Contribution to Petrochemical-mineralogical Characterization of Alteration Processes within the Marginal Facies of Rhyolitic Volcanics of Lower Permian Age, Thuringian Forest, Germany

Beitrag zur petrochemisch-mineralogischen Charakterisierung von Alterationsprozessen in der Randfazies unterpermischer rhyolithischer Vulkanite des Thüringer Waldes, Deutschland

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Abstract

Rhyolitic Rotliegend (lower Permian) -volcanics of the Thuringian Forest represent endogenous dome-like structures and some coherent lava flows. The outer part of their marginal facies, which forms the spherulite zone as an important facial part with dimensions in the decameter range, reflect processes of degassing and spherulitic crystallization at higher temperatures as well as alteration processes. Their petrochemical data differ significantly from those of the potassium-rich rhyolites in regular facies. Selected examples are given for the middle and northwestern range of the Thuringian Forest.

Star-shaped internal cavities of larger rhyolitic spherulites hosted within the spherulite zone demonstrate infillings of quartz, illite/chlorite, calcite and other paragenetic minerals sometimes. The rhyolitic wall rock, which surrounds the larger spherulites, has a distinct perlitic structure (altered residual volcanic glass).

The specific distribution of alkalis and alkaline-earth elements within the spheroidal shell of these rhyolitic spherulites is caused by crystallization processes of the so-called primary spherulites. After these post-magmatic distribution changes at higher temperatures, various alteration processes caused a further petrochemical and mineralogical discrimination, which was due to potassic alteration (K metasomatism), sodic albitization (Na metasomatism) and mainly low-temperature hydration (H respectively hydrogen metasomatism or argillic alteration) in different stages.

Silica enrichment within the rhyolites of the spherulite zone up to more than 80 wt.% SiO_2 was probably associated with K metasomatism. Regarding coherent lava flows silica assimilation may come further from the underlying sedimentary rocks.

The silicified spherulite zone served as the source for silica mobilization due to hydrogen metasomatism which caused deposition of chalcedony (agate) and macroquartz as one of the most important

alteration processes. This process generating infillings in the internal cavity of rhyolitic spherulites and in cracks is marked by suchlike secondary quartz mineralizations. It was caused by interactions of the rhyolites in the spherulite zone with meteoric and primary igneous waters as the source of the 6180-enriched solutions. Alteration processes affecting mafic minerals mobilized iron which was bond by formation of secondary hematite microlites. Illite accumulations reaching 3 to 18 wt.% within the altered residual volcanic glasses are characteristic for alkali mobilization. The mobilization of alkaline-earth elements reduced their contents within the spherulite zone, whereby calcium was bound at calcite in the internal cavity of larger rhyolitic spherulites. The scalenohedral calcite is considered to be cogenetic with the beginning of redeposition of silica as first wall-layered type agate.

Isotope compositions of agates and calcite III indicate low temperatures of formation (ca. 70-130 $^{\circ}$C). Alteration minerals (1 M-Illite) of the former residual volcanic glass within the spherulite zone, the Illite/chlorite association, calcite succession and secondary quartz in the internal cavity of rhyolitic spherulites, which were generated by low-temperature hydration, are characteristic for very low-grade metamorphism below 200 °C to demonstrate the low anchizone.

Kurzfassung

Nach Effusion der dom- bis stromförmigen rhyolithischen Rotliegendvulkanite hat sich im Ergebnis von Prozessen der Entgasung and sphärolithischen Kristallisation (Hochtemperatur-entglasung) sowie nachfolgender Alterationsprozesse eine charakteristische Randfazies im Deka-meterbereich herausgebildet, deren Gliederung and Merkmale beschrieben werden. Die zur äußeren Randfazies zählende Sphärolithzone, die einen wesentlichen Teil randfazieller Bildungen darstellt, weicht in ihren petrochemisch-mineralogischen Merkmalen von den weitgehend textur-losen Kalium-reichen Rhyolithen der Normalfazies ab, wie an ausgewählten Beispielen des mittleren bis nordwestlichen Thuringer Waldes dargelegt wird.

Gesondert betrachtet werden vor allem größere Sphärolithe innerhalb der Sphärolithzone, die im Inneren neben Quarz sowie Illit/Chlorit als weitere Mineralisationen Calcit and andere Para-geneseminerale enthalten, and von einem ausgeprägt perlitischen Rhyolith (alteriertes ehemaliges Restglas) umgeben sind. Abgesehen von der mit der Kristallisation dieser primären Sphärolithe verbundenen spezifischen Verteilung der Alkalien and Erdalkalien, unterlag die Sphärolithzone differenzierten Alterationsprozessen. Neben der potassic alteration (K-Metasomatose) bzw. sodic albitization (Na-Metasomatose), die mit einer sekundären Kalifeldspat- bzw. Albitbildung verbunden sind, bestimmen vor allem tiefthermale Hydratationsprozesse unter Beteiligung meteo-risch and magmatogen geprägter δ^{18}O-angereicherter Fluida im Sinne der Hydrogen-Metasomatose (argillic alteration) in unterschiedlichem Grad die petrochemischen Verhältnisse innerhalb der Sphärolithzone.

Die Anreicherung von SiO_2.auf über 80 Ma.% steht wahrscheinlich im Zusammenhang mit der Kalium-Metasomatose and ist darüber hinaus besonders bei romförmigen Vulkanitkörpern mit der Aufnahme aus dem Liegenden verbunden.

Das durch Silifizierung in der Sphärolithzone angereicherte SiO_2 wurde durch die Prozesse der Hydrogen-Metasomatose in der Folge von fluid/rock-Wechselwirkungen mobilisiert and als sekundärer Quarz (Achat, makrokristalliner Quarz) in Sphrälithen and Klüften akkumuliert. Durch Alteration der Mafite mobilisiertes Eisen liegt nach Oxidation vor allem in Hämatit-Mikrolithen in den randfaziellen Rhyolithen vor. Als charakteristische Mineralisation treten nach Mobilisierung der Alkalien vor allem Illite mit einem Anteil zwischen etwa 3 and 18 Ma.% im alterierten ehemaligen Restglas in Erscheinung. Die gleichfalls mobilisierten Erdalkalien weisen innerhalb der Sphärolithzone im wesentlichen ein Defizit auf, wobei Calcium wieder im Calcit innerhalb der rhyolithischen Sphärolithe gebunden wurde. Der skalenoedrische Calcit I gilt dabei als kogenetisch im Zusammenhang mit der beginnenden Redeposition des SiO_2 in Form des wandgebänderten Achats.

Unter anderem nach der isotopengeochemischen Charakteristik ist die Genese des Achats and Calcits der III. Abfolge zwischen etwa 70 and 130 °C einzuordnen. Alterationsminerale, wie insbesondere 1M-Illite im ehemaligen Restglas der Sphärolithzone sowie Illit/Chlorit, mehrere Calcit-Abfolgen and sekundärer Quarz im Inneren der rhyolithischen Sphärolithe, deuten unter den Bedingungen einer very low-grade Metamorphose auf die Ausbildung einer low Anchizone unter-halb 200 °C hin.

Introduction

Volcanic rocks and their tuffs are widespread as erosional remnants of intraorogenic Variscan volcanism of lower Permian age within an area of about 40 % of the Thuringian Forest (BENEK et al. 1987). As a whole of the volcanic sequences, rhyolitic rocks are prevalent in the so-called Ilmenau-, Oberhof- and Rotterode Formation of the Lower Rotliegend among the northeastern and southwestern borders of the Thuringian Forest (cf. Table 1). As MEISTER (1988, 1994) pointed out, lava domes are widely spread besides

Table 1. Survey to stratigraphy and position of selected marginal facies-sites within rhyolitic volcanics of the Ilmenau-, Oberhof -and Rotterode Formation (Lower Rotliegend), Thuringian Forest (cf. Fig. 1).

| Geological map (no.)	Locality (no.)	Stratigraphy	Position in petrofacies
Tambach-Dietharz (5229)	Köpfchen near Steinbach-Hallenberg (11)	Komberg Porphyry (Rotterode Formation)	upper (?) marginal facies
Waltershausen (5129)	Spießberghaus near Friedrichroda (5)	Regenberg Porphyry (Rotterode Formation)	lower marginal facies
Waltershausen (5129)	Brandkopf near Finsterbergen (19)	Regenberg Porphyry (Rotterode Formation)	lower marginal facies
Oberhof (5230)	Unteres Schwarzbachtal near Geraberg (15)	Younger Oberhof Quartz Porphyry (Oberhof Formation)	lower marginal facies
Waltershausen (5129)	Seebachsfelsen near Friedrichroda (4)	Older Oberhof Quartz Porphyry (Oberhof Formation)	upper (?) marginal facies
Oberhof (5230)	Mönchtal near Luisenthal (12)	Older Oberhof Quartz Porphyry (Oberhof Formation)	upper marginal facies
Suhl (5330)	Felsenschlag near Gehlberg (16)	Older Oberhof Quartz Porphyry (Oberhof Formation)	upper marginal facies
Tambach-Dietharz (5229)	Nesselhof near Tambach-Dietharz (7)	Older Oberhof Quartz Porphyry (Oberhof Formation)	lower marginal facies
Eisenach-Ost (5028)	Baumgartental near Thal (1)	Meisenstein Porphyry (Ilmenau Formation)	lower marginal facies
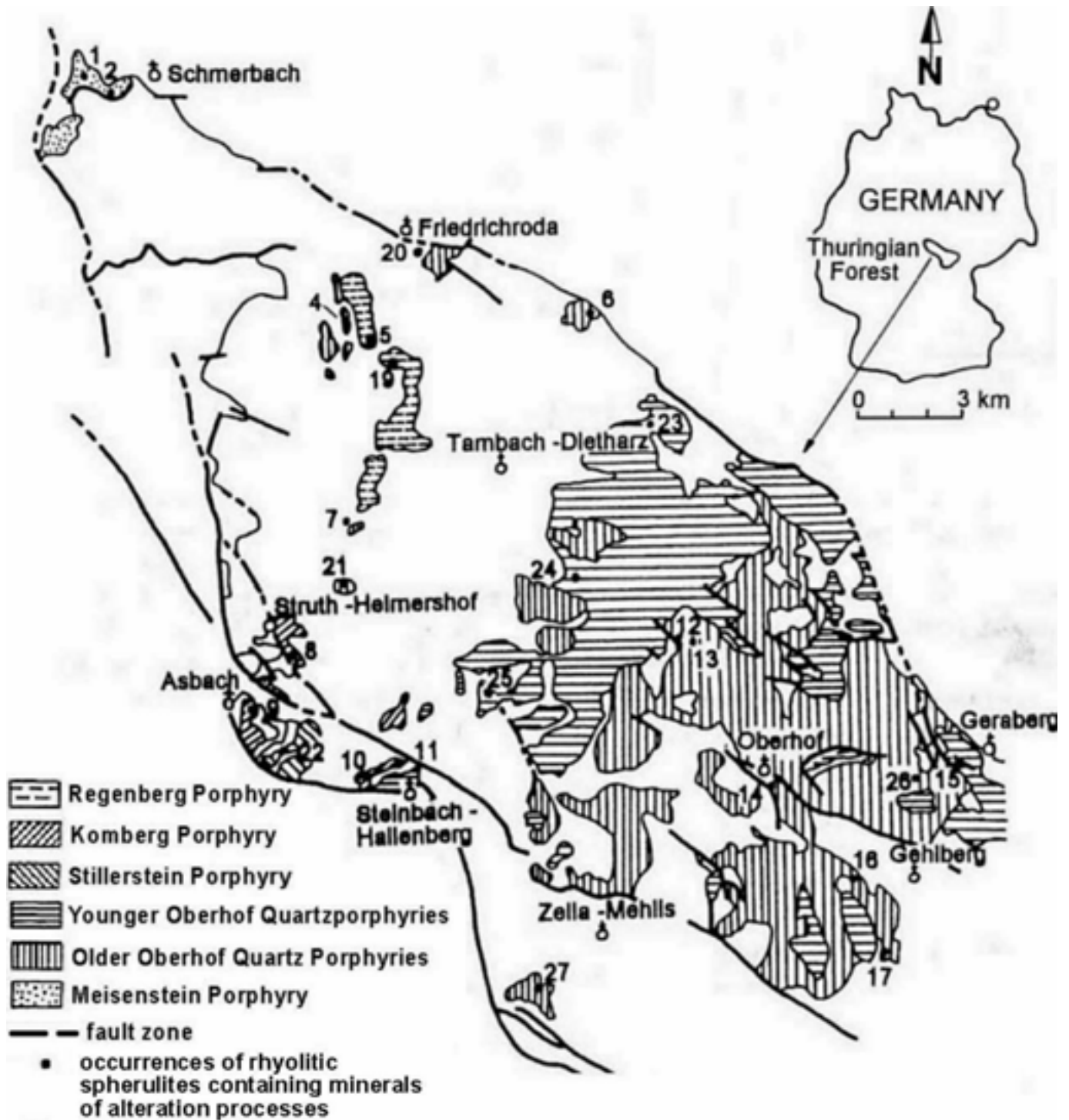
Figure 1. Sketch map of selected spherulite zones demonstrating larger rhyolitic spherulite-sites in relation to rhyolitic Lower Rotliegend-volcanics of the middle and northwestern range of the Thuringian Forest (localities cf. Table 1).

rhyolitic lava flows in the Oberhof region. The effusive to sub-effusive emplacement of these silica-rich volcanics was accompanied by the formation of a distinctive marginal facies. The specific petro-facial division of Oberhof Quartz Porphyries (ENDERLEIN and MÄDLER 1971)
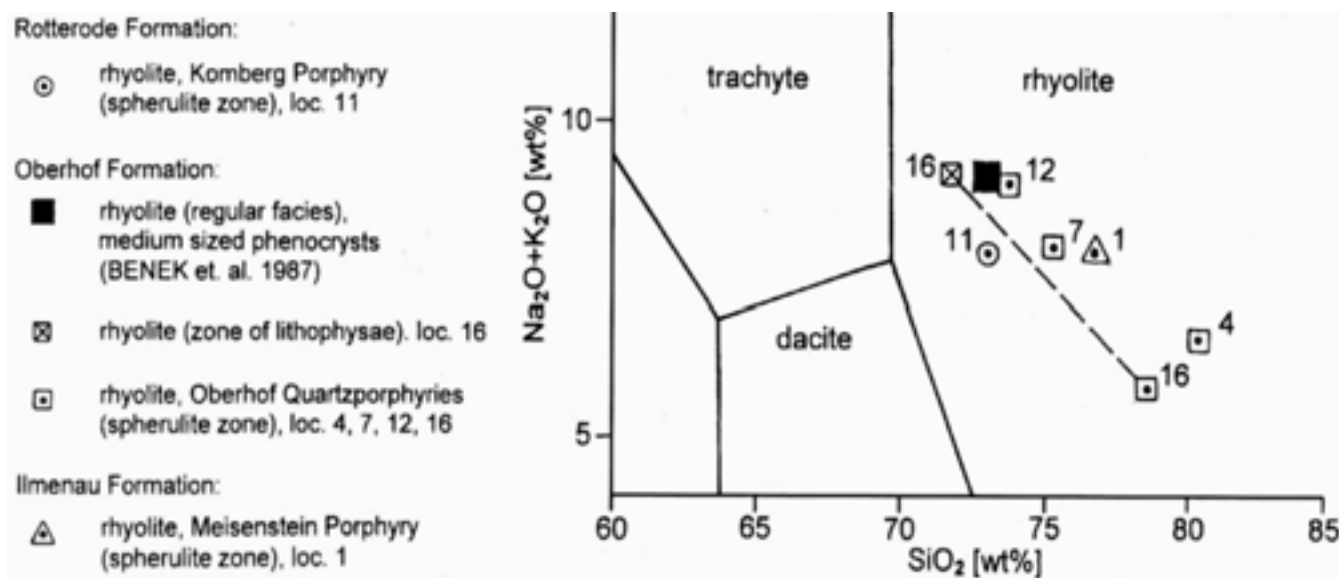
Figure 2. TAS diagram (LE MAITRE et al. 1989) of rhyolitic Lower Rotliegend-volcanics: Regular facies-rhyolite in comparison to selected marginal facies-rhyolites located in the Thuringian Forest.

facilitates to find out the boundaries of the volcanic sequences in question (cf. ENDERLEIN 1975). HOLZHEY (1993, 1994) and MEISTER (1988, 1994) extended and refined this facial division by taking into regard alteration processes following the devitrification and degassing processes within marginal parts of the rhyolitic volcanics.

In the past, a series of diploma theses at the Humboldt-University, Berlin (e.g. BARTMANN 1965; BEHRENDT 1961; BÖHNER 1966; FUNKE & SCHELLENBERG 1961; WEISSE 1965) were not (or not primarily) concerned with petrochemical relationships in general and post-magmatic processes in particular. Later on other related works refer to the regular- or normal facies of rhyolitic rocks (cf. ANDREAS et al. 1974; BENEK et al. 1987, ENDERLEIN and MÄDLER 1971; GRUNEWALD et al. 1990; LÜTZNER et al. 1995; MÄDLER. 1977; RÖLLIG and SCHIRMER 1978; SCHIRMER 1972). MÄDLER (1998a, b) specified the petrographic and petrochemical relationships also with respect to the marginal facies of Oberhof Quartz Porphyries in the area of Oberhof. GOLL (1996) determined ages of the low-temperature hydration of volcanics in the Thuringian Forest.

While former investigation dealt with other aspects (v. HOLZHEY 1993, 1999), this publication intends to present an initial chemical and mineralogical characterization of the spherulite zone of the marginal facies in lower Permian rhyolites in the Thuringian Forest (cf. MÄDLER 1998b). The spherulite zone (ENDERLEIN and MÄDLER 1971) of marginal facies will therefore be characterized qualitatively first time.

The data were measured and calculated at the former Zentralinstitut fur Physik der Erde (ZIPE), Potsdam.

According to BROWNE (1998), who points to investigations of "fluid-rock interactions" for silica-rich volcanics, the following considerations regard hydrothermal alteration processes, especially. As examples serve those localities (Table 1) which already can be distinguished in the field as spherulitic-perlitic rhyolites of the spherulite zone. The sketch map (Figure 1) provides an overview, where larger rhyolitic spherulites in terms of WILLIAMS et al. (1982) occur in the middle and northwestern range of the Thuringian Forest, which have a central internal cavity containing quartz and other alteration minerals.

Petrography/petrochemistry of rhyolitic Lower Rotliegend-volcanics (regular facies)

The rhyolitic volcanics of the Lower Rotliegend of Thuringian Forest are approximately uniform with respect to petrography and petrochemistry. However, they can be distinguished by mode and development of their phenocrysts. Post-magmatic re-crystallization processes caused the blurred, very fine to small-grained quartz/K feldspar implication texture of the groundmass which has nearly an eutectic composition (BENEK et al. 1987; LÜTZNER et al. 1995). MÄDLER (1998a) and MEISTER (1988) have demonstrated it for the Older Oberhof Quartz Porphyries (Oberhof Formation) especially.

The Oberhof Quartz Porphyries contain phenocrysts of K(Na-)feldspar, plagioclases, quartz, biotite and mostly pyroxene as well (v. ENDERLEIN and MÄDLER 1971; ANDREAS et al. 1974). BENEK et al. (1987) published petrochemical data displaying the dependency of phenocryst sizes. The Younger Oberhof Quartz Porphyries are distinguished from the Older by exhibiting only few and small phenocrysts of quartz and feldspar opposite to the medium to large sized phenocrysts (in general up to 10 mm, corresponding to the medium to coarse-grained facies after MEISTER 1988) in the Older ones. The phenocrysts of the Older Oberhof Quartz Porphyries make up 16 to about 41 vol.%. Plagioclase contents are almost exclusively reported only for the Older Oberhof Quartz Porphyries (ENDERLEIN and MÄDLER 1971; MEISTER 1988). SCHIRMER (1972) and ANDREAS et al. (1974) note 14 and 15 vol.% respectively as maximum.

Mafites (above all biotite and pyroxene) relating to rhyolites with larger phenocrysts reach contents of ca. 4.5 vol.% in contrast to the Younger Oberhof Quartz Porphyries (SCHIRMER 1972). Biotite altered preferably into hematite, whose microlites color the groundmass of rhyolites reddish-brown to reddish-gray. Alteration of feldspar phenocrysts may be partially recognized within the regular facies as well (cf. MÄDLER 1998a; MEISTER 1988).

The SiO_2 content of rhyolites with small phenocrysts is about 75 wt.%, whereas in those with larger phenocrysts it is lower with ca. 70 to 73 wt.% (BENEK et al. 1987; ENDERLEIN and MÄDLER 1971). The content of 73 % SiO_2 correspond to a normative quartz share (q, CIPW) of 35.6 wt.%. In the TAS diagram (Figure 2) all projection points fall within the discrimination field of rhyolitic rocks, including those of the rhyolites of marginal facies.
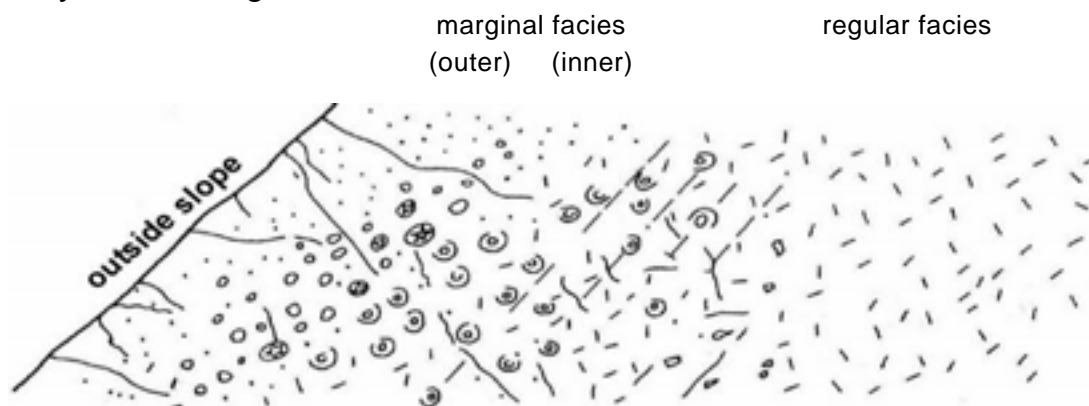

Figure 3. Schematic cross-section demonstrating the subdivision of the upper/lateral marginal facies concerning rhyolitic lava domes of Older Oberhof Quartz Porphyries.

As a characteristic feature of the major element chemistry the K_2O content generally increases up to 9 wt.% with decreasing phenocryst size (BENEK et al. 1987; ENDERLEIN and MÄDLER 1971; SCHIRMER 1972). MÄDLER (1977, 1998b) and LÜTZNER et al. (1995) report even higher K_2O contents up to 10 and 11 wt.% respectively.

The contents of Na_2O, TiO_2 and the low mass shares of CaO, Sr and Ba correlate inversely with K_2O (BENEK et al. 1987; MÄDLER 1977, 1998b). The analyses of BENEK et al. (1987) demonstrate an increase of the K_2O/Na_2O ratios from 5.4 and 6.2 respectively for rhyolites with large and medium sized phenocrysts, up to 20.4 for those with smaller ones, whereas MÄDLER (1977) even determined values up to 30. The potassium compensated sodium deficiency is attributed primary (BENEK et al. 1978; BUDZINSKI and GRUNEWALD 1990; MÄDLER 1977). With respect to this fact RÖLLIG and SCHIRMER (1978) pointed to "late-magmatic processes". In comparison to the rhyolites of the western part of the Oberhof Syncline those of the eastern part have higher values of the primarily increased Rb contents (MÄDLER 1977).

Characterization and subdivision of the marginal facies
of rhyolitic Lower Rotliegend-volcanics

Marginal facies which developed after effusion differs from the regular facies. Structural differences enable a subdivision of the marginal facies. The petrofacial position, as indicated in Table 1, documents marginal devitrification, degassing and alteration processes for different volcanic sequences as exemplified for several localities (v. HOLZHEY 1993, 1994, 1995).

Regarding the Older Oberhof Quartz Porphyries, formation of marginal facies was of prime importance for rhyolitic lava domes (cf. MEISTER 1988). K-feldspar phenocrysts are still partially sanidine within the rhyolites of marginal facies. The albitic shares of them have been determined by LÜTZNER et al. (1995) and GOLL (1996). According to MÄDLER (1998a), the Na_2O content of sanidine phenocrysts relating to Older Oberhof Quartz Porphyries comes in the mean to 2.8 wt.% close to locality 12.

It is to be expected, that the - primarily vitreous - basal, partly brecciated marginal zones of the rhyolitic sequences can reach thicknesaes of some 10 m up to 100 m (cf. LÁJCAKOVÁ and KRAUS 1993). MÄDLER (1998a) specified for the marginal facies of the Older Oberhof Quartz Porphyries apparent thicknesses up to ca. 25 m. At locality 15 near Geraberg (Table 1), marginal facies reaches a thickness of ca. 40 m (HOLZHEY 1996). Such thicknesses are in accordance with observations of FRIEDMAN and LONG (1984) as well as MANLEY and FINK (1987) for other regions.

The subdivision of the marginal facies of Oberhof Quartz Porphyries into a spherulite, perlite and a brecciated outer zone (ENDERLEIN and MÄDLER 1971; cf. LÜTZNER et al. 1995) revealed thickness variations including the disappearance of facial zones. MEISTER (1988) documented a subdivision into zones of an inner (lithophysal vug) and outer marginal facies regarding the rhyolitic lava domes.

With respect to the upper-, respectively lateral marginal facies, transitions occur from the internally almost massive (porphyric) facial zone (regular facies) to the inner marginal facies (lithophysal vug facies) or lithophysae zone. Figure 3 provides a cross section relating to the upper/lateral marginal facies of a rhyolitic lava dome. The zone of lithophysae shows joints parallel to the flow foliation (flow structure). It is followed outwards by a sharp defined zone characterized by a spherulitic-perlitic structure which is frequently olive-green colored. The groundmass of these rhyolites within the spherulite zone is micropoicilitic,
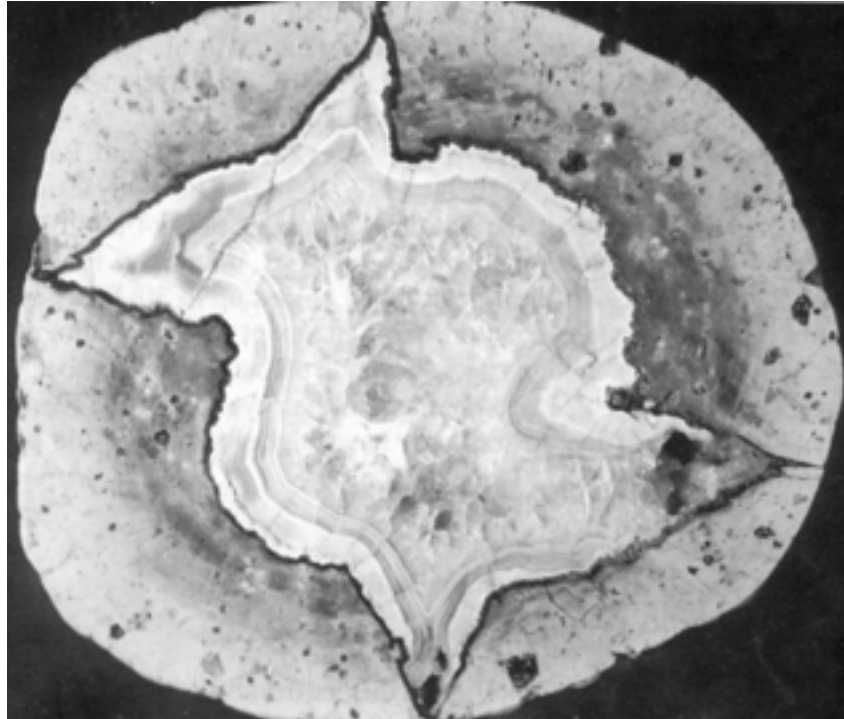
Figure 4. Polished section of a larger rhyolitic spherulite (∅ ca. 8 cm) from locality 7 which illustrates a wall-layered type agate - macroquartz succession as epigenetic infilling in the internal cavity; note: the rhyolitic spheroidal shell (H) reveals by change of color an outer shell (light gray, H 1) and an inner one (dark gray, H2).
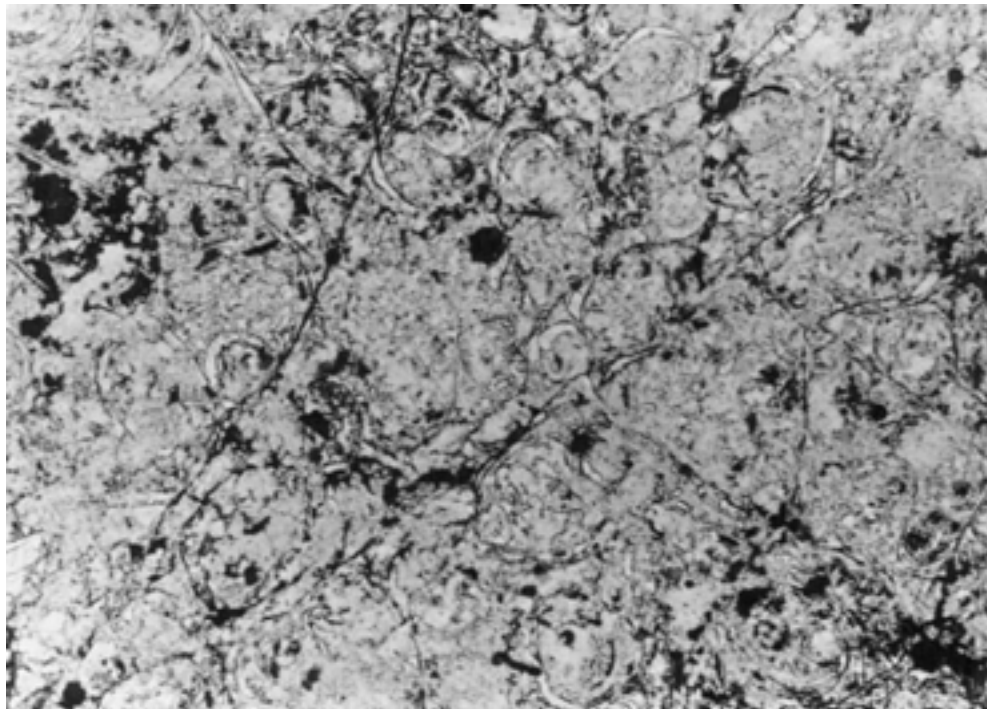

Figure 5. Thin section demonstrating perlitic rhyolite (altered residual volcanic glass, V2) which surrounds larger rhyolitic spherulites and includes alteration minerals (phyllosilicates; opaque: hematite microlites); locality 12; parallel polars, long edge of figure (l.e.f.) ca. 4 mm.

respectively partly fine- to coarse spherulitic (e.g. MÄDLER 1998a; MEISTER 1988) as a consequence of the spherulitic devitrification stage (LOFGREN 1971 a, b) probably passed through. The irregular contoured spherulite zone represents the outer marginal facies including the mainly perlitic, partly jointed and brecciated outermost zone of dome-like rhyolitic sequences in general. The distance of the spherulite zone to the margins of the investigated volcanic sequences varies between ca. 5 and 40 m (HOLZHEY 1993, 1994, 1996). The occurrence of larger spherulites with diameters up to decimeters within this facial zone is characteristic for selected sites which are illustrated at Figure 1. Processes of spherulitic crystallization may have produced masses of coalescing larger spherulites there. In this way, facial parts containing large rhyolitic spherulites represent an essential part of the spherulite zones.

Processes of crystallization/re-crystallization and alteration have superimposed the structure of rhyolitic spherulites (cf. HOLZHEY 1996; MÄDLER 1998a; MEISTER 1988). According to HOLZHEY (1993) an outer spheroidal shell (H1) can be distinguished already macroscopically from an inner one (H2) by their different discoloring (Figure 4). The larger spherulites surrounding wall rock enriched in clay minerals is marked "V2" as follows. Its color is predominantly-olive green, occasionally greenish-gray or violet- to reddish-brown and has a distinct perlitic structure (Figure 5). In accordance to this fact, the spherulite zones are differently colored as known from other regions as well (e.g. KELCH 1963; STETTNER and RICHTER 1993).

Post-magmatic changes within the marginal facies of rhyolitic Lower Rotliegend-volcanics

Post-magmatic processes lead to distribution changes of major- and trace elements within rhyolitic rocks regarding the marginal facies. The petrochemical and mineralogical characteristics of these partly spherulitic crystallized (devitrified), degassed and altered rocks differ markedly from those of the regular facies. Relevant changes, especially relating to the alkalis and alkaline-earth elements, are preferably caused by alteration processes as will be shown regarding the investigated spherulite zones. The following considerations comprise the spherulite zone as a whole as well as the unique larger rhyolitic spherulites in connection with perlitic rhyolite which surrounds them. The calcite succession in the central internal cavity of larger rhyolitic spherulites, which is characteristic for alteration processes, will be discussed below.

Petrochemical-mineralogical characteristics of the spherulite zone
Spherulitic-perlitic rhyolites

As for selected localities determined, spherulitic-perlitic rhyolites of the spherulite zone are SiO_2 enriched in common. In comparison to the regular facies (73 wt.% SiO_2) silica content is increased up to more than 80 wt.% SiO_2 (Table 2). MACLEAN (1990) states an average SiO_2 content increasing at 13.8 wt.% for most intense altered rhyolites of another region. The projection points of spherulitic-perlitic- to perlitic rhyolite, which surrounds the larger spherulites, fall between MACLEAN's alteration lines (Figure 6). The mass share of quartz inside the spherulite zone can increase up to more than 45 weight.%. The localities 4 and 6 (cf. Table 2) are examples demonstrating the enrichment (addition) of silica within the spherulite zone. Regarding the upper/lateral marginal facies of a rhyolitic lava dome (cf. Figure 3), only data for the lithophysae zone of locality 16 reveal partial de-silicification, indicated by a decrease of the SiO_2 content, whereas K_2O is increased in comparison to the regular facies- rhyolite.

Table 2. Petrochemistry (major and trace elements) of spherulitic-perlitic rhyolites (../V) of the spherulite zone at localities 1, 4, 7, 12, 16 and 11[1] in comparison to regular rhyolite facies[2] (data in % weight for major elements, in parts per million for trace elements).

	1/V	4/V	7/V	12/V	16/V	11/V	regular f.
SiO_2	76.6	80.4	75.2	73.6	78.6	73.0	73.0
Al_2O_3	11.1	10.8	12.7	12.7	10.2	12.8	12.8
TiO_2	0.11	0.14	0.12	0.31	0.19	0.30	0.19
Fe_2O_3	1.17	0.60	1.34	2.88	2.40	2.33	1.77
MnO	0.02	0.01	0.02	0.02	0.01	0.06	0.02
MgO	0.24	0.08	0.33	0.33	0.29	0.18	0.31
CaO	0.06	0.24	0.11	0.05	0.07	0.06	0.27
Na_2O	0.34	2.30	2.73	0.14	0.10	0.06	1.27
K_2O	7.60	4.20	5.30	8.90	5.70	7.90	7.83
P_2O_5	0.03	0.03	0.03	0.04	0.02	0.08	0.04
CO_2	0.17	0.48		0.56	0.36	0.23	
H_2O^+	1.72	0.75	1.15	0.66	1.56	1.92	
Σ	**99.16**	**100.03**	**99.03**	**99.69**	**99.50**	**99.82**	
F	400	115	80	80	632	870	
Cl	165	80	121	121	114	117	
B	71	41	16	16	60	85	
Ba	207	485	1467	1470	159	177	267
Be	3.6	7.4	2.4	3.8	2.6	3.4	
Cu	< 4	5	< 4	4	9	5	
Ga		10	12	12	11		
La	73	16	11	20	16	45	
Li	85	44	148	40	171	34	
Nb			10	9			
Pb		13	< 4	8	15		
Rb	240	173	154	546	449	297	278/428[X]
Sc	7.3	2.9	1.5	5.4	5.4	4.5	49
Sr	20	102	85	18	20	38	
V	10	3	< 3	12	9	21	
Y	24	56	27	23	21	36	
Zn	34	8	27	38	30	19	
Zr	141	181	217	278	262	236	250

[1] according to HOLZHEY (1993)

[2] rhyolites with medium size phenocrysts (BENEK et al. 1987)

[X] various Rb contents of rhyolites located in the eastern part of the Oberhof Syncline (MÄDLER 1977)

Table 3. Element ratios of spherulitic-perlitic rhyolites (../V) of the spherulite zone in comparison to regular facies rhyolite

	K_2O/Na_2O	$\dfrac{K_2O^{1)}}{(K_2O + Na_2O)}$	Ca/Sr	Rb/Zr
11/V	131.7	0.99	11.2	1.3
4/V	1.8	(0.65)	16.7	1.0
7/V	1.9	(0.66)	9.2	0.7
12/V	63.6	0.98	19.7	2.0
16/V	57.0	0.98	24.1	1.7
1/V	22.4	0.96	21.3	1.7
regular facies [2]	6.2	0.86	39.1	1.11/1.71[X]

[1] sericitization index

[2] rhyolites with medium sized phenocrysts (BENEK et al. 1987)

[X] concerning the different Rb contents of rhyolites located in the western and eastern part of the Oberhof Syncline (MÄDLER 1977)

The total alkali contents relating to the spherulitic-perlitic rhyolites of the spherulite zone are mostly reduced in comparison to the regular facies and point to a negative correlation in the TAS diagram (cf. Figure 2). The different alteration processes caused change of K_2O/Na_2O ratios and of sericitization index in terms of SHRIVER and MACLEAN (1993) as Table 3 demonstrates.

The Ca/Sr ratios are subjected to varying deviations inside the spherulite zone (Table 3) apart from the low Ca- and Sr contents of the regular facies (RÖLLIG and SCHIRMER 1978). The CaO content at locality 4, which is relatively raised in comparison to other localities (cf. Table 2), points to calcitization of feldspars (cc, CIPW = 0.37 wt.%) as discussed by MÄDLER (1998a) for the Older Oberhof Quartz Porphyries.

As Table 2 further shows, the Sr- and Ba contents may increase inside the spherulite zone, whereas Rb and F are decreased at localities in the western part of the Oberhof Syncline especially. The petrochemical discrimination between the western and eastern part of syncline referring to the Rb contents (MÄDLER 1977) is indicated by the Rb/Zr ratios as well (cf. Table 3).

In comparison to aluminum which is largely immobile with only low variations, contents of alkalis and alkaline-earth elements consequently point to a partly broad variation within the spherulite zone. According to the isocon-method, Figure 7 demonstrates mass changes of the major elements within the spherulite zone of the Older Oberhof Quartz Porphyry at localities 4, 7, 12, 16 and 11 (Komberg Porphyry). In comparison to the regular facies, depletions (losses) of CaO and partly MgO are characteristic altogether, whereas both K and Na contents are increased or reduced. Table 4 represents examples for a mass change calculation of the major elements. The used Al_2O_3 content is constant and equal to that of the regular facies (precursor composition: no addition or depletion of Al_2O_3). The mass change calculation includes the perlitic rhyolite (V2) which surrounds the larger spherulites. According to EWART (1971) it will be called as altered residual volcanic glass in the following text.
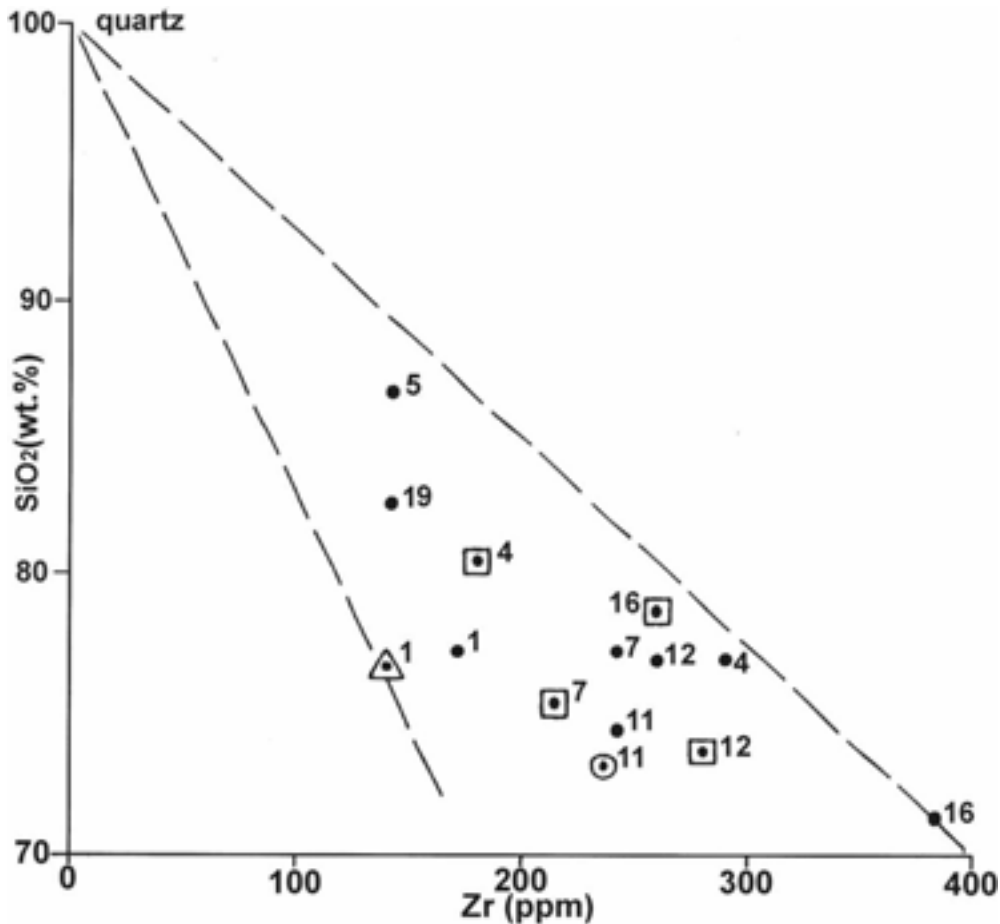
Figure 6. Plot of SiO$_2$ vs. Zr: Samples of spherulitic-perlitic rhyolites of the spherulite zone including altered residual volcanic glass (V2 - points) fall between the alteration lines; localities 1, 4, 5, 7, 12, 15, 16, 19 and 11 (data for localities 5 and 19: BLANKENBURG et al. 1983); explanation of symbols cf. Figure 2.

The spherulitic-perlitic rhyolite of the lower marginal facies relating to a coherent lava flow at locality 7 is characterized by a maximum of SiO$_2$ enrichment within larger spherulites represented by the highest quartz share as well (Table 5). Another difference, similar to locality 4, is indicated by an addition at 1,5 wt.% Na$_2$O and a depletion at 2.5 wt.% K$_2$O relating to the spherulitic-perlitic rhyolite (cf. Table 4). Albitic plagioclase prevails at localities 4 and 7 therefore. Correspondingly, the sericitization index is to low (cf. Table 3). This fact is in contrast to the predominance of K feldspar which characterize the spherulite zone of other localities (e.g. addition at ca. 2 wt.% K$_2$O at locality 12; cf. Tables 4 and 5). Altogether post-magmatic processes caused an increase of the Na$_2$O- and a decrease of the K$_2$O contents (e.g. localities 4 and 7) as well as the contrary (e.g. localities 12 and 16).

Frequently the Fe$_2$O$_3$ contents demonstrate enrichment processes inside the spherulite zone in comparison to the regular facies (cf. Table 2). Impregnations of hematite are accumulated within these altered spherulitic-perlitic rhyolites especially. Besides hematite as an alteration product of pyroxene (py, CIPW = 1.7 wt.% relating to rhyolites bearing medium sized phenocrysts), magnetite and chloritic mineralizations characterize the marginal facies of Older Oberhof Quartz Porphyries (MÄDLER 1998a).
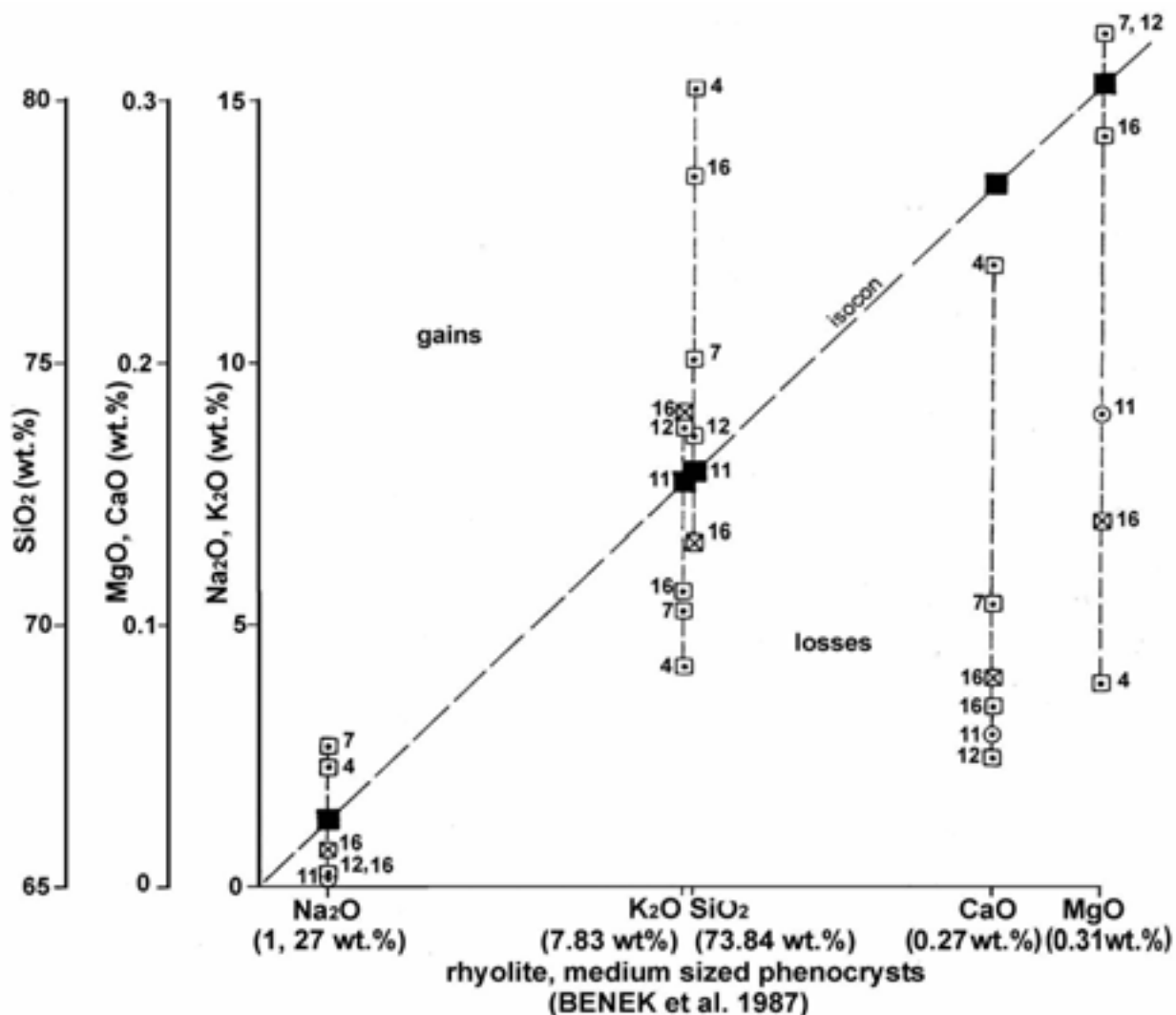
Figure 7. Enrichment (gains) and depletion (losses) of selected major elements within marginal facies-rhyolites in comparison to regular facies-rhyolite; localities 4, 7, 12, 16 and 11; explanation of symbols cf. Figure 2.

A further characteristic feature of alteration processes relating to the investigated spherulite zones is given in H_2O^+ contents up to nearly 2 wt.%. According to NOCKOLDS (1984) unto WEDEPOHL (1969) not, respectively only weakly altered rhyolites contain 0.8 wt.% of water in the mean. Rhyolitic lava flows originally contain 0.3 wt.% (FRIEDMAN and LONG 1984).

Altered residual volcanic glass/rhyolitic spherulites

As pointed out, there are differences between the perlitic rhyolite (V2 - altered residual volcanic glass) and the embedded unique larger rhyolitic spherulites relating to structure and petrochemistry. The residual volcanic glass surrounding the spherulites was altered by processes of low-temperature hydration (EPELBAUM and SALOVA 1988). It contains 4 wt.% of H_2O^+ at maximum. Normative quartz shares (q, CIPW) are partially increased up to 55 wt.% (e.g. locality 1). In a singular case (locality 7) SiO_2

content of the rhyolitic spherulites may be higher than that of the residual volcanic glass. Normally it is lower or equal within the spheroidal shells (H1 and H2, respectively H) of rhyolitic spherulites (cf. Table 5, Figure 8).

The total content of alkalis within the altered residual volcanic glass is lower than those regarding the spheroidal shells (localities 1, 5, 12, 15, 16) or equal (localities 4 and 11). Such results have been determined by BRYAN (1954) for another region. Reverse to this fact, the maximum of alkalis was detected within the altered residual volcanic glass at locality 7 only (Figure 9).

The K_2O and Ba contents and therefore of K-feldspar as well decrease from the outer spheroidal shell (H1) to the inner one (H2). The same fact is to be mentioned in case of TiO_2, whereas the Na_2O content (albitic plagioclase) increases (cf. Figures 8, 9). Comparable results were published by EWART (1971). The decrease of the Na_2O/K_2O ratios from the inner spheroidal shell to the outer one demonstrating at Table 6 is due to the predominance of Na_2O during the early stage of spherulitic crystallization (cf. VOLJANJUK 1972; YANEV 1988).

This enrichment of Na_2O within the inner part of the rhyolitic spherulites (inner spheroidal shell) is accompanied by a relative enrichment in CaO and MgO (HOLZHEY 1993). Calcium was enriched in a different manner within spherulites during spherulitic devitrification stage according to EWART (1971). The relatively high Na_2O, CaO and MgO contents decreased gradually during spherulitic crystallization from the inner (H2) to the outer shell (H1) of spherulites (cf. Figure 9) which is in accordance with results of FRIEDMAN and LONG (1984). Li/Mg ratios increased in progress of crystallization (HOLZHEY 1993). Enrichment of CaO points to the highest observed value (0.41 wt.%) within the inner spheroidal shell (H2) at locality 4. However, at localities 11 and 16 which represent most intense alteration processes regarding the spherulite zone located within upper marginal facies of lava domes, the maximum of CaO content can be proved for the altered residual volcanic glass (V2).

The MgO maximum relates to altered residual volcanic glass (V2) at all investigated localities (Figures 9 and 10). This is in accordance with results from other regions reported by BAIN (1926), BLANKENBURG

Table 4. Enrichment (gains) and depletion (losses) of major elements relating to spherulitic-perlitic rhyolites (../V) of the spherulite zone including perlitic rhyolite -altered residual volcanic glass (../V2) - at localities 7 and 12 and rhyolite of the lithophysae zone (l6/V^X) at locality 16 (data in wt.%).

	7/V	7/V2	12/V	12/V2	16/V ^{X}
SiO_2	+2.75	+8.52	+4.18	+13.84	-1.44
Al_2O_3	0	0	0	0	0
TiO_2	-0.07	-0.04	+0.14	+0.16	+0.10
Fe_2O_3	-0.42	-0.44	+1.25	+0.46	+1.03
MnO	0	-0.01	0	-0.01	0
MgO	+0.02	-0.15	+0.04	+0.22	-0.17
CaO	-0.16	-0.17	-0.22	-0.21	-0.19
Na_2O	+1.48	+1.36	-1.12	-0.69	-1.10
K_2O	-2.49	-2.12	+2.02	+0.33	+1.27

et al. (1983), Ewart (1971) and Junge et al. (1986). A zone of a few mm thickness which directly surrounds the spherulites near the border to the outer spheroidal shell is characterized by the highest MgO content. MgO is enriched up to 0,94 wt.% at locality l. This layer described by Philipp (1921) represents the so called "impurity layer" in terms of Lofgren (1971b).

Except localities 4 and 7, Fe_2O_3 contents reach a maximum up to 3.30 wt.% for the spherulites. Therefore, impregnations of hematite are observed within spherulites (Figures 5, 11) in accordance to Mädler (1998a). They were detected occasionally inside the altered residual volcanic glass as well (cf. Table 5). Probably due to low oxygen fugacity, gray to greenish colors of perlitic rhyolites prevail at locality 7. Red rock colors are restricted there on some parts of flow banded perlitic rhyolite which surrounds spherulites hosted within the coherent lava flow. Using the CIPW standard norm, the normative minerals hematite and magnetite are calculated for 1.0 and 0.4 wt.%, respectively. These concentrations are too low for quantification by X-ray diffractometry (cf. Table 5).

According to Byers et al. (1989) and Jentsch (1979), a release of halogens was connected with spherulitic crystallization during high-temperature devitrification in terms of Lofgren (1971a, b.). The enrichment in flourine, which is bond inside biotite and apatite as well as the altered

Table 5. X-ray powder diffraction analysis (XPD) and normative corundum (c, CIPW) of spherulitic-perlitic rhyolites (../V) of the spherulite zone including altered residual volcanic glass (../V2) and spheroidal shells of rhyolitic spherulites (H1 and H2, respectively H) at localities 1, 4, 7, 12, 16 and 1 (data in wt.%)[1].

	1/V	1/V2	1/H	4/V	4/V2	4/H1	4/H2	7/V	7/V2	7/H1	7/H2
quartz	42	43	40	46	33	44	39	36	33	57	56
K feldspar	55	40	54	38	55	47	49	39	45	30	27
albitic plagioclase	n	n	2	16	9	9	12	25	19	13	16
hematite	n	n	1	n	n	n	n	n	n	n	n
illite	3	17	3	n	3	n	n	n	3	n	1
c(CIPW)	2.33	4.03	1.33	2.13	2.88	1.80	1.37	2.40	2.08	1.62	1.44

	12/V	12/V2	12/Hl	12/H2	16V[x]	16/V	16/V2	l6/Hl	16/H2	11/V	11/V2	11/H
quartz	24	36	20	18	28	48	23	8	24	37	36	35
K feldspar	64	49	76	76	69	41	51	90	73	44	46	54
albitic plagioclase	n	3	n	3	n	n	6	n	n	n	n	n
hematite	2	n	2	n	3	2	2	2	3	2	1	2
illite	10	12	2	3	n	9	18	n	n	17	17	9
c(CIPW)	2.38	2.66	1.05	1.45	2.14	3.90	4.60	3.67	2.39	4.30	3.30	3.90

[1] according to Holzhey (1993)

16/V[x] - rhyolite of the lithophysae zone, locality 16
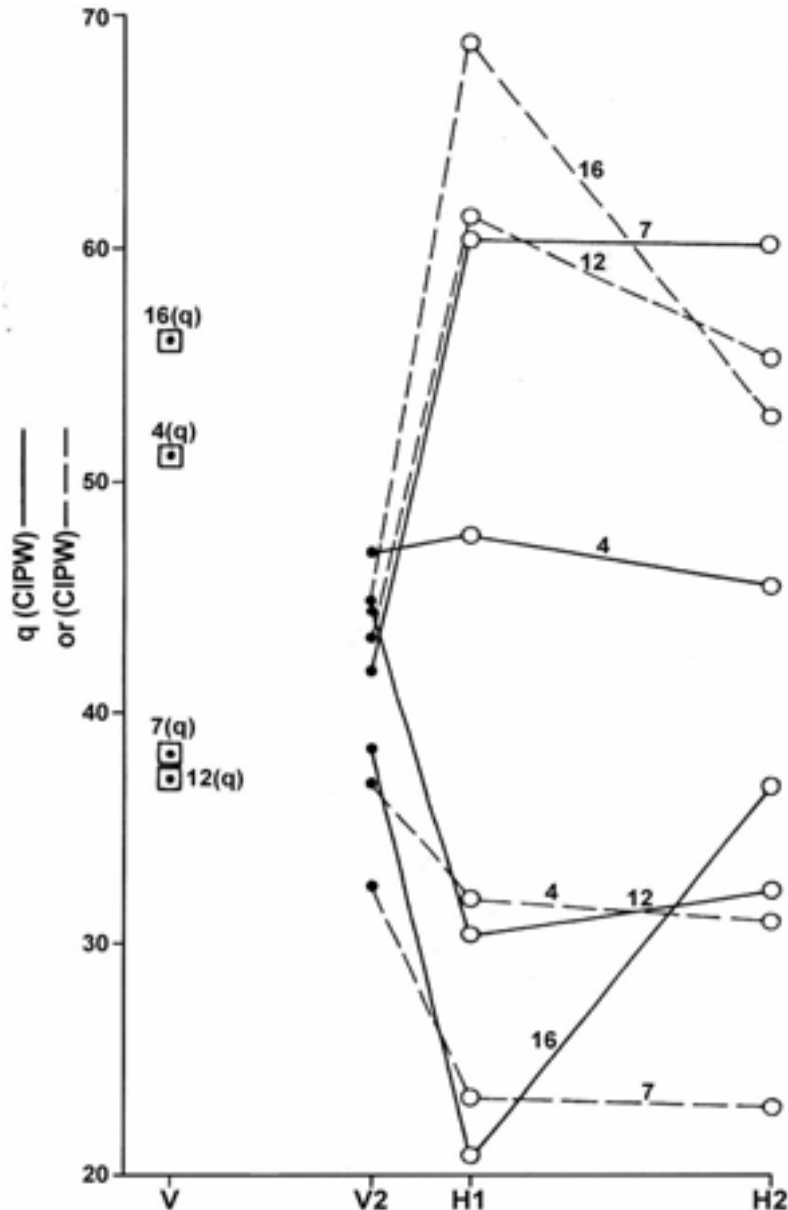
n - not detectable using XPD

Figure 8. Mass changes of the normative minerals quartz (q) and K feldspar (or) concerning spherulitic-perlitic rhyolites (V), spheroidal shells of rhyolitic spherulites (H1 and H2 - circles) and altered residual volcanic glass (V2 - points); localities 4, 7, 12, 16 (explanation of symbols cf. Figure 2).

residual volcanic glass (V2) themselves, can be proved for localities 1, 7, 12, 16 and 11. The maximum of fluorine concentration (1116 ppm) is reached within the "impurity layer" at locality 1. In opposite to this fluorine enrichment within the residual volcanic glass near the spherulites (Figure 12), high F- and CaO contents of the inner spheroidal shell (H2) point to the presence of fluorite- and calcite sequences which were detected in the central cavity of larger spherulites at locality 4 (HOLZHEY 1993, 1995). In general, the contents of fluorine and boron are relatively higher within the inner spheroidal shell (H2) as pointed out at figures 12 and 13. In comparison to the B content of rhyolites [in average 30 ppm after HARDER (1959)], boron is enriched within the spherulite zones mostly (cf. Table 2). Similar to fluorine, boron is enriched for a maximum within the altered former glass phase (V2) near the spherulites (Figure 13). The high boron contents are fixed at illite essentially (cf. HARDER 1961).

Table 6. Na_2O/K_2O ratios of spherulitic-perlitic rhyolites (V) of the spherulite zone including altered residual volcanic glass (V2) and spheroidal shells of rhyolitic spherulites (H, respectively H 1 and H2).

Locality (no.)	Na_2O/K_2O				
	V	V2	H	H1	H2
11	0.01	0.02	0.02	-	-
19 [1]	-	0.32	0.21	-	-
4	0.49	0.16	0.385 [X]	0.36	0.41
5 [1]	-	0.28	0.18	-	-
7	0.46	0.41	0.420 [X]	0.40	0.44
12	0.01	0.07	0.055 [X]	0.03	0.08
16	0.02	0.07	0.015 [X]	0.01	0.02
1	0.04	0.03	0.08	-	-

[1] according to data published from BLANKENBURG et al. (1983)

[X] average of H1 and H2

Table 7. Ca/Sr ratios of spherulitic-perlitic rhyolites (V) of the spherulite zone including altered residual volcanic glass (V2) and spheroidal shells of rhyolitic spherulites (H, respectively H1 and H2).

Locality (no.)	Ca/Sr				
	V	V2	H	H1	H2
11	11.2	24.4	16.6	-	-
19 [1]	-	0.32	0.21	-	-
4	16.7	11.8	34.3 [X]	20.8	47.8
5 [1]	-	3.9	3.1	-	-
7	9.2	7.0	7.4 [X]	7.1	7.6
12	19.7	12.7	21.8 [X]	18.4	25.1
16	24.1	51.4	5 1.8 [X]	47.7	55.8
1	21.3	14.2	13.4	-	-

[1] according to data published from BLANKENBURG et al. (1983)

[X] average of H1 and H2

Besides the characteristics of post-magmatic changes described above, phyllosilicates, above all illite accumulations, characterize the spherulite zones including the altered residual volcanic glass (V2) in particular. The highest contents of illite and normative corundum (c, CIPW) were detected within most intensively altered spherulite zones at localities 11 and 16 (cf. Table 5). Shares of normative corundum are about 0.8 wt.% lower within rhyolitic spherulites than those of the surrounding altered residual volcanic glass (Figure 14). According to X-ray powder diffractometry, illite mineralization represents concentrations from 3 up to 18 wt.%, regarding the altered glass and
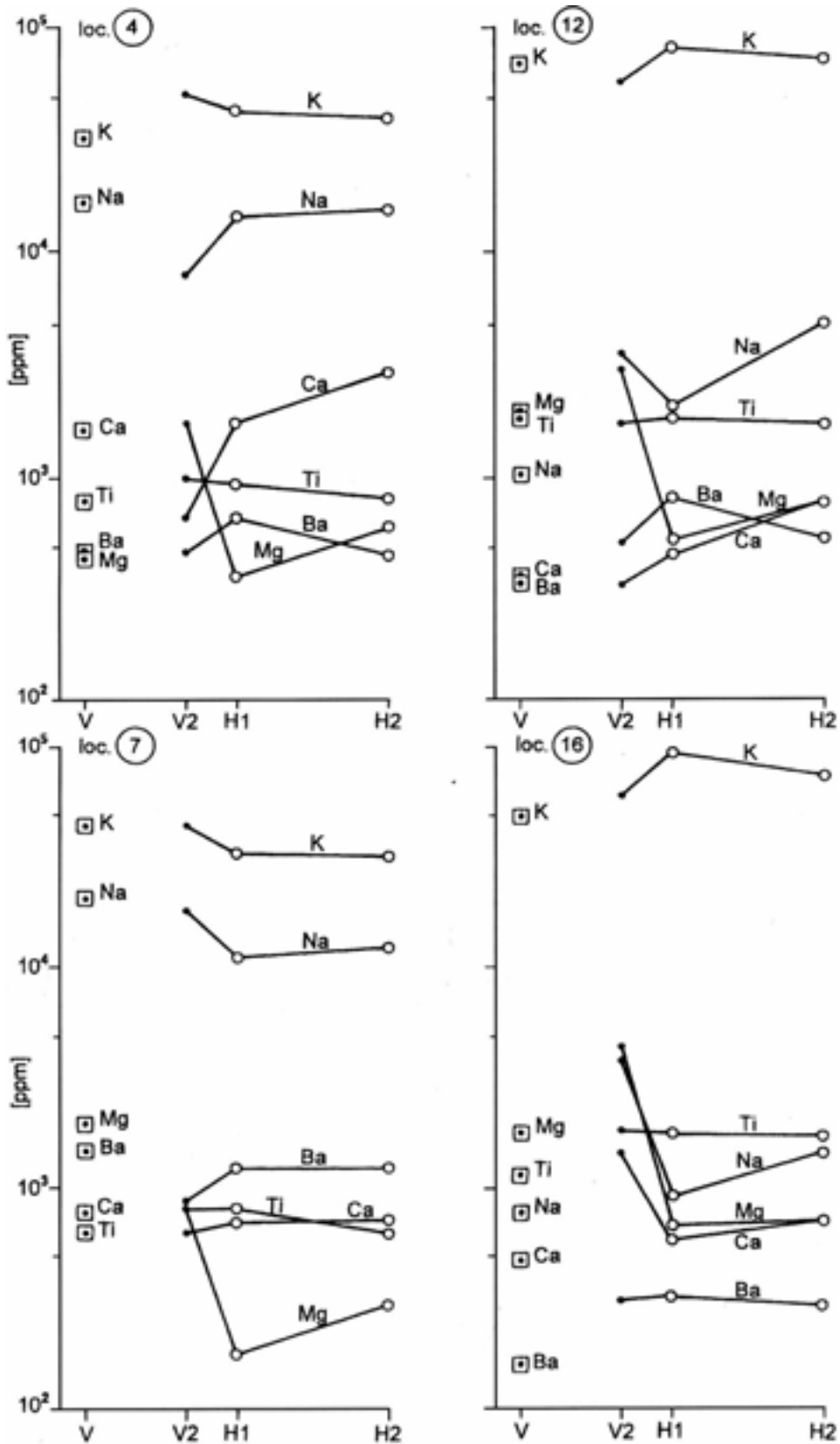
Figure 9. Mass changes of selected major elements concerning spherulitic-perlitic rhyolites (V), spheroidal shells of rhyolitic spherulites (H1 and H2 -circles) and altered residual volcanic glass (V2 -points); localities 4, 7, 12 16 (explanations of symbols cf. Figure 2).
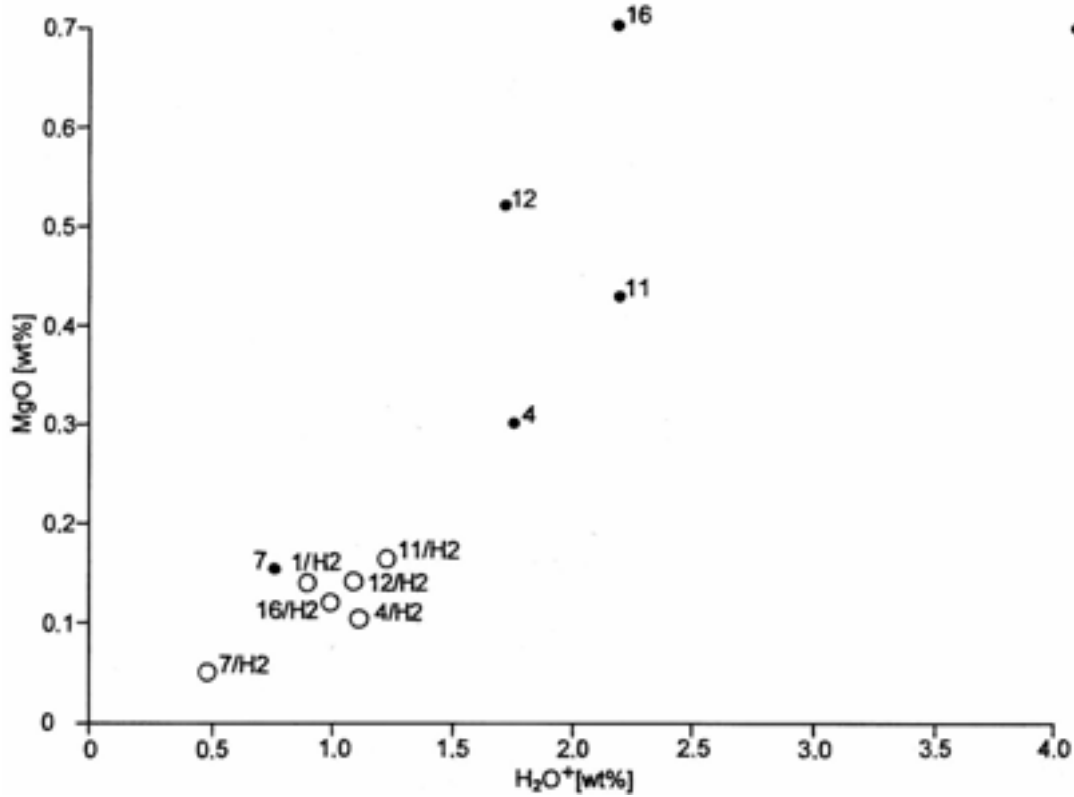
Figure 10. Plot of MgO vs. H_2O^+ of altered residual volcanic glass (V2- points) in comparison to the inner spheroidal shell (H2- circles) of rhyolitic spherulites; localities 1, 4, 7, 12, 16 and 11.
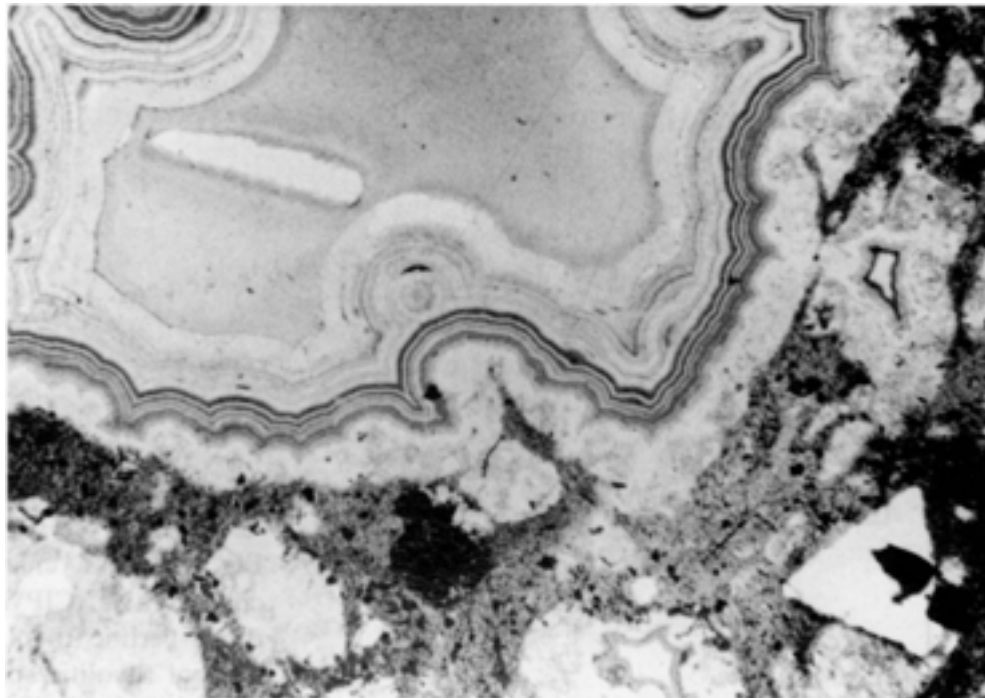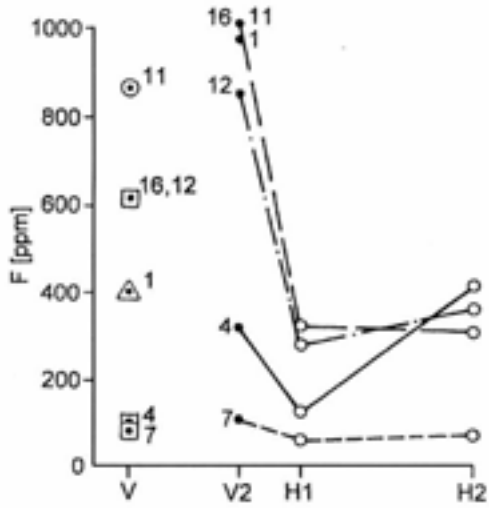

Figure 11. Thin section demonstrating wall-layered type agate as epigenetic infilling in the internal cavity and opaque hematite within the spheroidal shell of a small spherulite (*lithophysal)*; locality 1; parallel polars, l.e.f. ca. 8 mm.

Figure 12. Mass changes of flourine concerning spherulitic-perlitic rhyolites (V), spheroidal shells of rhyolitic spherulites (H1 and H2- circles) and altered residual volcanic glass (V2- points); localities 1, 4, 7, 12, 16 and 11 (explanation of symbols cf. Figure 2).
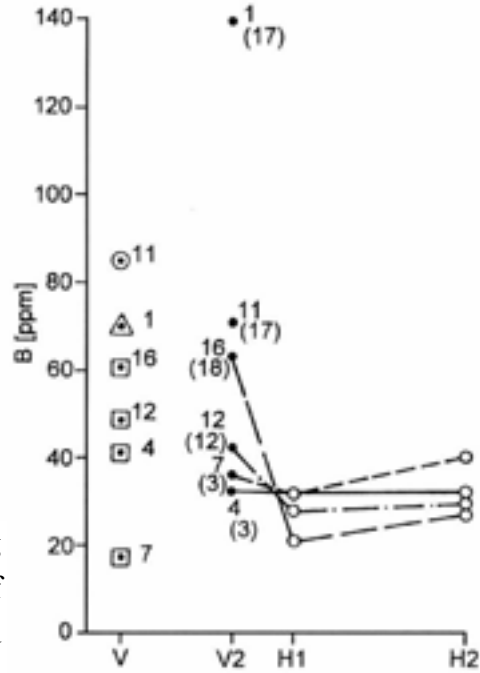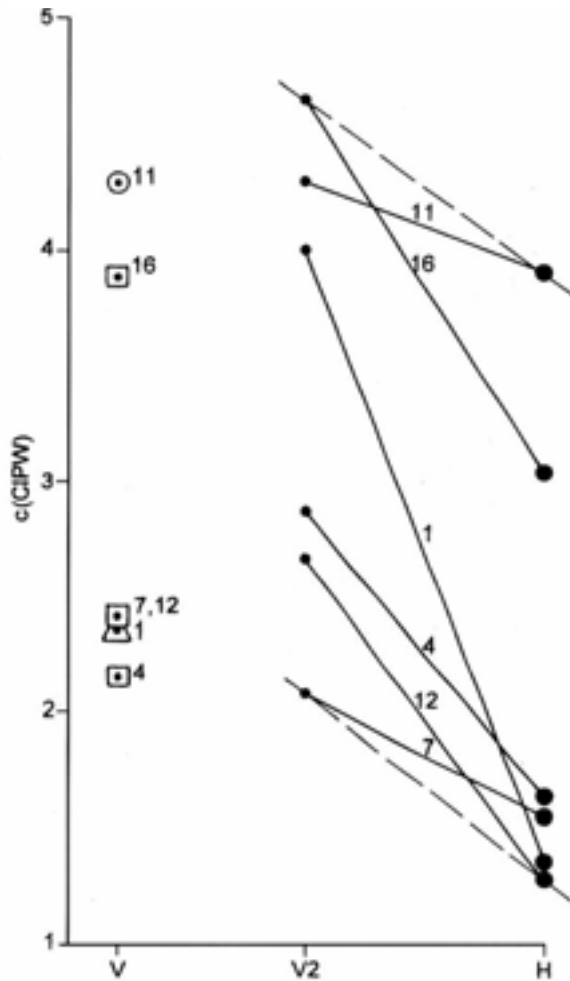

Figure 13. Mass changes of boron concerning spherulitic-perlitic rhyolites (V), spheroidal shells of rhyolitic spherulites (H1 and H2- circles) and altered residual volcanic glass (V2- points; in brackets: weight % illite); localities 1, 4, 7, 12, 16 and 11 (explanation of symbols cf. Figure 2)

Figure 14. Mass changes of normative corundum (c,CIPW) concerning spherulitic-perlitic rhyolites (V), spheroidal shell of rhyolitic spherulites (H= average of H1 and H2 - large points) and altered residual volcanic glass (V2 - small points); localities 1, 4, 7, 12, 16 and 11 (explanation of symbols cf. Figure 2).
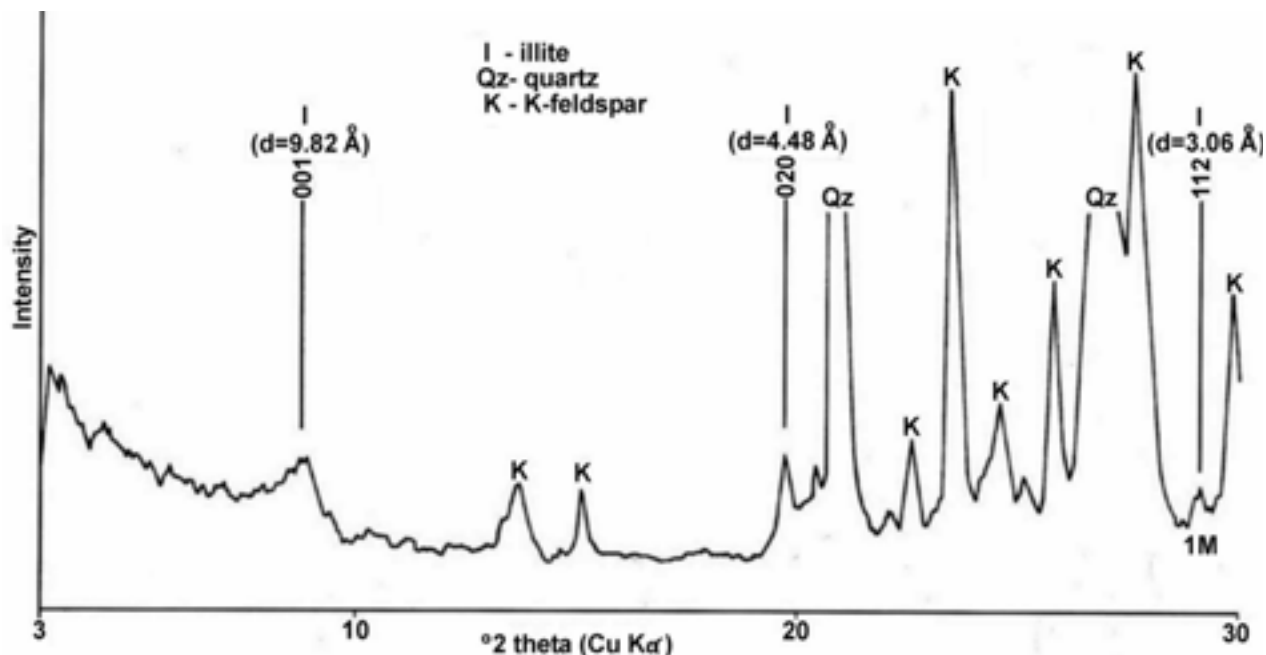
Figure 15. X-ray powder diffraction pattern (XPD) of altered residual volcanic glass (V2) which surrounds larger rhyolitic spherulites; locality 16.
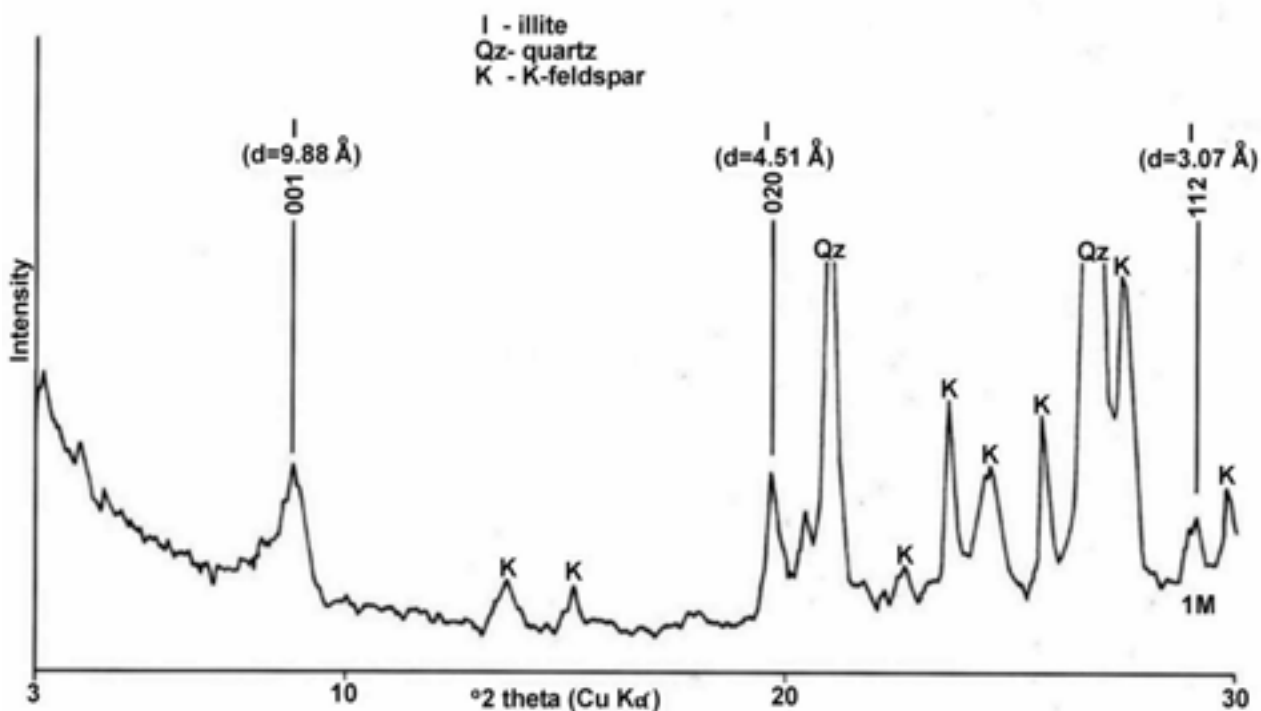

Figure 16. X-ray powder diffraction pattern (XPD) of the "impurity layer" near the border to the rhyolitic spherulite; locality 12.
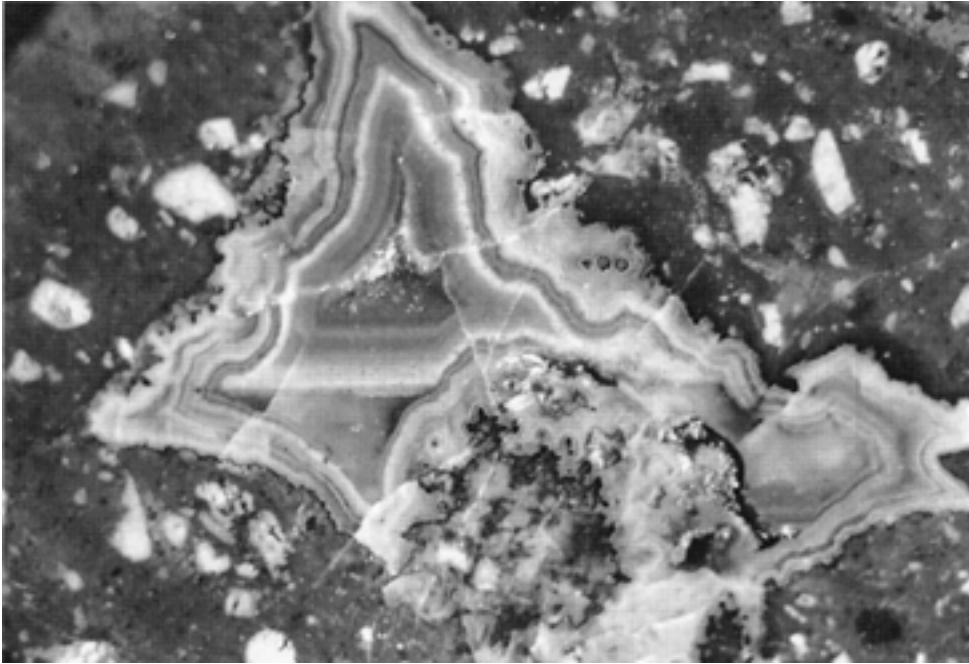
Figure 17. Polished section of a larger rhyolitic spherulite (cutting) from locality 12 which illustrates as epigenetic infilling in the internal cavity a phyllosilicate - agate - macroquartz succession; note: the "skin" of phyllosilicates (black) is followed by wall-layered and horizontally-layered type agate; l.e.f. ca. 5 cm; coll. Museum of Nature, Gotha (MNG 7557).

Figure 18. Polished section of a larger rhyolitic spherulite (Ø ca. 6 cm) from locality 7 which illustrates an internal breccia at the "bottom" of the cavity (composed of rhyolite-clasts embedded in a quartz/illite matrix), followed by a wall-layered type agate.

about 20 wt.% in particular for the "impurity layer" mentioned above. BLANKENBURG et al. (1983) published clay mineral shares of 4 and 5 weight % (locality 5 and locality 19 respectively). In comparison to the Thuringian Forest-rhyolites, a concentration of 10 weight % was published by SCHNEIDER (1968) for altered rhyolites located in the southern Harz Mountains. The illite accumulations within altered residual volcanic glass are based on processes of low-temperature mobilization, transport and redeposition of silica. The redeposition of silica as quartz infillings in the cavity of larger rhyolitic spherulites is derived from the intensively altered glass parts surrounding these spherulites (HOLZHEY 1993, 1995, 1999).

X-ray powder diffraction pattern of the altered residual volcanic glass show the illite 001-reflection at d ~ 10 Å and further reflections at d ~ 4.5 Å and d ~ 3.06 Å besides reflections of quartz and K feldspar (Figures 15, 16). The 112-reflection at d ~ 3.06 Å indicates the illite to be the 1M-polytype which is the characteristic alteration mineral hosted within perlitic cracks of the residual volcanic glass. The $2M_1$-polytype of illite is much less common as known hitherto. It has been identified by GOLL (1996) within marginal facies-rhyolites of the Jägerhaus Porphyry (Oberhof Formation).

Phyllosilicate mineralizations as first infilling in the internal cavity of larger rhyolitic spherulites are observed frequently as a green "skin" (Figure 17). Internal breccias at the "bottom" of these cavities (Figure 18) consist in the main of micro-granular quartz and of illite up to more than 10 weight % (HOLZHEY 1993). X-ray powder diffraction pattern points to the 1 M-polytype (Figure 19).

In addition, phyllosilicates, essentially illite and chlorite as characteristic alteration minerals, can be observed within pseudomorphs of quartz after scalenohedral calcite (Figures 20, 21, 22) as well as inside of the horizontally-layered type agate (Figure 23) in the internal cavity of larger rhyolitic spherulites (HOLZHEY 1997). Sequences of phyllosilicate mineralizations may be completed by micro-platy chlorite/1M-illite following on quartz as infillings in the internal cavity of larger spherulites are documented by X-ray powder diffraction pattern of a texture preparate (Fig. 24).
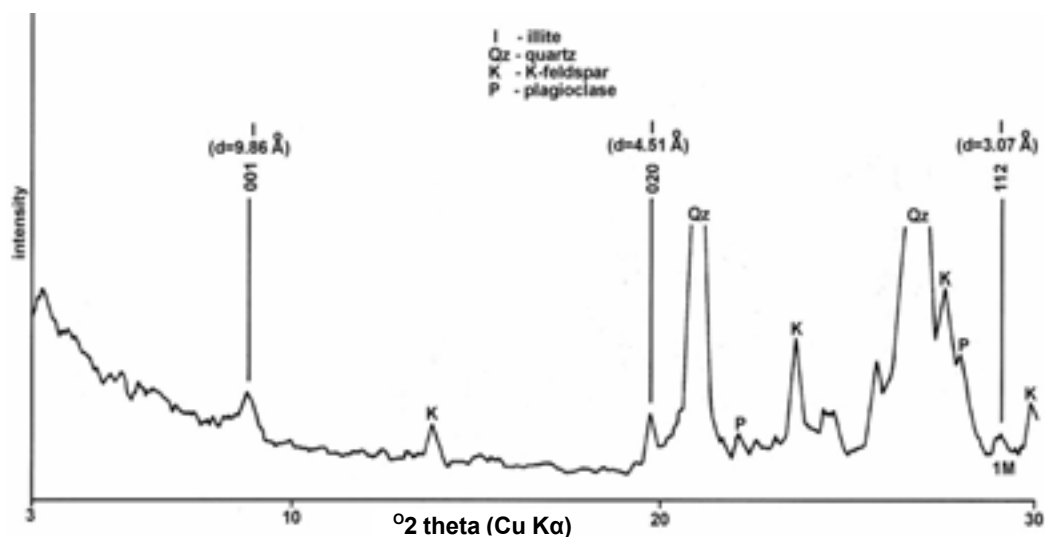

Figure 19. X-ray powder diffraction pattern (XPD) of an internal breccia in the internal cavity of a rhyolitic spherulite illustrated at Figure 18; locality 7.

Figure 20. Polished section of a larger rhyolitic spherulite (Ø ca. 7 cm) from locality 11 which illustrates as epigenetic infilling in the internal cavity a wall-layered type agate-macroquartz succession; note: quartz pseudomorph after scalenohedral calcite I (black) on the left hand wall of the cavity.

Figure 21. Polished section of a larger rhyolitic spherulite (cutting) from locality 16 which illustrates as epigenetic infilling in the internal cavity a repeated wall-layered type agate-macroquartz succession; note: quartz pseudomorph after scalenohedral calcite I (dark outline) on the lower-right wall of the cavity; l.e.f. ca. 5 cm. Collection Museum of Nature, Gotha (MNG 7396).
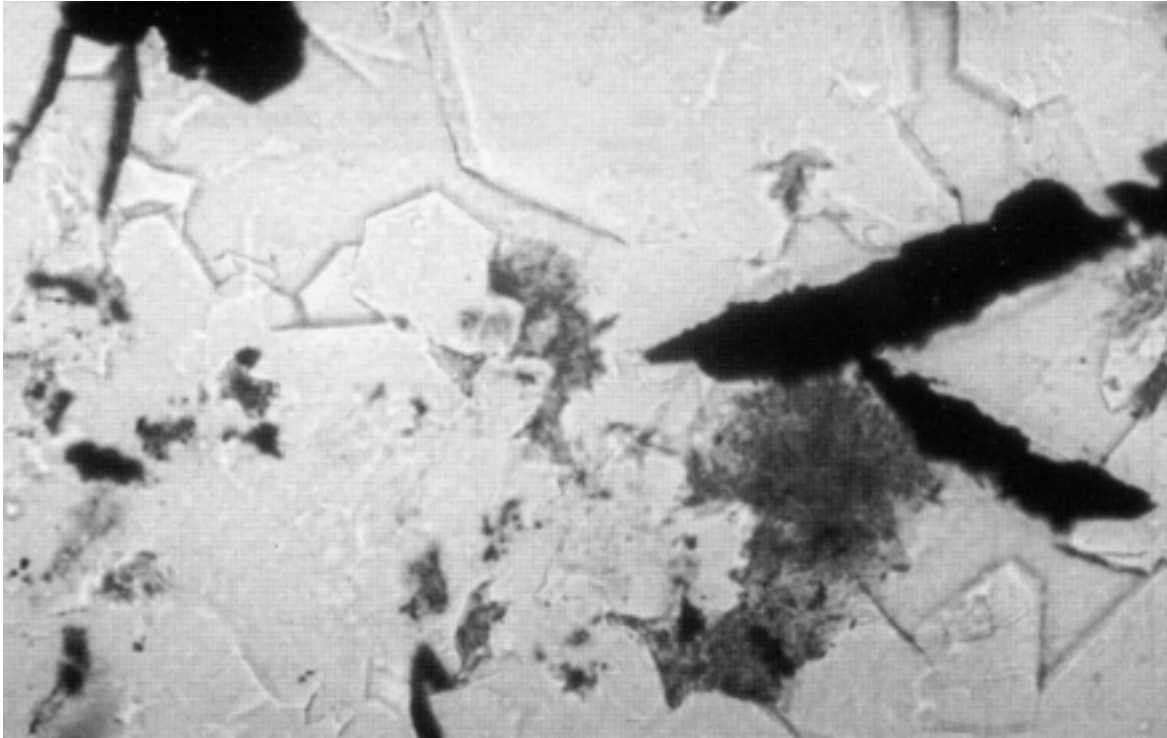
Figure 22. Thin section demonstrating phyllosilicates (gray-black) besides opaque hematite within macroquartz pseudomorph after calcite I from inside of a rhyolitic spherulite (cf. Figure 21); locality 16; parallel polars, l.e. f. ca. 0.6 mm.

Figure 23. Thin section demonstrating phyllosilicates (gray-black) within macroquartz of horizontally-layered type agate immediately below the border to macroquartz (upper field of micrograph) from inside of a spherulite; locality 4; parallel polars, l.e.f. ca. 0.6 mm.
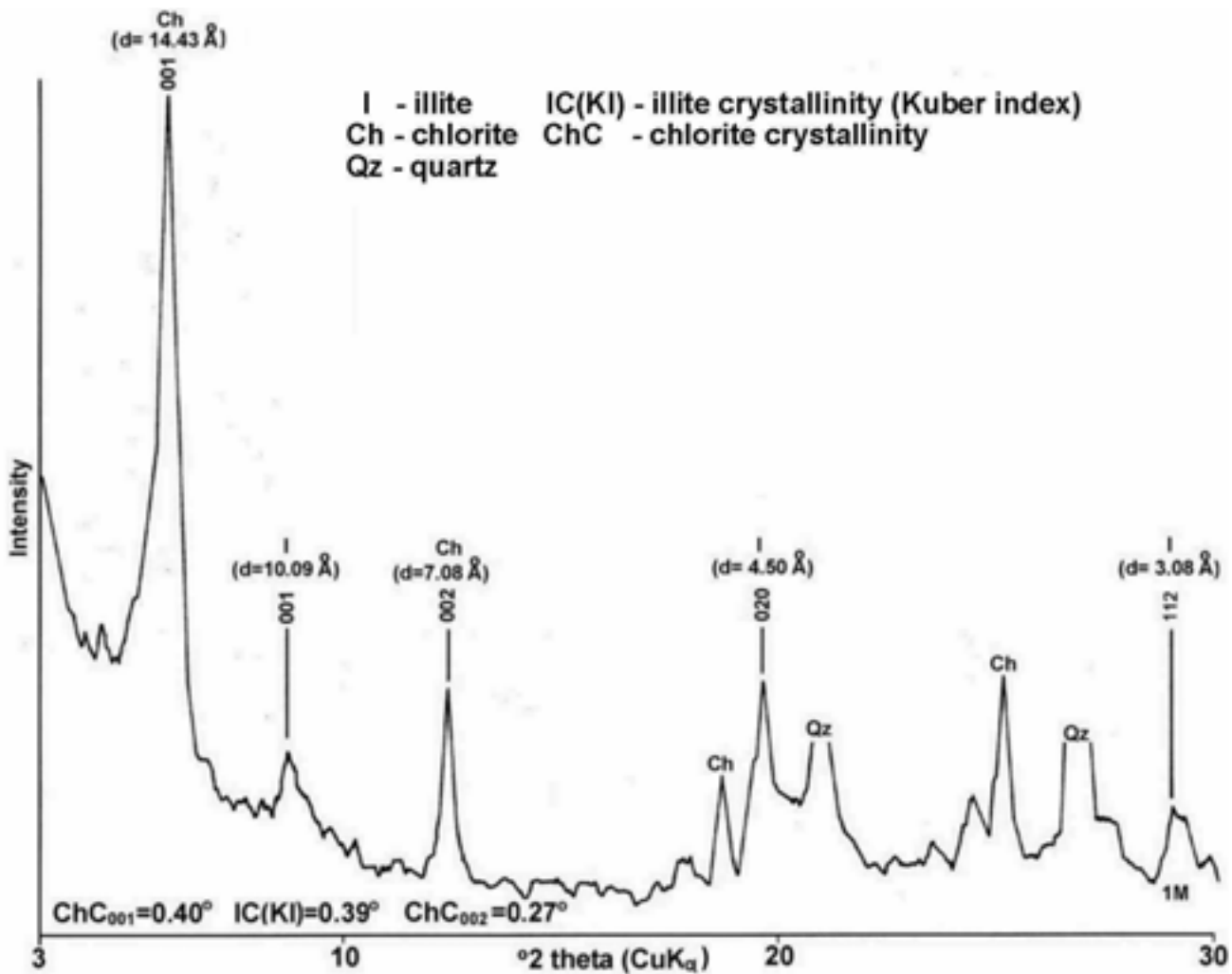
Figure 24. X-ray powder diffraction pattern (XPD) of macroquartz and alteration minerals (chlorite/illite) as epigenetic infillings in the internal cavity of a rhyolitic spherulite; locality 16.

Table 8. Succession of calcite as epigenetic infillings in the cavity of larger rhyolitic spherulites.

Locality (no.)	Sequence					
	Ia	Ib	IIa	II b	III	IV
11	Ps	-	-	-	Ca	-
4	-	P	-	P/Ps	Ca	Ca
7	-	P	-	-	-	-
12	Ps	Ps	-	p	-	-
16	Ps	P	Ps	P	Ca	-
1	P	-	-	Ps	-	-

Ca - calcite

P - encrustation pseudomorphs of calcite

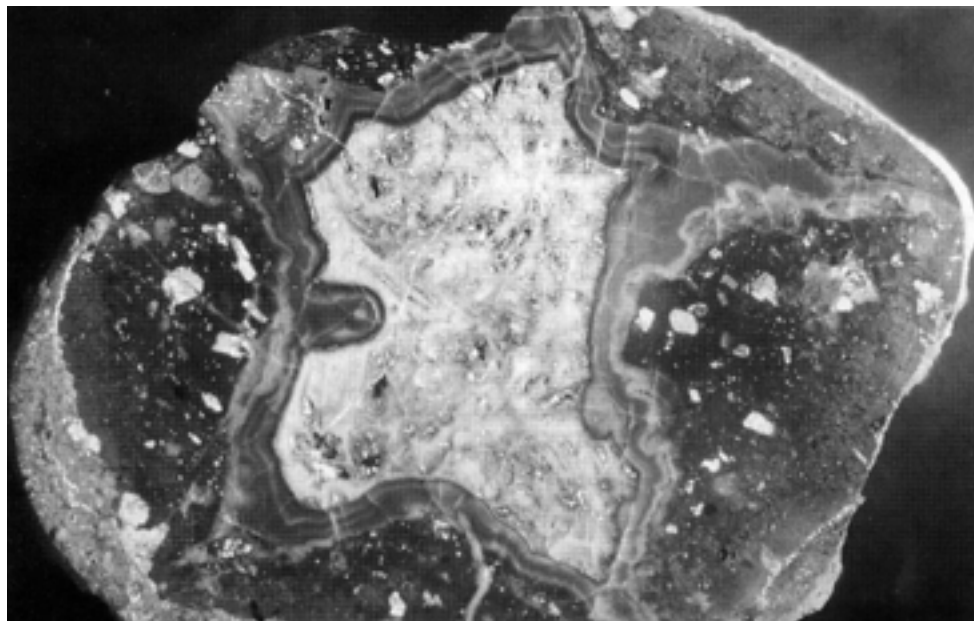Ps - pseudomorphs of quartz after calcite

Figure 25. Polished section of a larger rhyolitic spherulite from locality 16 which illustrates as epigenetic infilling in the internal cavity the succession wall-layered type agate - macroquartz; note: quartz demonstrates pseudomorphs after platy calcite (?); l.e.f. ca. 10 cm.

Sequences of calcite in the internal cavity of rhyolitic spherulites

An important characteristic of alteration processes to be mentioned especially, is hypidiomorphic calcite including the formation of encrustation pseudomorphs/pseudomorphs after calcite as infillings in the internal cavity of larger rhyolitic spherulites. Additionally, sequences of fluorite can be observed at localities 4, 7 and 16 for instance (HOLZHEY 1993, 1995, 1999).

Based on the hitherto used division (v. HOLZHEY 1993), calcite sequence II shall be subdivided into sequences IIa and IIb. The sequence IIa demonstrates pseudomorphs of quartz after platy calcite (?) at locality 16 (Figure 25). The sequence IIb shows encrustation pseudomorphs/pseudomorphs after predominantly rhombohedral calcite. The sequence IV (prismatic calcite at locality 4) was added at Table 8. The habit of original calcite sequences changes from scalenohedral (I), platy (IIa), predominantly rhombohedral (IIb) and exclusively rhombohedral (III) to prismatic (IV). Encrustation pseudomorphs/pseudomorphs after scalenohedral calcite are preferably observed as typical remnants of the first (oldest) calcite sequence (I) at localities 11 (Figure 20), 12 and 16 (Figure 21). Pseudomorphs of the second sequence (II) are much more seldom. Whereas calcite of the sequences I and II has been replaced by quartz, it was preserved regarding the sequences III and IV (cf. Table 8).

Table 9 represents the isotope composition of rhombohedral calcite III and of paragenetic quartz mineralizations in the internal cavity of larger rhyolitic spherulites. Samples 4/37 and 11/19 verify a δ^{13}C-signature of calcite III which corresponds more or less with the isotope composition of calcite infillings relating to amygdules and veins as it has been worked out by SCHMITT-RIEGRAF (1996) for another region [arrow (1) at Fig. 26]. This points to the partly igneous isotopic signature

Table 9. Isotope ratios[1] and calculated deposition temperatures of quartz and calcite as epigenetic infillings in the cavity of larger rhyolitic spherulites (using the equations of CLAYTON et al. 1972: system quartz - H_2O and of O'NEIL et al. 1969: system calcite - H_2O); localities 4, 16, 11 and 19.

	$\delta^{18}O$ [‰ SMOW]	$\delta^{13}C$ [‰ PDB]	$T_{max.}$ [C]
11/5; internal breccia	+22.3	-27.5	+113
11/4-2; agate, wall-layered type	+21.0	-23.8	+124
11/4-3; macroquartz	+22.5	n. d.	+111
I I/19; calcite, rhombohedral	+19.4	-5.7	+107
19/1; calcite, rhombohedral	+23.2	-14.2	+74
4/19; internal breccia	n. d.	-23.6	-
4/38; agate, horizontally-layered type	+28.6	-11.3	+68
4/36; macroquartz	+25.7	-6.9	+87
4/37; calcite, rhombohedral	+21.5	-5.3	+96
16/5; agate, horizontally-layered type	+20.6	-26.0	+128

[1] isotope measurements: former Zentralinstitut für Isotopen- und Strahlenforschung Leipzig n. d.- not determined

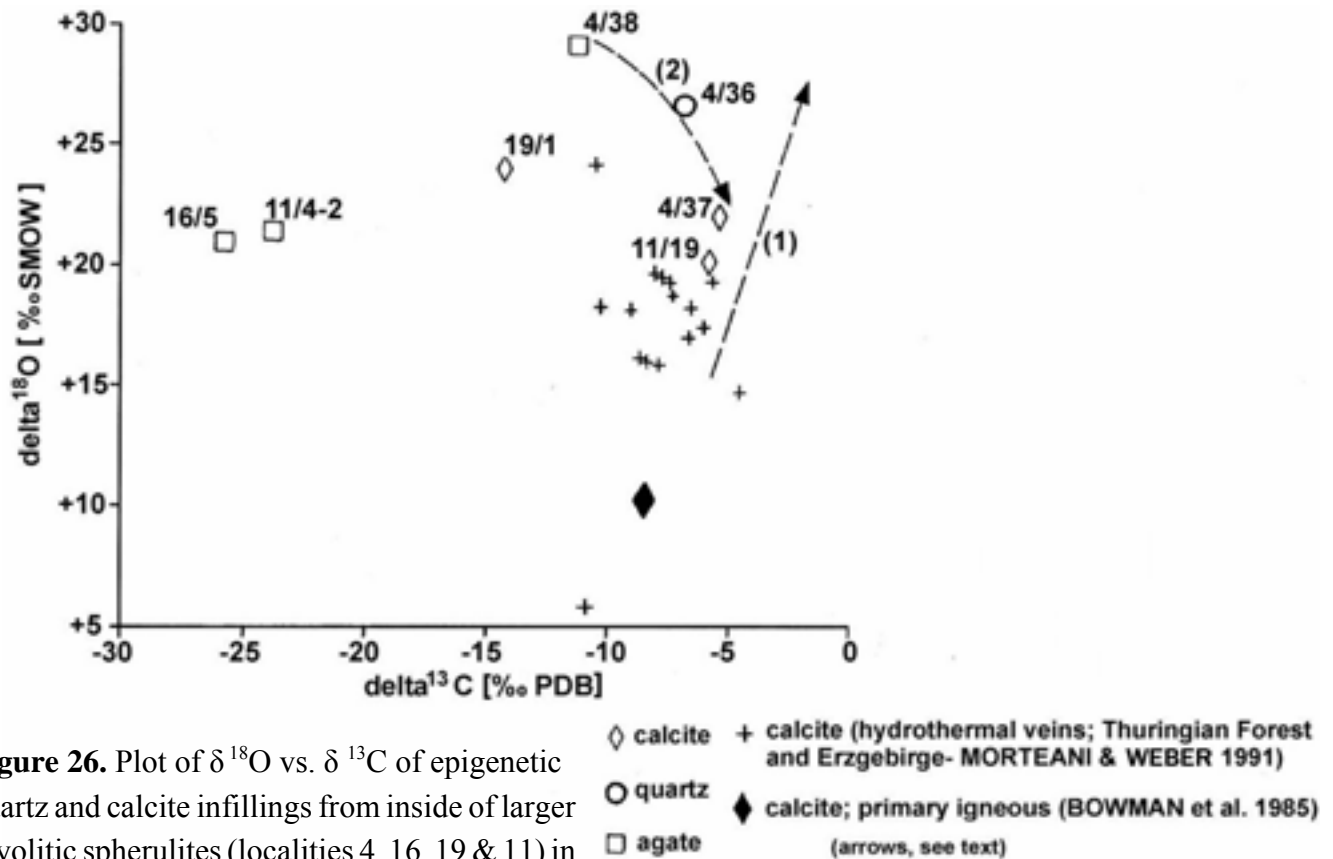**Figure 26.** Plot of $\delta^{18}O$ vs. $\delta^{13}C$ of epigenetic quartz and calcite infillings from inside of larger rhyolitic spherulites (localities 4, 16, 19 & 11) in comparison to the isotopic composition of hydrothermal calcite veins.

of solutions (cf. BOWMAN et al.1985; HOEFS 1987) represented by various hydrothermal veins as well (cf. LEEDER 1981; MORTEANI and WEBER 1991; SCHMITT-RIEGRAF 1990). Calcite III (sample 19/ 1) shows a deviation in isotopic composition in comparison to hydrothermal veins. The projection point of this sample, plotted at diagram $\delta^{18}O$ vs. $\delta^{13}C$ (cf. Figure 26), indicates a restraint of the influence of primary igneous (magmatogenic) solutions in favor of meteoric water. The deposition temperature (T_{max}.) of this calcite sample, using the equation of O'NEIL et al. (1969), was calculated with 74°C as the lowest one (cf. Table 9).

Remarkable differences are documented by isotope composition of quartz mineralizations as well. The maximum of $\delta^{18}O$-values attains + 28,8%o regarding agate infillings in the internal cavity of larger rhyolitic spherulites (HOLZHEY 1993; STRAUCH et al. 1994). The agate samples 11/4-2 and 16/5 are characterized by depletion of isotopic heavy, primary igneous carbon in result of the increasing admixture of organogenic carbon via meteoric water (cf. HOLZHEY 1993). Corresponding with the succession agate - quartz - calcite (III) and the rise in calculated deposition temperatures, isotopic heavy oxygen is depleted and that of heavy, primary igneous carbon is increased relating to locality 4 (cf. Table 9 and arrow (2) at Figure 26).

Conclusions to sequence and classification of post-magmatic changes concerning the spherulite zone

As described, spherulite zones are defined by structural, petrochemical and mineralogical characteristics, developed within the marginal facies in the latest phase of emplacement of rhyolitic volcanics. Principally, post-magmatic changes have to be subdivided in those resulting from spherulitic crystallization and those which have occurred later on during alteration processes. Crystallization of rhyolitic spherulites took place in parts of the outer marginal facies (cf. Figure 3), where an enrichment in volatile components was to be stated during high-temperature devitrification. These, in terms of POLDERVAART (1971) primary spherulites crystallized during an early stage of devitrification according to EWART (1971) still above the solidus temperature of lava (cf. HOLZHEY 1993, 1994). NASSEDKIN (1988) states that devitrification processes normally are followed by processes of secondary hydration. Alteration minerals, which characterize post-magmatic changes within spherulite zone-sites of the Thuringian Forest, are secondary K feldspar, secondary albitic plagioclase as well as secondary quartz, illite/chlorite, calcite and sometimes fluorite, respectively barite in the cavity of larger rhyolitic spherulites. Conclusions to run off and classification of alteration processes, under them processes of low-temperature hydration above all, are given as follows.

Potassium metasomatism (GIGGENBACH 1988), respectively the potassic alteration type in terms of CLARKE (1992), caused an enrichment in potassium. This early process of alteration probably started at 600°C (BOWES 1989). High concentrations of K_2O, respectively K feldspar and correspondingly losses of Na_2O and CaO, are measured therefore within the marginal facies at localities 1, 12 and partly 16 (cf. Tables 4, 5). In these cases K feldspar occurs frequently and characteristically as adularia (LÜTZNER et al. 1995). GIGGENBACH (1984, 1988) discussed these petrochemical changes for other regions as characteristic effects of cooling hydrothermal solutions during ascent. They may have caused a partial silification of the spherulite zone (cf. Table 2 and Figure 7). According to HOLZHEY (1993, 1995) further

assimilation of silica may come from the underlying sedimentary rocks (e.g. locality 7). KAY (1981) described it for another region as well. Already SZÁDECZKY-KARDOSS (1958) pointed to trans-hydration/trans-vaporization processes in connection with processes of silica mobilization at the base of coherent lava flows.

Probably with decreasing temperature, the spherulite zones of localities 4 and 7 exhibit a sodium metasomatism as the so-called sodic albitization (CLARKE 1992) following generally the potassium metasomatism. Therefore, appearance of secondary albitic plagioclase (cf. Table 5) results besides the low anorthitic plagioclase content ≤ 1 wt. % (cf. HOLZHEY 1993, 1994). The formation of albitic shares within K feldspar (GOLL 1996; LÜTZNER et al. 1995; MÄDLER 1998a) is to be seen in this context.

Essentially for illite genesis was the hydrogen metasomatism (BARTON et al. 1991; GIGGENBACH 1984), respectively a hydrolytic metasomatic process (cf. HEMLEY and JONES 1964). More than 90 wt.% of phyllosilicates, generated within altered rhyolites, are illites in result of such hydrothermal fluid-rock interactions (CATHELINEAU and IZQUIERDO 1988). This can be confirmed for the spherulite zone of the investigated localities.
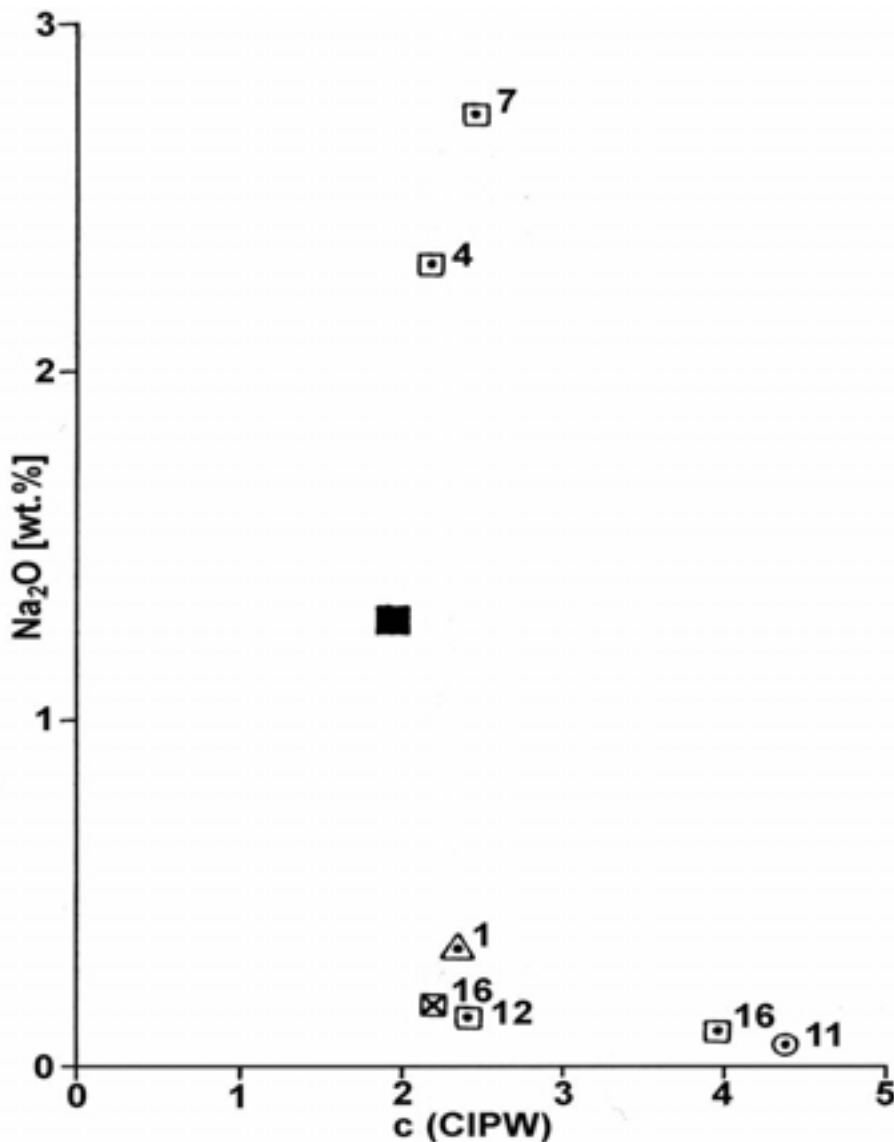

Figure 27. Plot of Na_2O vs. normative corundum (c, CIPW) of spherulitic-perlitic rhyolites (localities l, 4, 7, 12, 16 and 11) in comparison to regular facies rhyolite (explanation of symbols cf. Figure 2).

Whereas potassium gains in the course of potassium metasomatism are proved for the spherulite zone of localities 1 and 12, hydrogen metasomatism caused losses in K_2O at localities 4 and 7 (cf. Tables 2, 4 and Figure 7). This may be partly argued for locality 16 as well. In addition, figure 27 verifies losses in Na_2O in accordance with increasing normative corundum (c, CIPW) as a result of hydrogen metasomatism regarding the spherulite zone of localities 1, 12, 16 and 11. Above all, in these cases the so-called argillic alteration (MEYER and HEMLEY 1967) generated illite and some chlorite as alteration minerals. EWART (1971) pointed out, that mobilization of sodium above all and oxidation of iron are effects of such a low-temperature hydration. Correspondingly with progress of argillic alteration, increasing of c(CIPW) correlates with Na_2O losses (Figure 27). Mobilization and losses of sodium and calcium commonly occur during mobilization/leaching of silica corresponding with sericitization and chloritization (SHRIVER and McLEAN 1993). Therefore, losses of CaO as shown in figure 7, may be not only an effect of potassium metasomatism but also and preferably of argillic alteration. According to a different release and losses of CaO as well as Sr (cf. Tables 2, 4) from the plagioclases, Ca/Sr ratios are decreased (cf. Table 3).

Like contents of boron and fluorine, MgO remains enriched within the altered residual volcanic glass (cf. Figures 9, 12, 13). A positive correlation is indicated between increasing MgO- and H_2O^+ contents which is the result of a low-temperature hydration (hydrogen metasomatism). It is observed for mafic minerals of the inner spheroidal shell of rhyolitic spherulites as well (cf. Figure 10). Probably the same alteration process has contributed to a maximum of fluorine enrichment within the residual volcanic glass.

The progress in alteration by hydrogen metasomatism (stage II of low-temperature hydration) is documented by a maximum of normative corundum (c, CIPW) within spherulitic-perlitic rhyolites probably because of reinforced mobilization of silica (Figure 28). CLARKE (1992) classifies this process as going on above 50°C. The maximum of sericitization index, especially registered at localities 11 and 16 (cf. Table 3), corresponds with the second, most intense stage of low-temperature hydration. The negative correlation shown at diagram c (CIPW) vs. SiO_2 could be a hint to different influences of the alkali- and hydrogen metasomatism.
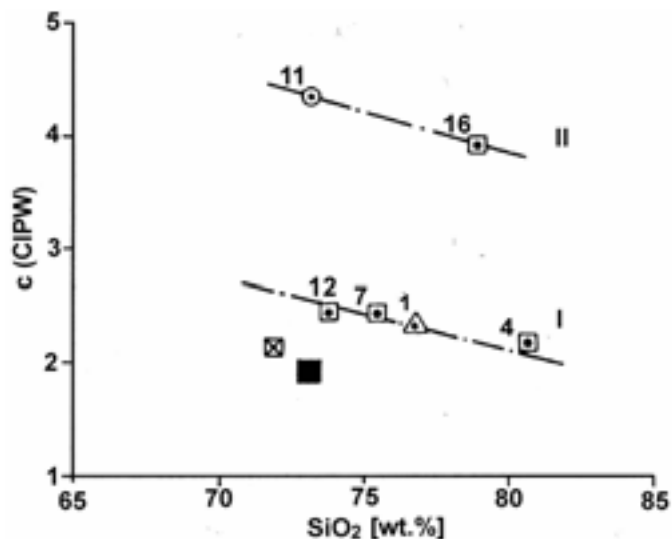

Figure 28. Plot of normative corundum (c, CIPW) vs. SiO_2 of spherulitic perlitic rhyolites (localities 1, 4, 7, 12, 16 and 11) which demonstrate the alteration stages I and II in comparison to regular facies-rhyolite as well as lithophysae zone-rhyolite from locality 16 (explanation of symbols cf. Figure 2).

Therefore, alteration processes of hydrogen metasomatism are most important for petrochemical processes of mobilization and accumulation/deposition within the marginal facies, above all for the epigenetic silica accumulation in cracks and as infillings in the cavity of larger rhyolitic spherulites (HOLZHEY 1995, 1999). Processes of hydrogen metasomatism (argillic alteration) has been formulated in different chemical reactions (e.g. GIGGENBACH 1980, 1981, 1984, 1988; MEYER and HEMLEY 1967; VON PLATEN and HOFMEISTER 1993; SCHMITT-RIEGRAF 1996; YARIV and CROSS 1979). At the end of alteration processes relating to residual volcanic glass (V2), mineral assemblage containing K feldspar, albitic plagioclase, quartz, illite and calcite indicates the assumption of an equilibrium with water according to GIGGENBACH (1984, 1988). The carbon dioxide partial pressure (pCO_2) was controlled by the following reaction (GIGGENBACH 1980, 1981):

$$\text{Ca plagioclase} + CO_2 \rightarrow \text{calcite} + \text{clay minerals} \tag{1}$$

Representative reaction of the hydrogen metasomatism are given as follows (GIGGENBACH 1984; SIMMONS & CHRISTENSON 1994):

$$\text{Ca plagioclase} + \text{K feldspar} + CO_2 + H_2O \rightarrow \text{calcite} + \text{K mica(illite)} + 2SiO_2 \tag{2}$$
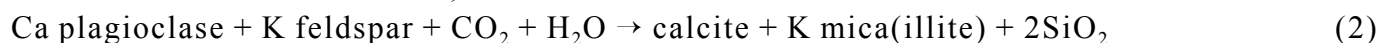
Relating to reaction (2), for these processes of hydrogen metasomatism H^+ is consumed, whereas silica and potassium (generating illite) are released (YARIV and CROSS 1979). H_2CO_3 is the major carbon species which promotes this low-temperature hydration (GIGGENBACH 1981, 1984, 1988). According to ZARAISKY (1995) solution, transport and redeposition of silica are restricted to these processes within the marginal facies. In connection with the diffusion controlled hydration, FISHER and SCHMINCKE (1984) pointed out, that mobilization of alkalis initially produces an alkaline environment which is required for silica solution and formation of illite. The upper limit of illite stability is drawn at 300 °C by SIMMONS and BROWNE (1998) which is in accordance with NASSEDKIN (1988), who put the beginning of such a secondary hydration process (hydrogen metasomatism) at ca. 290 °C. Temperatures of the low-temperature hydration of Thuringian Forest-volcanics are limited at 200 °C (GOLL 1996).

Besides the isotope composition of quartz- and calcite infillings in the cavity of rhyolitic spherulites, information about temperatures of fluid-rock interactions are to be expected by measuring of illite crystallinity (KÜBLER 1967, 1968) and chlorite crystallinity (FREY 1987). These indices of crystallinity are characteristic for WINKLER's (1974) very low-grade metamorphism (anchimetamorphism; KÜBLER 1968) ranging between 100 and 300 °C (MERRIMAN and PEACOR 1999). The illite crystallinity (IC) of phyllosilicates in the cavitiy of a rhyolitic spherulite was determined using the 001-reflection. The chlorite crystallinity (ChC) was determined using the 001- and the 002-reflection respectively (Figure 24). The illite (001) crystallinity is in accordance with chlorite (001) crystallinity (0.39 ° and 0.40 ° respectively). These values are greater than that relating to chlorite (002) crystallinity (cf. ARKAI 1991; FREY 1987). According to ARKAI (1991), MERRIMAN and PEACOR (1999), illite (001)- and chlorite (001)- crystallinity respectively, verify the anchizone below 200 °C (low anchizone in terms of KISCH 1991) which is characteristic for the most intense argillic alteration (stage II) relating to the spherulite zone at locality 16 for instance. The other X-ray powder diffraction pattern (Figures 15, 16 and 19) indicate the existence of 1M-illite as well. However, the existence of the $2M_1$-polytype corresponding with temperature conditions $\gg 100$ °C cannot be excluded.

Scalenohedral calcite, whose have been formed later on encrustation pseudomorphs/ pseudomorphs within the internal cavity of rhyolitic spherulites (cf. Figures 20, 21), represents the first (oldest) sequence as determined above (calcite Ia/b, Table 8). This typomorphic calcite I is considered to be cogenetic with the beginning of redeposition of mobilzed silica as first wall-layered type agate in the cavity of rhyolitic spherulites (cf. HOLZHEY 1993). Results of the investigations of zones in geothermal systems rich in illite (v. SIMMONS and BROWNE 1998) point to crystallization temperatures of calcite I still above 150 °C. In connection with deficiency of CaO, respectively of anorthitic plagioclase especially at localities 11 and 16 (cf. HOLZHEY 1993, 1995), calcite Ia/b originally crystallized as epigenetic infillings at those localities, where most intense alteration (stage II) was to be stated (cf. Figure 28). In accordance with GODOVIKOV et al. (1987) encrustation pseudomorphs/pseudomorphs are characteristic for the alteration by hydrogen metasomatism. According to reactions mentioned above, calcitization of plagioclase may be regarded as a formation of replacement calcite in the sense of BROWNE and ELLIS (1970) as well as SIMMONS and CHRISTENSON (1994). It indicates temperatures below ca. 170 °C (SIMMONS and CHRISTENSON 1994). After GISLASON and ARNORSSON (1993) plagioclases become unstable below 180 °C.

At considerably lower temperatures (cf. Table 9), associated with a shift in pH which made calcite of the first sequence unstable, formation of agate began after redeposition of silica as an epigenetic infilling in the cavity of larger rhyolitic spherulites. Calcite I was replaced by micro- to macroquartz (cf. Figures 20, 21). Among other investigations which support low-temperature genesis of agate sequences, isotope composition indicates formation temperatures between 70 and 130 °C (HOLZHEY 1993, 1995, 1999). Based on a value of $+ 3‰$ for the $\delta^{18}O_{H2O}$ signature of hydrothermal solutions, which were efficient in hydrogen metasomatism (cf. HOLZHEY 1999), this range of temperature is nearly in accordance with GOLL's (1996) results of feldspar alteration in the range of 70 to 150 °C. Conditions illustrated above are in accordance with comments of FOURNIER (1973, 1985), that chalcedony cannot be formed in dependence of pH above 180 °C generally. In addition, the microstructure of agates is significantly and irreversibly destroyed under hydrothermal conditions above 200 °C (GRAETSCH 1985).

As described, besides quartz pseudomorphs after scalenohedral calcite, pseudomorphs of quartz after platy calcite (?) occur in the cavity of larger rhyolitic spherulites at least at locality 16. This calcite sequence, according to the state of knowledge signed as IIa, probably precipitated from local boiling CO_2-enriched solutions through exsolution of carbon dioxide (cf. BROWNE 1978, 1998; SIMMONS and BROWNE 1998; SIMMONS and CHRISTENSON 1994). While platy calcite originally forms in "fluid-dominated environments" within open cavities, replacement calcite mentioned above forms in "rock-dominated environments where sub-boiling liquids contain relatively concentrations of dissolved carbon dioxide" (SIMMONS and CHRISTENSON 1994). Therefore, calcitization of plagioclase and on the other hand formation of calcite IIa as well as calcite of the following sequences later on, point to changes of the interaction between hydrothermal solutions and rhyolitic host rocks located within the marginal parts of lava domes especially.

Table 10. Alteration processes and important mineralizations within the spherulite zone of the rhyolitic Rotliegend-volcanics of Thuringian Forest.

Type of alteration	Temperature (°C)	Processes (mineralizations)
Potassic alteration (K metasomatism)	(~ 600?) ↓	- mobilization especially of Na, (Ca); silicification; adularization (K feldspar; secondary)
Sodic albitization (Na metasomatism)		- mobilization especially of K (albitic plagioclase; secondary)
Argillic alteration (H metasomatism)	(~ 300?) 200 ↓ 70	- mobilization especially of SiO_2, K, Na, Ca, Mg; oxidation of Fe_2^+; calcitization (illite/chlorite, secondary quartz, calcite and hematite characterizing the low anchizone)

Based on isotope composition, formation temperatures of calcite may be calculated only for calcite III/IV which has been preserved. Calcite III crystallized, partly influenced by primary igneous solutions, at temperatures at or below 100 °C (cf. Table 9). This calcite formation is, in opposite to calcite I however, recognizable in no direct relation to the beginning of argillic alteration. In course of genesis of the four calcite sequences environmental temperature probably decreased from > 200 to 70 °C with regard to the obvious changes in crystal habit.

Table 10 summarizes post-magmatic changes in the sense of various alteration processes described above, which determine petrochemical-mineralogical characteristics of the spherulite zone. At higher temperatures metasomatic processes point to local differences as described, whereas low-thermal alteration processes, that means hydrogen metasomatism, generated the predominant mineralization of the low anchizone.

Acknowledgments

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