanite, and picro-basalt composition); and basic (basalt and basalt-trachyandesite composition) volcanic rock types (classification of the rock types were based on the scheme suggested by Le Maitre et al., 1989, as well as Gillespie and Styles 1999, see Fig. 3). Na(Ca)-plagioclase (albite-andesine) (Fig. 1B) was in mineral assemblages with amphibole with no to dark CL (Fig. 1C). Ca(Na)-plagioclase (labradorite-bytownite) (dark brown-green CL) (Fig. 1C, F) was in mineral assemblages with zoisite (intense yellow-green CL) (Fig. 1C) or K-feldspar (intense blue CL) (Fig. 1F) and white mica (no to dark CL). Apart from those listed above, such minerals as pyroxene, chlorite, nepheline, olivine, and clay minerals (smectite) also occurred in the samples of Group I. This type of basic volcanic rock was altered by the secondary carbonate (calcite) with an intense orange CL (Fig. 1C, F). Accessory minerals such as apatite, titanite, ilmenite (Fig. 1E), and pyrite were present. The presence of quartz was very rare in Group I.

Rock types of Groups II and III belonged to basic (basalt and trachybasalt composition), intermediate (andesite composition) and/or acid (trachyte-trachydacite and rhyolite

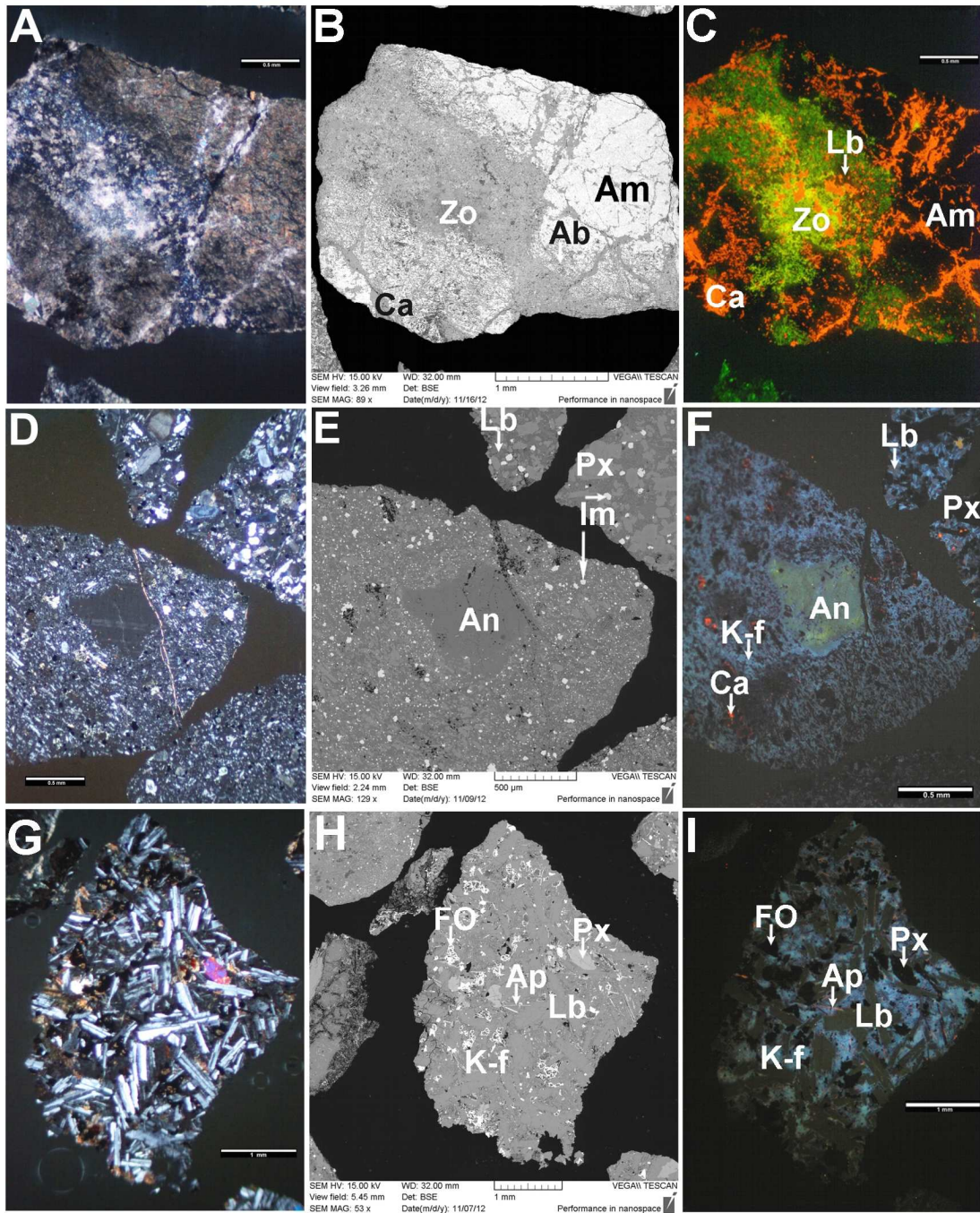


Figure 1. Overview of the microscopic images (from XPL: A, D, G; from SEM-BSE: B, E, H; and from CL: C, F, I) of Samples No. CZ22 (A, B, C), CZ29 (D, E, F), CZ18 (G, H, I). Mineral phases: Ab - albite; Am - amphibole; An - andesine; Ap - apatite; Ca - calcite; Ch - chlorite, K-f - K-feldspar; Im - ilmenite; Lb - labradorite; Px - pyroxene; Q - quartz; Zo - zoisite.

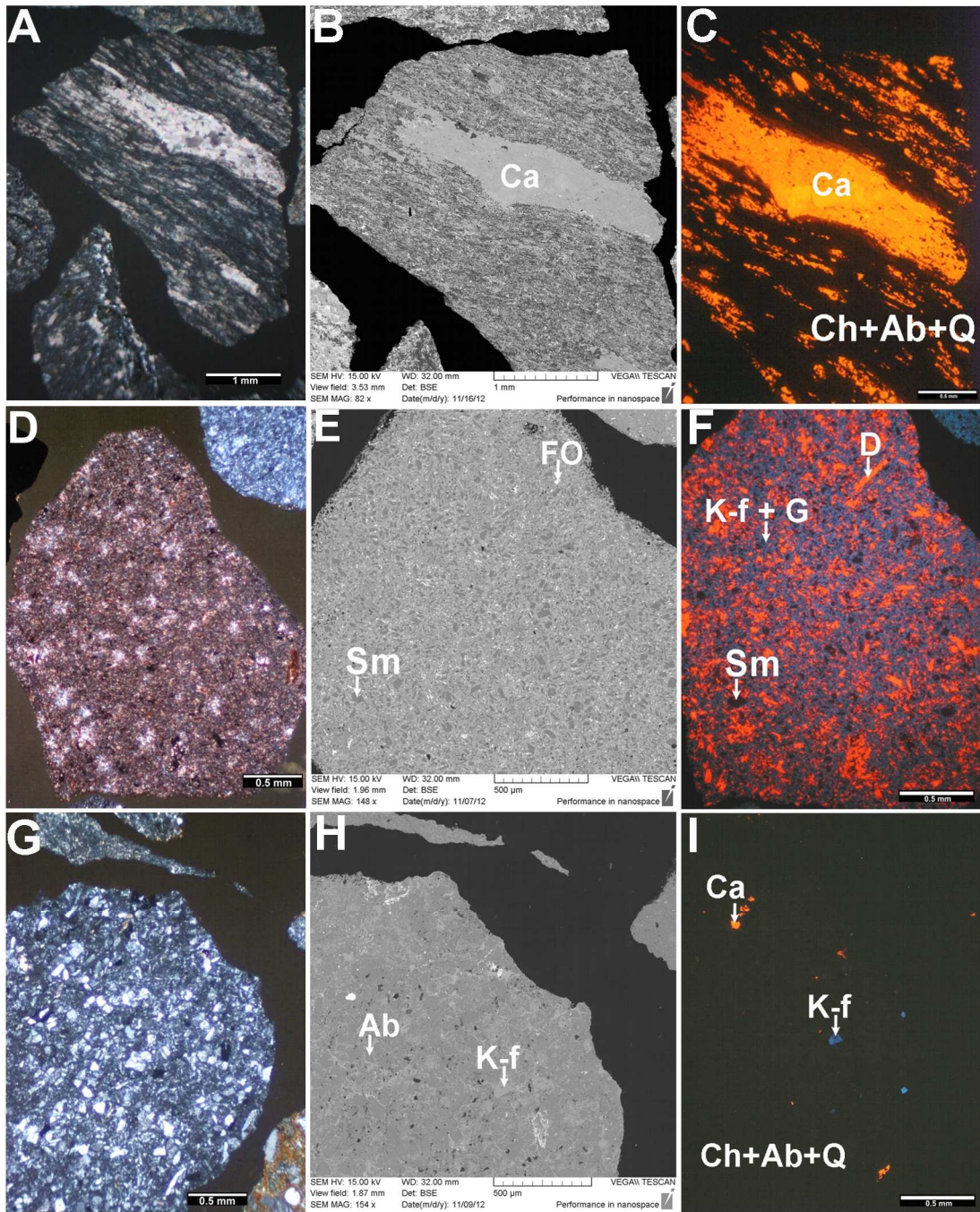


Figure 2. Overview of the microscopic images (from XPL: A, D, G; from SEM-BSE: B, E, H; and from CL: C, F, I) of Samples No. CZ46 (A, B, C), CZ17 (D, E, F), CZ25 (G, H, I). Mineral phases: Ab - albite; Ca - calcite; D - dolomite; FO - Fe-oxides; G - SiO₂-rich glass; Ch - chlorite, K-f - K-feldspar; Q - quartz; Sm - smectite.

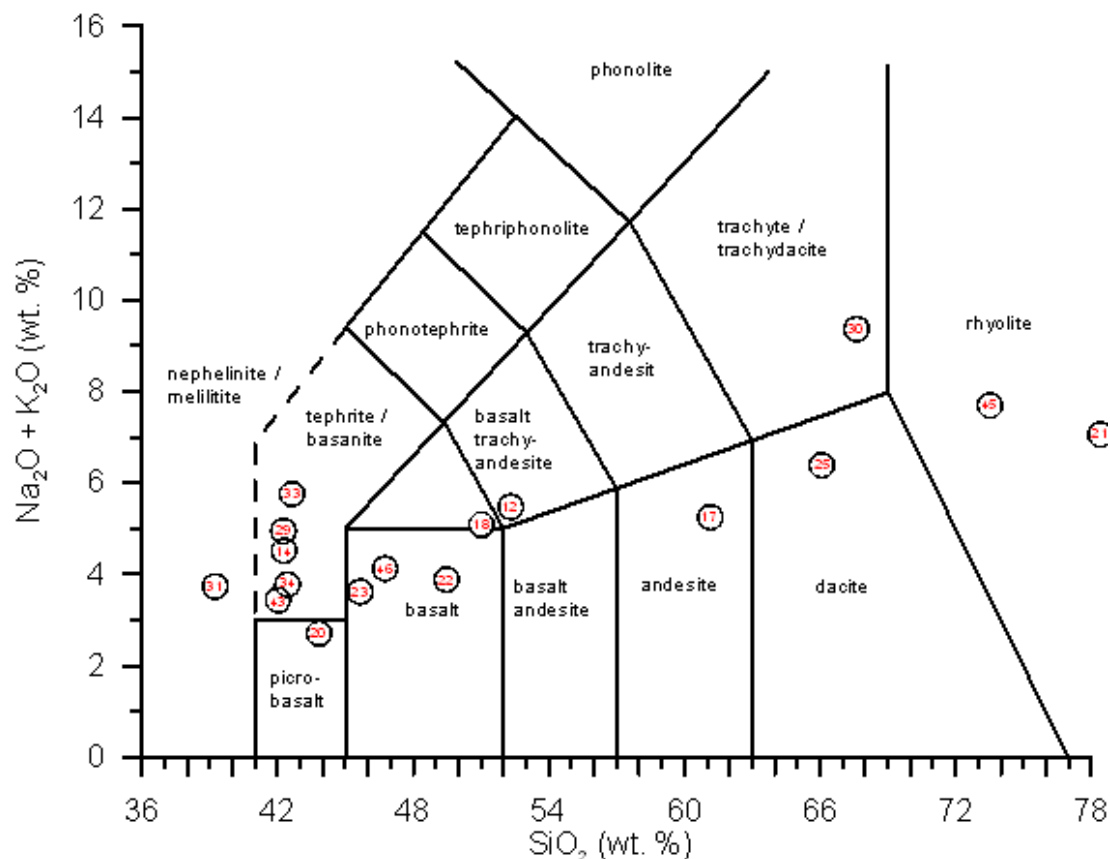


Figure 3. The TAS diagram for the studied samples. For sample numbers and associated quarries see Tab. 1.

composition) volcanic rocks (Fig. 3), which contained the Na-rich- (with no to dark CL), as well as Ca-rich- (dark brown-green CL) plagioclase feldspar (albite-labradorite) (Fig. 1I; 2C). K-feldspar (intense blue CL) was often accompanied by SiO₂-rich glass (no to dark CL) (Fig. 2E, F). Cryptocrystalline to fine-grained quartz (no to dark CL) was frequently present in the matrix in mineral assemblages with chlorite and albite (Fig. 2B, C). Various silicate minerals such as pyroxene (Fig. 1H, I), white mica, chlorite (Fig. 2C, D), and clay minerals (smectite) (Fig. 2E, F) exhibited no to dark CL. Calcite (intense orange CL) (Fig. 2C) and dolomite (intense red CL) (Fig. 2F) formed carbonate veins and intergranular fillings. Minor Fe- and Ti-oxides were non-luminescent on CL (Fig. 1H-I; 2E-F) and apatite exhibited yellow-green to orange CL (Fig. 1I).

Sample No. CZ 25, of acid composition (classified as dacite), occurred in Group IV (Fig. 2G-I, Fig. 3). The non-luminescent mineral assemblage including cryptocrystalline to fine-grained quartz, SiO₂-rich glass, Na-plagioclase (albite), chlorite, white mica, and clay minerals prevailed in these cases. Isolated grains of K-feldspar exhibited an intense blue CL (Fig. 2I). Pyrite and Fe oxide-hydroxides (all with no to dark CL) occurred as accessory minerals.

The volcanic rock types of all groups showed features of alteration. The spilitization was the most common process here when albitization of feldspar (plagioclase) and chloritization of

mafic minerals (pyroxene, amphibole) formed new mineral phases such as chlorite, calcite, epidote, zoisite, and other low-temperature hydrous crystallization products (Fig. 1A-C; 2A-C, G-I). Studied samples were often carbonatized including the very intense orange CL of calcite, which covered the CL of other mineral phases (see Fig. 1C and 2C).

DISCUSSION

Mineralogy of volcanic rocks affecting ASR

The main difference in the mineral composition of the aggregates was observed in the different compositions of plagioclases, presence of K-feldspars, presence of SiO₂-rich phases (quartz, cryptocrystalline quartz, and SiO₂-rich glass), as well as the presence of various mafic minerals. The mineralogical characteristics obtained by a combination of polarizing and cathodoluminescence microscopy proved to be helpful in the identification of the various mineral phases and microstructure, which has been discussed elsewhere (e.g. Götze, 2009; Štátná et al., 2012).

No correlation was found in the presence of carbonates, chlorite, mafic minerals (e.g. pyroxene, amphibole, olivine), accessory minerals (e.g. apatite, titanite, pyrite, Fe-oxides, Ti-oxides), and the ASR potential of the samples. All of the minerals mentioned above occur in all groups of the samples investigated. Katayama and Kaneshige (1987) attributed a decreasing ASR potential of volcanic rocks to an increasing degree of alteration and increasing content of chlorite. Our observations are not in accordance with the later statement. Chlorite was found in most of the investigated samples (e.g. chlorite occurred in significant amounts in the matrix of sample No. CZ25, which exhibited the highest ASR potential).

Significant differences were found in the presence of plagioclase, K-feldspars, quartz, and SiO₂-rich glass. Alkali-silica reactive samples (samples from Groups II - IV) preferentially contained albite and K-feldspar. In contrast, samples from Group I prevalingly contained plagioclase of (albite)andesine-to-labradorite composition and minor K-feldspars. The presence of SiO₂-rich glass and quartz was restricted to the samples from Groups II - IV. The high ASR potential of SiO₂-rich phases is well known (e.g. Wakizaka, 2000; Çopuroğlu et al., 2009). The influence of K-feldspar and albite is more complicated. Bérubé et al., (2002) documented the possible leaching of alkalis from alkali feldspars, and their contribution to ASR. This hypothesis has only been confirmed in a few cases (Constantiner and Diamond, 2003; Locati et al., 2010), and is explained by the role of cleavage zones, twins, and grain-grain contacts.

Reduction of alkalinity

The influence of mineral composition on R_C values was less visible, compared to its influence on ASR potential. Samples from Group I indicated slightly lower R_C values, compared to other investigated samples. There was expected to be a possible effect of SiO₂-rich phases (SiO₂-rich glass) on the R_C values. Increasing content of SiO₂-rich glass can increase R_C values (Wakizaka, 1998). The possible influence of clay minerals (smectites) on R_C has been found by several authors (e.g. Morino et al., 1987; Wakizaka et al., 1989; Wakizaka, 2000). The R_C values were suggested to be controlled by the cation exchange

capacity, derived from expanding clay minerals. In our study, smectite and other clay minerals were preferentially found in the samples indicating R_C values exceeding 300 mmol/l (e.g. samples Nos. CZ18, CZ25, CZ31, and CZ33), which were higher, compared to the rest of the samples investigated.

CONCLUSIONS

A combination of various microscopic techniques with both the accelerated mortar bar test and chemical test enabled us to distinguish the minerals contributing to the ASR potential of studied volcanic rocks from the Czech Republic. Rocks of ultrabasic and basic composition preferentially containing plagioclase and mafic minerals confirmed almost no ASR potential. ASR potential increased with increasing content of SiO₂-rich phases (SiO₂-rich glass and cryptocrystalline to fine-grained quartz), as well as K-feldspar. No correlation was found between ASR potential and the chlorite content. Reduction of alkalinity of the accelerating solution was found to be affected by the presence of clay minerals. On the contrary, no correlation was found between a reduction of alkalinity and the presence of SiO₂-rich phases.

The simple application of a chemical test underestimated alkali-reactivity of volcanic rocks coming from the Czech Republic. The alteration of the samples studied influenced the chemical test results. The application of microscopic techniques showed deleterious mineral phases in the samples, classified as non-reactive when the chemical test was employed. Moreover, mineralogical-petrographic results corresponded well with data from the accelerated mortar bar test.

ACKNOWLEDGEMENTS

This study, which makes part of Zuzana Nekvasilová Ph.D. study, was supported financially from the research project “Creating a database for measuring properties of rocks used for the production of crushed stone” provided by the Ministry of Environment of the Czech Republic; from project MSM 0021620855 “Material flow mechanisms in the upper spheres of the Earth”, Grant Agency of the Charles University No. 671112; as well as Project No. P104/12/0915 of the Czech Science Foundation.

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