

Petrogenesis and alteration of tuffs associated with continental flood basalts from Putorana, northern Siberia

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(Received 25 November 2002; accepted 12 August 2003)

Abstract – In the Putorana region of the Siberian continental flood basalt province, tuffs form thin layers or small bodies between single basaltic lava flows. Based on our fieldwork, these ash fall deposits have relatively small volumes (< 100 000 m³) compared with the associated basaltic flows and the tuffs of the adjacent Noril'sk region in the north. Six tuff units with different degrees and modes of alteration were analysed by XRD, SEM and XRF in order to determine mineralogical and chemical changes which occurred during progressive alteration. Pyroxene compositions and immobile element ratios suggest that the tuffs were derived from a basaltic lava like the flood basalts. Post-eruptive, low-temperature alteration processes have significantly changed the primary composition of the tuffs. Therefore the different tuffs have variable petrography, mineralogy and geochemistry (MgO 5.2–9.2 wt %, SiO₂ 33.6–69.1 wt % and TiO₂ 0.6–1.6 wt %) compared to the tholeiitic basalts in which they are interbedded. Crystallization of secondary minerals, such as carbonate, clay minerals, zeolites and analcime, occurred from circulating fluids. The results show that the fluid compositions varied significantly between the different tuffs. This implies that the elements behaved differently depending on the circulating agent, which led to the formation of different minerals. In addition, two samples show an input of quartz, derived either by wind from terrigenous sediments or generated by magma–sediment interaction, and one sample was deposited in a subaqueous, possibly lacustrine environment. These results indicate that the conditions during alteration varied despite the close spatial relationship of the tuffs and that a generalization about the alteration processes cannot be made in the Putorana region. The analyses of the clay minerals show alteration of chlorite to vermiculite. Interestingly, corrensite (a regularly stacked, 50/50 mixed layered clay mineral composed of chlorite and vermiculite) is still preserved in two samples. This indicates different alteration stages in the different tuff outcrops. The state of alteration deduced from immobile element ratios, plagioclase compositions and mineral assemblages shows contradictory results. This suggests that the state of alteration is best deduced from clay minerals, as one can follow this process step by step.

Keywords: tuff, alteration, clay mineralogy, Siberian platform, flood basalts.

1. Introduction

Understanding the behaviour of elements during alteration of volcanic rocks is very important, as only relatively immobile elements that were not influenced by secondary (post-eruptive) processes can be used to infer mantle source compositions, degree of melting and crustal-level processes such as differentiation and assimilation. Tuffs are also used as tephrostratigraphic markers and can provide clues to the tectonomagmatic setting (e.g. Königer & Lorenz, 2002). Previous studies have shown that the behaviour of elements during weathering and alteration depends on the relative stability of the parent mineralogy, pressure, temperature, redox potential and the type of leaching agent (Nesbitt, 1979; Gouveia *et al.* 1993; Ohlender *et al.* 1996; Minarik *et al.* 1998; Tapia, Tosiani & Loubet, 1998). Malpas, Duzgoren-Aydin & Aydin (2001) showed in a

study on a crystal-vitric tuff that not only the degree of weathering but also the abundance of clay minerals and the type and abundance of sesquioxides control the behaviour and mobility of chemical elements. It is generally accepted that different minerals have different degrees of resistance against weathering (e.g. Goldich, 1939; Laughman, 1969; Surdam & Sheppard, 1978; Triplehorn & Bohor, 1981; Heim, 1990; Deer, Howie & Zussman, 1992; Bohor & Triplehorn, 1993). The degree of weathering of the same mineral may vary from minor to complete alteration on a thin-section scale.

Generally, the mobility of elements is assessed from percentage changes in ratios of elements from weathered samples, relative to those from unaltered rocks. These ratios are calculated by dividing a value for each element by that of an immobile element. There are a growing number of studies suggesting that elements which are generally thought to be immobile during weathering and alteration (e.g. rare earth elements (REE), Zr, Ti and Al) may in fact be mobile under

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certain conditions (Gardner, Kheoruenromne & Chen, 1978; Gardner, 1980; Van der Weijden & Van der Weijden, 1995; Cornu *et al.* 1999). More precisely, the light REE (La–Gd) are commonly immobile, whereas the heavy REE (Tb–Lu) are generally depleted in alkaline solutions but immobile in more dilute pore fluids (Winchester & Floyd, 1977; Zielinsky, 1982; Summa & Verosub, 1992).

‘Tuffs’ are consolidated equivalents of volcanic ash deposits with > 75 vol. % pyroclasts. In contrast, ‘tuffites’ are the consolidated equivalents of mixed pyroclastic–epiclastic sediments that contain 25–75 vol. % pyroclasts, independent of the content of secondary minerals formed by alteration. Both terms ‘tuffs’ and ‘tuffites’ are used independently of the depositional environment or post-depositional alteration processes (Fisher & Schmincke, 1984, and references therein). This study investigates the effect of alteration and weathering on the mineralogy and chemistry of tuffs from the Siberian flood basalt province. The tuffs are highly altered compared with the associated basalts, presumably due to their lower consolidation and higher porosity, which makes them more susceptible to alteration. As a result, the tuffs provide excellent samples for studying the effects of alteration on basaltic rocks.

In this study, we examine six tuff units, which show different degrees and modes of alteration, in order to determine the mineralogical and chemical changes that occurred during progressive alteration. We investigate the extent to which the chemical effects of alteration differ according to the mode of alteration and the initial composition of the rock. In addition, we examine whether the state of alteration can be best deduced from mineral assemblages, clay mineral analyses or from whole rock compositions. To address these questions, mineral and whole rock chemical compositions of six different tuff outcrops were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) or X-ray fluorescence (XRF).

2. Geological setting

The 250 Ma old (e.g. Wooden *et al.* 1993) continental flood basalts of northern Siberia cover an area of about 1.5×10^6 km² (Sharma, Basu & Nesterenko, 1991) and can be divided into three main regions (Fig. 1): the Putorana Province (90 % of the area), the Noril’sk region (7 % of the area) and the Meimecha–Kotui region (3 % of the area). Most flows are composed of tholeiitic basalts, but in the Noril’sk region, picritic to tholeiitic and subalkaline basalts as well as basaltic andesites also occur (Sharma, Basu & Nesterenko, 1992).

In contrast to many other flood basalt provinces, the eruption of the Siberian continental flood basalts was accompanied by significant explosive basaltic

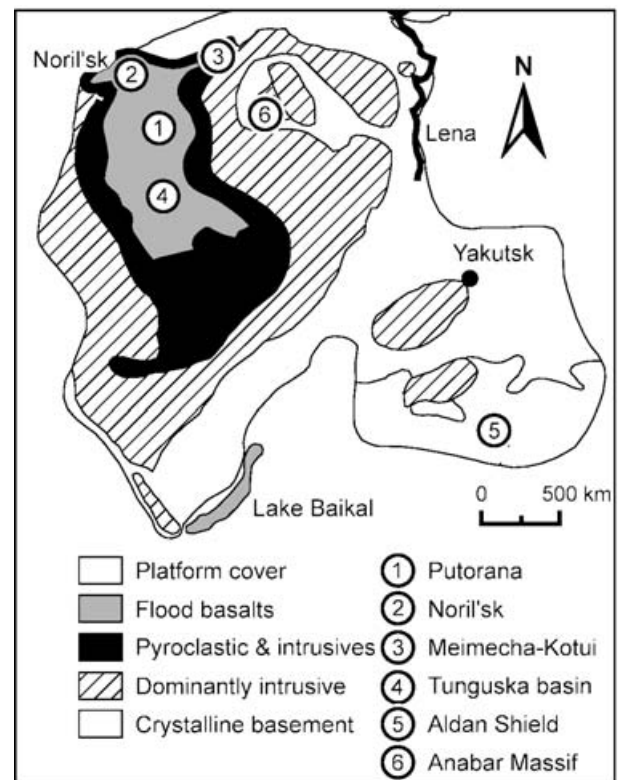


Figure 1. Schematic geological map of Permian–Triassic Siberian Traps (modified from Renne & Basu, 1991).

volcanism. Large quantities of basaltic tuffs are distributed widely but irregularly within the Tunguska basin in which the Siberian continental flood basalts are mainly present (Zolothkhin & Al'mukhamedov, 1988). The pyroclastic deposits reach a maximum thickness of 700 m in the centre of the Tunguska basin and thin towards the north and west where the lavas are well developed. In contrast, in the south of the Tunguska basin, the tuffs are present without accompanying lava (Sharma, 1997). In the Noril'sk region, phreatomagmatic eruptions occurred before the eruption of the basalts (Sharma, Basu & Nesterenko, 1992). These tuffs are up to 800 m thick (Khain, 1985). Subsequently, smaller pyroclastic eruptions occurred intermittently during emplacement of the flood basalts (Basaltic Volcanism Study Project, 1981). The tuffs stratigraphically located in the lower third of the Noril'sk region were formed in water-filled basins, whereas the tuffs of the upper two-thirds were emplaced subaerially (Federenko, 1991). In the Noril'sk area the lava–tuff ratio is approximately 8:1 (Lightfoot *et al.* 1993). Wooden *et al.* (1993) estimated a 4:1 lava–tuff ratio for the whole continental flood basalt province. This would imply a higher volume of tuffs in the Putorana region than in the Noril'sk area. However, in contrast to the Noril'sk Province in the Putorana and Meimecha–Kotui provinces, thick tuff units do not occur at the base of the lava pile. In the Putorana region of the Siberian continental flood basalts, tuffs

form small layers or bodies between single basaltic lava flows. These tuffs have relatively small volumes ($< 100\,000\text{ m}^3$), compared with the associated basaltic flows and the tuffs of the neighbouring Noril'sk region.

Even though the occurrence of tuffs associated with the Siberian continental flood basalts in the Noril'sk region has been described by several authors (e.g. Khain, 1985; Zolothkhin & Al'mukhamedov, 1988; Federenko, 1991; Sharma, Basu & Nesterenko, 1992; Lightfoot *et al.* 1993; Sharma, 1997), their genetic relationship as well as the mineralogy, petrology and geochemistry of the tuffs has not been investigated previously in detail.

3. Analytical methods and samples

3.a. Analytical methods

Minerals were determined using a polarizing microscope, and SEM was used for quantitative mineral analyses. Before analysis, the alteration rims of the samples were removed. Sample pieces 0.5 cm in size were then fixed on a sample holder and coated with carbon. The data were obtained with a JEOL JSM-6400 at an accelerating voltage of 20 kV and a beam current of 80 to 100 nA at the University of Vienna. The analytical system was a LINK EDX. ZAF-4 corrections were made.

Major and trace element compositions of the whole rocks were determined using XRF. The data were collected by a Philips PW 2400 spectrometer with a rhodium tube and a 3 kW generator from 60 kV/50 mA to 24 kV/125 mA at the University of Vienna. For preparation of the fused pellets, 1.2 g of the dried sample powder was mixed with 6 g of Li-tetraborate (MERCK Spektromelt A10). After homogenization, about 100 μl of LiBr_2 were added. The fused pellets were then generated by the Philips Perl' X3. Pressed pellets were prepared by mixing 0.5 ml polyvinyl alcohol (2% MERCK Mowiol) with 10 g of sample powder and stirring ten minutes. This mixture was put in the hydraulic press for three minutes at 0.6 t/cm³. Trace element concentrations were calculated using the Traces program (Petraakis & Dietrich, 1985).

The bulk and clay mineralogy of the samples was determined by XRD. Diffraction data were collected with a Philips diffractometer (PW 3710, goniometer PW 1820), $\text{CuK}\alpha$ radiation (45 kV, 35 mA), step scan (step size $0.02^\circ 2\theta$, 1 s per step) at the University of Vienna. For the separation of the clay fraction, the samples were crushed to a size of 3 mm and treated with a 400 W ultrasonic probe for further disaggregation. The $< 2\ \mu\text{m}$ fractions were separated by sedimentation. The clay fractions were saturated with 1N KCl-solutions and 1N MgCl_2 -solutions by shaking overnight and afterwards washed in distilled water. Oriented preparations of the $< 2\ \mu\text{m}$ fractions for XRD were made by dispersing approximately

7 mg of clay separate in 1 ml of water, pipetting the suspension onto a round glass slide, and drying at room temperature. Oriented XRD mounts were analysed air-dried and after vapour solvation with ethylene glycol or glycerol at 60 °C for 12 h (Moore & Reynolds, 1997).

3.b. Samples

In the study area of the Putorana Province, the tuffs occur only rarely as thin layers or small bodies between the tholeiitic flows. The thickness of the tuffs in the outcrops varies from a few centimetres up to 40 m. Horizontally, the layers can be traced for a distance of a few metres to several tens of metres. Although the basaltic lava flows of single eruptions cover a wide area, the tuffs have much smaller volumes of $< 100\,000\text{ m}^3$. The boundaries between the tuffs and the enclosing lava flows are sharp and therefore detrital admixing can be excluded. In addition, the tuffs do not show any flow structures, and therefore most likely represent ash fall deposits. Six different tuff units (T1–T6; Fig. 2) were investigated in detail. Large samples were taken from each outcrop, as it was not possible to take samples at regularly spaced intervals along a bed because of limited access and/or very small size of outcrops. The analyses should be representative because of the large sample sizes. The grain size classification and nomenclature follows Wentworth (1922).

Three samples of the tholeiitic flows were included in this study for comparison; for details see Büchl (A. Büchl, unpub. Diploma thesis, Univ. Vienna, 1999). The tholeiitic flows are very homogeneous in composition (e.g. Büchl, Ntaflou & Ryabchikov, 1999). They extend horizontally over hundreds of kilometres with thickness between a few metres and tens of metres. Single flows exhibit sharp contacts with neighbouring flows and sediments are absent between them.

4. Results

4.a. Mineralogy

The mineral phases occurring in the tuffs are listed in Table 1; mineral identifications were made by XRD, SEM and microscopy.

Clay mineral analyses were carried out by XRD. To distinguish between the expandable clay minerals smectite and vermiculite, the samples were saturated first with Mg and afterwards with glycerol. After this treatment vermiculite should expand to about 14.5 Å, whereas smectite should expand to 18 Å (Moore & Reynolds, 1997). As can be seen in Figure 3 ($< 2\ \mu\text{m}$ fraction of T1), the peak remains at 14.0 Å after Mg and glycerol treatment. Therefore, the expandable clay mineral in T1, and also in T3, T4 and T5, was identified as vermiculite. Ethylene glycol

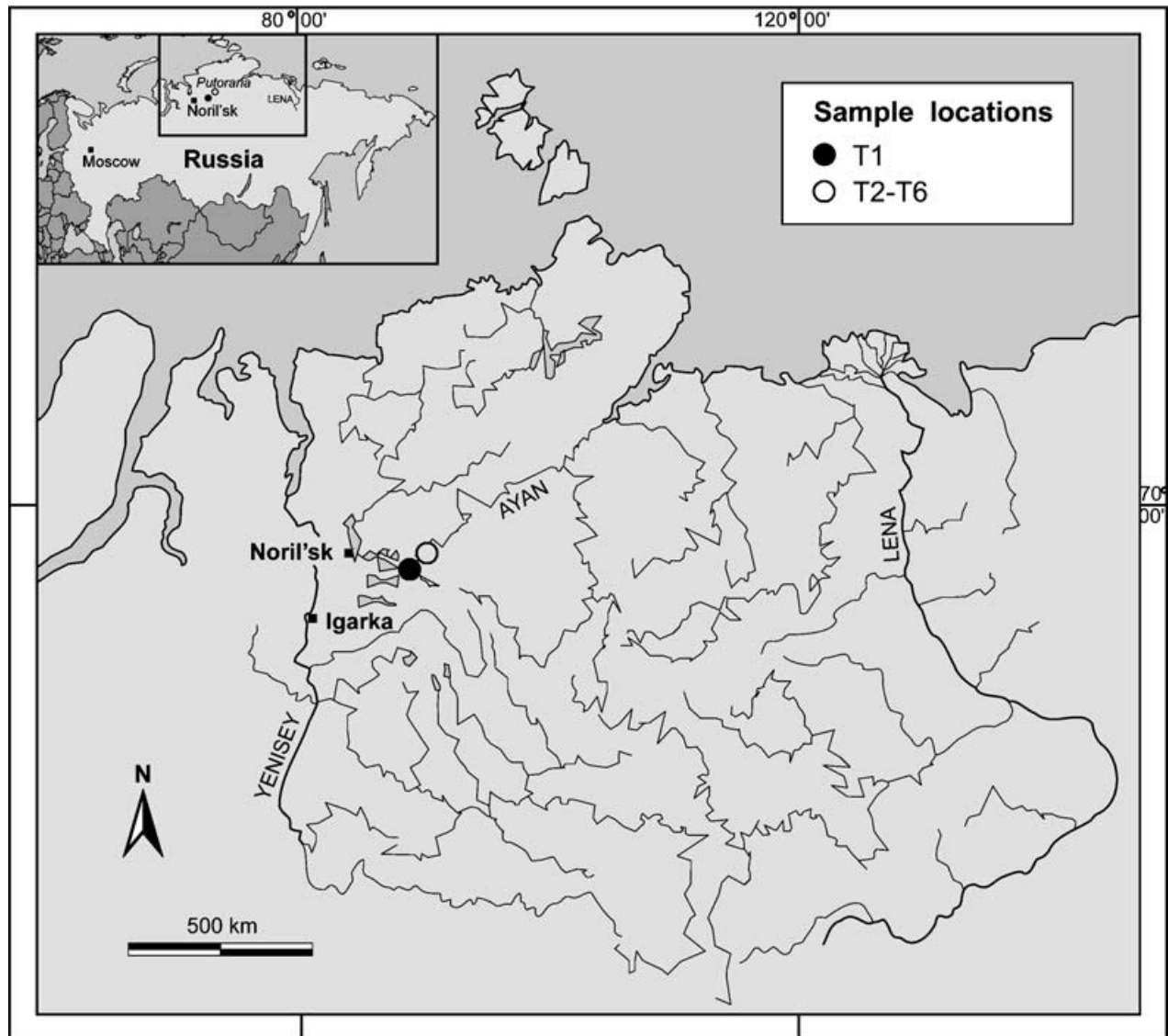


Figure 2. Map of the study area, which lies in the Putorana region of the Siberian continental flood basalts. The samples locations are marked by dots. Six tuffs have been investigated.

(EG)-saturation of the vermiculite causes an expansion to 16.5 Å, K-saturation a collapse to 12.4 Å (Fig. 3), which indicates low-charged vermiculite. This is quite ambiguous, because the behaviour after Mg and glycerol treatment points to high-charged vermiculite (Moore & Reynolds, 1997).

The $< 2 \mu\text{m}$ fractions of T2 (Fig. 4) and T6 show an unusual clay mineral, corrensite. This corrensite is a regularly stacked (R1 ordered), 50/50 mixed layered clay mineral composed of chlorite and vermiculite. The vermiculite was again identified after Mg and glycerol saturation; the vermiculite component in chlorite/vermiculite remains at about 14 Å. The air dried and Mg- and glycerol-treated forms (Fig. 4) produce rational patterns (lower curve); the superstructure 001 has a spacing of 28.2 Å = 14.2 + 14. For the ethylene glycol solvated example the superstructure has a spacing of 31 Å (upper curve).

4.b. Geochemistry

Major and trace element chemistries of the tuffs and three associated basalts were determined by XRF, and results are listed in Table 2.

In contrast to associated basaltic flows which are very homogeneous in their geochemical composition and only moderately altered (Büchl, Ntaflös & Ryabchikov, 1999), the tuff samples are highly altered and their major and trace element compositions vary significantly among each other, for example, MgO contents range from 5.3 to 9.2 wt %, SiO₂ from 33.7 to 69.2 wt %, TiO₂ from 0.6 to 1.7 wt %, Zr from 63 to 201 ppm and Cr from 97 to 315 ppm (Table 2). The changes in major and trace element composition of the samples are very complex and seem not to change systematically.

The plagioclase compositions of T1, T2 and T4 are poorer in calcium, whereas measurements of T5 are

Table 1. Mineral compositions of the tuffs

Sample	Minerals	Percentages	Description
T1	Plagioclase	20 %	Mostly broken
	Augite	5 %	
	Titanomagnetite	7 %	
	Ankerite	7 %	Hypidiomorphic crystals in cavities
	Vermiculite	15 %	
	Matrix	46 %	Very fine grained
T2	Plagioclase	5 %	Slightly altered
	Augite	2 %	Slightly altered
	Quartz	3–5 %	Well rounded (up to 0.1 mm)
	Ore	3 %	Altered to leucoxene, skeletal crystals
	Pyrite	<1 %	
	Glass	3–5 %	Altered, perlitic structure
	Corrensite	35 %	
	Matrix	45 %	Fine grained
	T3	Plagioclase	3 %
Augite		2 %	
Quartz		3 %	Well-rounded (up to 0.2 mm)
Ore		2 %	Altered into leucoxene
Glass		30 %	Altered
Carbonate		8 %	Xenomorph, interstitial
Vermiculite		30 %	
Matrix		22 %	Fine grained
T4	Plagioclase	2 %	Altered
	Augite	1 %	Altered
	Ore	10 %	Agglomerations
	Glass	20 %	Altered
	Hematite	7 %	
	Calcite	50 %	Xenomorph, cement in matrix
	Vermiculite	10 %	Agglomerations
	T5	Plagioclase	2 %
Augite		2 %	
Ore		3 %	
Carbonate		1 %	Hypidiomorphic in cavities
Zeolite		1 %	Hypidiomorphic in cavities
Vermiculite		60 %	
Matrix		31 %	Fine grained
T6		Plagioclase	5 %
	Augite	5 %	
	Ore	3 %	
	Carbonate	3 %	Hypidiomorphic in cavities and interstitial cement
	Analcime	2 %	In amygdales
	Laumontite	2 %	In amygdales
	Corrensite	35 %	Angular and lithic
	Matrix	45 %	Fine grained

Mineral phases were determined by XRD, SEM and microscopy; given percentages are mineral volumes determined by thin section microscopy.

richer and of T6 are partly richer and partly poorer in calcium than those of the basalts (Table 3, Fig. 5). In T2, and partly in T6, the plagioclases are more sodium rich and reach up to pure albites. Except for T6 (and T4 with only one analysed plagioclase), the intra-sample variation of the plagioclases is much less than the variation between samples.

Pyroxenes were analysed from all samples, except samples T1 and T3, where the mineral grains were not large enough (Table 4). The variations of the pyroxene analyses of the tuffs and of representative associated basalts are shown in Figure 6. All pyroxenes are augites and there is very little chemical variation in this mineral between the different tuffs. The pyroxenes of the tuffs fall in the field defined by the associated basalts (Fig. 6).

5. Discussion

5.a. Characteristics in single tuffs

A number of tuff samples show distinctive characteristics that only occur in single samples. Well-rounded quartz grains, which occur in T2 and T3, have no genetic relationship to the other minerals. The rounded shape of the quartz grains indicates transport and abrasion of the grains. One explanation is that the sediment cropping out stratigraphically below the flood basalts is the source region for the quartz grains. This source area is approximately 200 km northwest of the sample outcrops. Since there is no evidence for an ancient fluvial dispersal system, this would imply that the quartz is of terrigenous origin and was transported by wind. Interestingly, quartz does not

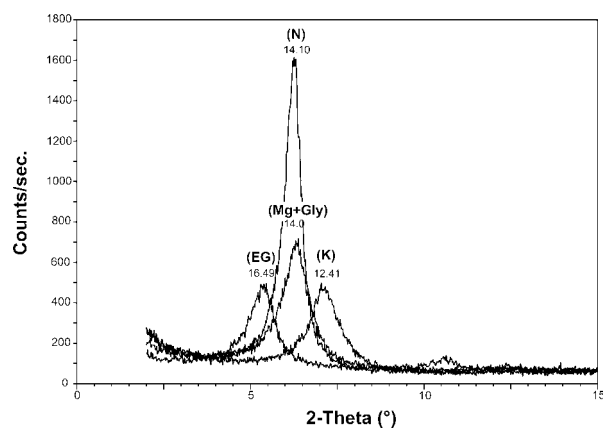


Figure 3. XRD patterns of the orientated $<2\ \mu\text{m}$ fraction of sample T1 after different treatments (see text). Air-dried (N), ethylene glycol-saturated (EG), first Mg-, then glycerol-saturated (Mg + Gly), K-saturated (K). d-values in Å.

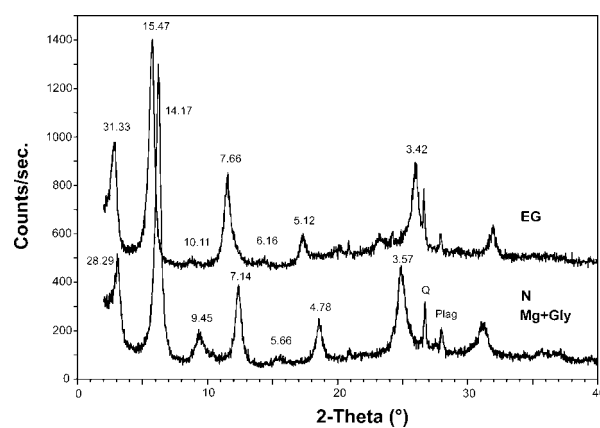


Figure 4. XRD patterns of the orientated $<2\ \mu\text{m}$ fraction of sample T2. Air-dried (N), ethylene glycol-saturated (EG), first Mg-, then glycerol-saturated (Mg + Gly). d-values in Å. Q = quartz, plag = plagioclase.

occur in T4, which is situated on top of T3. Therefore, the input of quartz must have occurred periodically. Also the basaltic tuffs of the lower areas in the Noril'sk region contain 10–15 % of 0.1–1 mm large xenocrysts from the underlying sediment (Wooden *et al.* 1993). An alternative explanation involves magma–sediment interaction, whereby quartz is included in the pyroclastic rocks because of interaction between the rising magma and a neighbouring country rock prior to tuff formation. This sort of phenomenon has been described by Leat & Thompson (1988); Elliot & Hanson (2001); Skilling, White & McPhie (2002) and others.

This process could also explain the angular argillaceous lithic fragments that occur in T6. In this case there would have been some sediment that was completely disaggregated into the magma, appearing as individual quartz grains or lithic fragments within the tuffs.

T2 shows millimetre-scale planar lamination. This structure together with the green colour of the sample indicates the presence of Fe^{2+} and reducing conditions, suggestive of deposition in a subaqueous, possibly lacustrine environment. These aquatic conditions support the formation of albite because of a high volatile content in the water.

Table 2. Major and trace element chemistry of the tuffs and three associated basalts

Sample	T1	T2	T4	T5	T6	Basalt Pu-3a*	Basalt Pu-35*	Basalt Pu-55*
SiO ₂ (wt %)	52.09	69.12	33.67	54.46	52.00	48.91	49.67	49.59
TiO ₂ (wt %)	1.41	0.62	1.19	1.28	1.69	1.18	1.17	1.15
Al ₂ O ₃ (wt %)	16.30	11.62	10.47	15.87	17.21	15.28	15.42	15.55
Fe ₂ O ₃ (wt %)	7.77	5.94	7.44	7.21	7.60	12.41	12.64	12.40
MnO (wt %)	0.27	0.13	0.25	0.28	0.31	0.18	0.19	0.19
MgO (wt %)	6.56	8.89	5.25	9.24	8.10	7.41	7.66	7.57
CaO (wt %)	12.62	1.69	38.69	8.16	9.67	11.75	11.48	11.53
Na ₂ O (wt %)	2.39	1.52	1.26	2.88	2.14	2.03	2.14	2.06
K ₂ O (wt %)	0.32	0.41	1.52	0.44	1.10	0.25	0.32	0.32
P ₂ O ₅ (wt %)	0.24	0.06	0.15	0.11	0.12	0.13	0.14	0.13
Total	99.96	99.99	99.87	99.93	99.92	99.53	100.83	100.49
Nb (ppm)	5	n.d.	n.d.	n.d.	7	4	5	4
Zr (ppm)	96	93	63	81	201	83	85	85
Y (ppm)	26	11	17	20	23	22	23	24
Sr (ppm)	190	49	192	371	301	205	211	219
Rb (ppm)	n.d.	10	21	9	26	7	8	7
Ga (ppm)	17	12	9	13	17	20	20	21
Zn (ppm)	87	38	47	85	107	89	88	86
Cu (ppm)	161	99	17	149	126	129	130	128
Ni (ppm)	85	57	76	121	157	123	121	123
Co (ppm)	80	58	50	101	114	51	48	52
Cr (ppm)	151	97	121	147	315	146	145	151
Sc (ppm)	46	26	24	45	39	32	33	31

Major (wt %) and trace (ppm) element concentrations determined by XRF; n.d. = not detected.

*Data from A. Büchl, unpub. Dipl. thesis, Univ. Vienna, 1999.

Table 4. Pyroxene compositions of the tuffs and three associated basalts

Sample	T2	T4	T5	T6	T6	T6	Basalt Pu-3a*	Basalt Pu-35*	Basalt Pu-55*
SiO ₂ (wt %)	50.47	50.75	51.33	50.50	48.83	49.56	50.32	50.67	49.96
TiO ₂ (wt %)	0.56	1.02	1.56	1.79	0.58	0.89	0.84	0.84	1.6
Al ₂ O ₃ (wt %)	0.80	3.77	2.25	7.80	4.13	4.40	2.78	1.98	2.48
FeO (wt %)	14.74	10.58	9.03	7.67	13.69	10.33	9.2	10.79	17.82
MnO (wt %)	0.34	n.d.	0.41	n.d.	0.64	n.d.	0.21	0.27	0.41
MgO (wt %)	16.09	16.05	16.88	15.24	17.66	15.89	14.42	14.96	12.83
CaO (wt %)	16.26	16.38	18.30	14.97	13.90	18.32	21.16	19.48	15.02
Na ₂ O (wt %)	n.d.	0.84	n.d.	n.d.	n.d.	n.d.	0.22	0.23	0.26
K ₂ O (wt %)	n.d.	0.43	n.d.	1.16	n.d.	n.d.	0.02	0.02	0.02
Total	99.26	99.82	99.77	99.12	99.43	99.39	99.17	99.24	100.4
Wollastonite	32.42	34.89	37.47	35.52	28.27	37.78	43.71	39.99	32.11
Enstatite	44.63	47.54	48.09	50.29	49.99	45.60	41.45	42.73	38.16
Ferrosilite	22.95	17.58	14.43	14.19	21.74	16.63	14.84	17.29	29.73

Pyroxene compositions were determined by SEM; n.d. = not detected.

*Data from A. Büchl, unpub. Dipl. thesis, Univ. Vienna, 1999.

include mainly carbonate, clay minerals, zeolites, analcime, pyrite and hematite (Table 1). The mineral chemistry of the tuffs shows that the altered plagioclases in one tuff unit (T1) are very homogeneous, but among the tuff units their compositions vary considerably (Fig. 5). In the associated basalts, the compositions of the plagioclases only vary over a small range. The chemical variation of the plagioclases in the tuffs is therefore most likely influenced by different degrees of alteration.

The highly altered nature of the tuffs compared to the associated basalts is presumably due to their lower consolidation and therefore higher permeability of the tuffs, which makes alteration processes, such as those induced by fluids, more likely. T3, T4 and T6 are cemented by carbonate and in T1, T5 and T6, carbonate appears as hypidiomorphic minerals in cavities. The carbonate cementation as well as the carbonate in the cavities is derived from local circulation of hydrothermal fluids. In T4 only, it is possible that the whole tuff was soaked with an iron-rich fluid which led to the formation of hematite.

This shows that fluid compositions varied considerably in the different tuffs despite their close spatial relationship. Different fluids probably caused the formation of different minerals in the tuff samples. Malpas, Duzgoren-Aydin & Aydin (2001) suggested that different leaching agents can lead to different behaviour of such elements.

5.c. Do tuffs and basalts have a common source?

Even though the association of the tuffs with the basaltic lava flows in the Noril'sk region has been described by several authors (e.g. Basaltic Volcanism Project (1981), Khain (1985), Zolothkhin & Al'mukhamedov (1988), Federenko (1991), Lightfoot *et al.* (1993), Sharma (1997), Sharma, Basu & Nesterenko (1992)), their genetic relationship has not been shown previously. Alteration processes which

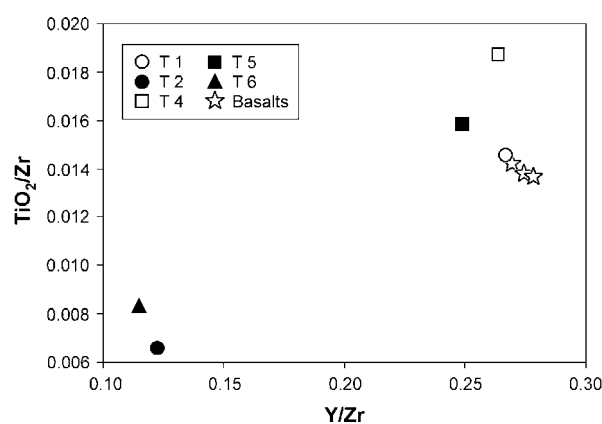


Figure 7. TiO₂/Zr and Y/Zr ratios in the tuffs and associated basalts from the Putorana region. T1, T4 and T5 broadly have similar ratios compared with the associated basalts. In contrast, T2 and T6 have lower ratios.

led to growth of secondary minerals (carbonate, zeolites, clay minerals, etc.) involving selective enrichment/depletion of major and trace elements, have significantly changed the original compositions of the tuffs after their deposition. Therefore, whole-rock compositions (Table 2) cannot be considered representative of the parental magmas of these rocks. For example, T4 contains 38 wt % CaO and cannot be classified according to chemical criteria as any recognizable volcanic rock. However, elements considered to be relatively immobile (e.g. TiO₂, Zr and Y) are possibly not affected by low-temperature secondary alteration and could therefore be used as tracers for the original magma compositions (Pearce, 1983; Tatsumi, Hamilton & Nesbitt, 1986; Pearce & Peate, 1995). In addition, the mineral compositions of the pyroxenes, which are more stable during low-temperature alteration than plagioclases, could be used to estimate original compositions. The augite compositions of the tuffs are within the narrow field defined by the associated basalts (Fig. 6). Together with Y/Zr ratios (Fig. 7), which are similar in T1, T4 and T5,

and TiO_2/Zr ratios, which are similar in T1 and T5 and lie close to the associated basalts, this might indicate that these tuffs were originally derived from the basaltic magmas. T2 and T6 have lower TiO_2/Zr versus Y/Zr ratios and in contrast to the other samples, albite occurs in these samples (Fig. 5). In magmatic rocks, albite forms due to alteration of plagioclase (Larsson *et al.* 2002). In comparison to the other tuffs, the occurrence of albite in T2 and T6 together with lower TiO_2/Zr and Y/Zr ratios could imply that the immobile elements were mobilized due to a very high degree of alteration during the formation of albite. These two tuffs could have had the same parental magmas than the other tuffs and associated basalts. This assumption is supported by the similar immobile element ratios of these two tuffs compared with the other tuffs. These results suggest that the tuffs and basalt lavas had one common source.

5.d. Clay minerals as indicators for the state of alteration

The samples show disparate chemical starting compositions (Tables 1, 2). Thus, whole rock major and trace element as well as mineral analyses cannot be used to investigate the state of alteration, as has been shown above (see Sections 5.a, 5.b, 5.c).

The entire Siberian flood basalt province with a volume of $1.5 \times 10^6 \text{ km}^3$ (Sharma, Basu & Nesterenko, 1991) was formed within 600 000 years (Campbell *et al.* 1992). There is no evidence for soil formation, therefore no clay formed during a soil formation process in the time intervals between single basaltic flow eruptions, and palaeosoils were not found in the working area. This is consistent with the presence of vermiculite which is an alteration product of chlorite in a humid and cold climate without soil formation.

The formation of the clay minerals can be divided into three different stages in the tuffs.

Stage 1. Alteration of glass and olivine to chlorite. Pyroxene is fresh in the samples and cannot be the precursor of the chlorite.

Stage 2. Further alteration of chlorite leading to a partially replacement of the interlayer hydroxyl sheet by hydrated cations. Development of corrensite, a regular mixed layer clay mineral composed of chlorite/vermiculite.

Stage 3. Vermiculite formation as alteration proceeds (Chamley, 1989).

Corrensite was found in T2 and T6 and vermiculite in the other four tuffs. This implies that the alteration process towards vermiculite in T2 and T6 is still ongoing. It also suggests that the stage of alteration is lower in T2 and T6 than in the other tuff outcrops.

Surprisingly, in the tuffs with immobile element ratios lower than the associated basalts and which contain albites, corrensite occurs as clay mineral. These results are intriguing, as corrensite suggests a lower state of alteration whereas the immobile element ratios

and albite suggest a higher state of alteration compared with the other tuffs. Interestingly, T4 contains 50 % calcite, but has immobile element ratios similar to the associated basalts. This can only be explained if the circulating fluid did not affect the immobile elements and implies that only specific alteration conditions affect the mobility of the immobile elements. Consequently, the degree of alteration cannot be deduced from the immobile elements.

These results imply that the state of alteration deduced from the clay minerals cannot be directly associated with the state of alteration deduced from the plagioclases, the immobile element ratios or the mineral assemblage. This suggests that the alteration processes are extremely complex. The progressive alteration to different clay minerals can be followed step by step in contrast to the other alteration processes. Therefore, we suggest that the state of alteration can be best deduced from the clay minerals. Using this approach implies that T2 and T6 have a lower state of alteration than the other tuffs even though their immobile element ratios differ more from the basalts than from those of the other tuffs. This supports the idea that immobile elements are mobilized selectively only by some alteration processes.

6. Conclusions

Tuffs of the Putorana region, interbedded with tholeiitic basalt flows of the Siberian continental flood basalts province have volumes $< 100\,000 \text{ m}^3$. The composition of augite crystals and immobile element ratios (TiO_2/Zr , Y/Zr) probably imply that the tuffs were derived from basaltic magmas similar to those of the flood basalt lavas.

Subsequent sedimentary, hydrothermal and low-temperature alteration processes have modified the original mineralogy and geochemistry of the tuffs significantly. Post-eruptive alteration led to complex changes in major and trace elements. The primary mineralogy consisted of clinopyroxene, plagioclase, olivine, glass and spinel. Olivine and glass were almost completely replaced and crystallization of carbonate, zeolites, clay minerals, and analcime was triggered by circulating fluids. The fluid compositions varied significantly despite the close spatial relationship of the tuff outcrops. This points to locally restricted fluids with different compositions that led to the formation of different minerals. The environments of deposition of the tuffs were most likely variable, since, for example, only one sample was deposited in an aqueous, possibly lacustrine environment, contributing to the different alteration histories of the tuffs, and it is not possible to generalize the alteration conditions for the tuffs from the Putorana region. Therefore, alteration conditions must always be studied individually in each outcrop and cannot be assumed to be spatially invariant.

We suggest that the state of alteration can be best verified in highly altered rocks by clay mineral analysis. In two samples, corrensite, the transition mineral from chlorite to vermiculite, is still preserved and this implies a lower stage of alteration in these samples compared to the other tuffs. Interestingly, the samples which are most altered, based on their immobile element ratios (TiO_2/Zr , Y/Zr) and their plagioclase compositions, contain corrensite. This contradicts the state of alteration deduced from the clay minerals and shows the complexity of the alteration process. It also shows that (1) the immobile elements were depleted/enriched, and (2) the plagioclase minerals altered selectively only due to specific alteration conditions. We suggest that the clay minerals are more reliable in determining the state of alteration than the other parameters, because their mineral type can be followed step by step through the alteration process.

Acknowledgements. This work was partly financed by the FWF (Fonds zur Förderung der wissenschaftlichen Forschung) and the Austrian Federal Ministry of Education, Science and Culture. Many thanks to Theodoros Ntaflos (University of Vienna) for the opportunity to collect the samples and also for his support during sample collection, Eugen Libowitzky (University of Vienna) for assistance on the SEM and Hans Kurzweil (University of Vienna) and Lawrence Amy (University of Bristol) for many constructive discussions. Also we would like to thank Erich Draganits (University of Vienna) for improving the figures. Thank you to the reviewers Drs P. T. Leat and S. Königer; their comments helped to improve the manuscript.

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Appendix 1. Detailed sample descriptions

Tuff 1 (T1) has a thickness of a few metres and is located 555 m above sea-level at N 69°24.121' and E 93°29.359'. It is a siltstone and has a light brown colour. The matrix contains ~1 mm size dark brown vermiculite minerals.

Tuff 3 (T3) and *Tuff 4 (T4)* occur together and are located at N 69°49.080' and E 93°51.044' with T4 (280 m above sea-level) lying on top of T3 (240 m above sea-level). The outcrop T3 comes from has a thickness of up to 40 m, whereas the maximum thickness of T4 is only several centimetres. T3 has a black colour and its grain size varies from mudstone to siltstone. This tuff contains many black clay and ore agglomerations.

Tuff 2 (T2) is located 2 km east of T3 and T4 next to the Ayan River (elevation 255 m). It is 1–50 cm thick and has a green colour. It shows a fine grain-size grading in several sequences which are concordant to each other. This multiple grain-size grading and the concordant layering are typical for

the successive deposition of several individual primary ash fall tuffs. The grain size varies from mudstone to medium sandstone.

Tuff 5 (T5) and *Tuff 6 (T6)*, cropping out together at N 69°48.442' and E 93°49.784', are located directly at the Ayan River, with a horizontal distance of 30 m and a vertical distance of 10 m apart. They occur at 320 m and 330 m above sea-level. The thickness of each unit is about 15 m. The colour of T5 is dark brown and it is a sandstone. The grains are well rounded and closely spaced with a low porosity. The grey-green T6 is a fine sandstone to coarse sandstone and shows graded bedding. This tuff contains many angular (Shepard, 1963) red and green particles, but in general the particles are well rounded.

Three basalts associated with the tuffs were also analysed. They are from the following locations: Pu-3a (460 m above sea-level) is located at N 69°24.121' and E 93°29.359', Pu-35 (463 m above sea-level) at N 69°24.121' and E 93°29.359', Pu-55 (385 m above sea-level) at N 69°48.434' and E 93°49.778'.