

# Hydrothermal alteration of the Ediacaran Volyn-Brest volcanics on the western margin of the East European Craton

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## Abstract

The Ediacaran continental flood basalts and associated tuffs were studied to identify and quantify alteration processes by means of XRD and chemistry, supplemented by Mössbauer and FTIR spectroscopies, petrography, oxygen and iron isotopes, K-Ar dating, and organic geochemistry. Two superimposed alteration processes were identified: the Ediacaran hydrothermal alteration, induced by meteoric waters, heated and put in motion by the cooling basalt, and the Caledonian and/or Variscan potassic alteration. The degree of basalt alteration was quantified using as an index the sum of primary minerals in the bulk rock. The sequence of minerals dissolved and crystallized during the hydrothermal alteration was established. The alteration resulted in the loss of Ca (dissolution of plagioclases), compensated by the gain of

water and Mg (crystallization of clays), and proceeded from the edges of the basalt flows in an oxidizing environment, evidenced by the increasing amount of hematite and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio of the bulk rock. Cyanobacteria were active in the hydrothermal system, most probably responsible for the measured negative  $\delta^{56}\text{Fe}$  values and more reducing conditions at the stage of intense alteration. Chlorophaeite (palagonite), following quartz as the earliest petrographically identifiable basalt alteration product was found to vary systematically from fully isotropic to birefringent. The chlorophaeite was identified as a mixture of Fe-montmorillonite and Fe-saponite, identical with griffithite and oxysmectites, probably preceded by a finer-grained ferrosaponite at the isotropic stage. REE content of chlorophaeite indicates basaltic volcanic glass (sideromelane) as the major source of material. REE in clays are contained mostly in the dioctahedral smectite, while in the bulk rock mostly in phosphates. The smectite characteristics and Mg enrichment are indicative of the hydrothermal basalt alteration process, which perhaps was dominant also on Mars.

Both mineral and chemical composition of tuffs vary continuously from basaltic to felsic, the latter close to the measured rhyodacite composition, dominated by quartz and feldspars. The basaltic tuffs resemble the most altered basalts but contain also abundant albite and chlorite, indicative of higher alteration temperatures, up to 220°C. Tuff composition indicates stronger component of felsic volcanism in the trap formation than evidenced by the preserved bodies of effusive rocks.

**Key words:** aluminoceladonite; chlorophaeite; cyanobacteria; griffithite; ferrosaponite; Martian smectite, palagonite.

## Introduction

Sub-surface (non-related to weathering) alteration of basalts is a widespread and intensely studied phenomenon, known from three major Earth environments: submarine hydrothermal, burial diagenetic/metamorphic, and continental hydrothermal.

A good example of submarine hydrothermal alteration within a 60-165°C measured temperature range is the 1300 m profile of DSDP Hole 504B south of the Costa Rica Rift in the Pacific (Alt et al., 1986; Shau and Peacor, 1992). A clear alteration sequence was observed: iron oxides, saponite, celadonite, phillipsite, anhydrite, and aragonite formed below 150°C, and mixed-layer saponite-chlorite, corrensite, corrensite/chlorite, and finally chlorite, minor talc, quartz, pyrite, epidote, laumontite, heulandite, prehnite, actinolite, and albite formed in deeper, hotter parts. Altered basalt becomes a sink for Mg and K from seawater, affecting the element mass balance of the oceans. From the saponitic to chloritic end of the trioctahedral clay sequence, Si/(Si+Al) ratio decreases, while Fe/(Mg+Fe) increases. In another submarine site (801), Alt et al. (1992) observed a range of alteration products from pure saponite to almost pure dioctahedral smectite, accompanied by pyrite and calcite. Other samples contain celadonite, glauconite, and iron oxides. With progressing alteration (measured by  $\text{H}_2\text{O}^+$ ), an increase in  $\delta^{18}\text{O}$ , iron oxidation and  $\text{K}_2\text{O}$  is observed, while  $\text{CaO}$  decreases, but  $\text{MgO}$  does not show a clear trend.

A particularly clear sequence of burial metamorphic alteration zones was documented (Schmidt, 1993; Schmidt and Robinson, 1997) from the 8 km thick pile of the Keweenawan Middle Proterozoic continental subaerial rift basalts, outcropping on the shore of Lake Superior, and known for native copper deposits. At the top of sequence, saponite is dominant, and going down section, random chlorite-smectite and corrensite appear, accompanied by laumontite and albite, then chlorite with prehnite and pumpellyite, and finally epidote and actinolite (greenschist facies). Albite is the most abundant alteration product of Ca-rich plagioclase. Fe oxides were not reported. Celadonite occurs sporadically. Like in the

submarine alteration, from the saponitic to chloritic end of the trioctahedral clay sequence Si/(Si+Al) ratio decreases, while Fe/(Mg+Fe) increases. Strong control of porosity and permeability over the extent of alteration is evident: massive flow centres have less advanced alteration than porous, thus permeable tops and bottoms.

Subaerial hydrothermal alteration of basalts has been most thoroughly studied in Iceland, where data measured in active hydrothermal systems were used to assess temperature ranges of subsequent alteration zones, analogous to burial and marine hydrothermal (Franzson et al., 2008): smectite+zeolites correspond to the 50-200°C range, trioctahedral mixed layer clays dominate over the 200-220°C range, then chlorite takes over and albitization starts, epidote appears at ca. 240°C, actinolite at 275°C, and amphibole above 350°C. Analogous basalt alteration sequences have been identified in other hydrothermal fields, e.g. in a geothermal well in Hawaii (Stone and Fan, 1978).

This review demonstrates that the alteration of basalts in three different environments proceeds via a very similar sequence of mineral assemblages, which indicates dominant control of the rock chemistry over the alteration mineralogy, with porosity and permeability affecting the reaction progress, and in particular the pathway of smectite to chlorite transition (Robinson et al., 2002).

Similar qualitative mineralogical data (e.g. Juskowiakowa, 1974; Kuzmenkova, 2005; Derevska et al., 2006; Emetz et al., 2006; Kuzmenkova et al., 2006; Melnychuk, 2006; Shumlyanskyy and Tsymbal, 2006; Skakun et al., 2006) are available also for the Ediacaran Volyn-Brest volcanics of the East European Craton (EEC; Figure 1) and they inspired the present study. Our study was focused on adding a quantitative mineralogical dimension to the knowledge of hydrothermal basalt alteration, on understanding the conditions of this alteration, and on discriminating the effects of younger alteration phenomena. The clay alteration products were studied in most detail to characterize the substrate on which the

Ediacaran weathering of basalts took place (Liivamägi et al., 2018). It was also hoped that better understanding of the Ediacaran basalt hydrothermal alteration may be useful as a model for the origin of clays on Mars. They have been detected both by remote and in-situ methods as the main products of basalt alteration in the Noachian age (e.g., Ehlmann et al., 2011a,b; Carter et al., 2013; Chemtob et al., 2015). The origin of these clay minerals is currently debated, and potential formation environments include subsurface hydrothermal systems, subaerial weathering profiles, lacustrine environments, and steam or a supercritical atmosphere of water and CO<sub>2</sub> (e.g., Ehlmann et al., 2011a,b; Vaniman et al., 2014; Bishop et al., 2018; Cannon et al., 2018). Here, we identify mineralogical and geochemical signatures of subsurface hydrothermal clay deposits that can be used to constrain clay formation environments on Mars.

## **Study area**

The Volyn-Brest Ediacaran flood basalts, up to 500 m of lavas and volcanoclastics, cover 140,000 km<sup>2</sup> of the western margin of the East European Craton. The original volcanic cover extended much further east and north, as evidenced by isolated erosional remnants in these areas (Figure 1). Towards the southeast, the volcanic cover continues to an unknown distance, deeply buried below Paleozoic sediments of the Teisseyre-Tornquist Zone (Paczeńska, 2010), which separates the Precambrian from the Paleozoic platform. In Volyn (northwest Ukraine north of Lvov), the Ediacaran basalts occur over ca. 80 km<sup>2</sup> at the surface or under a thin cover of the Cretaceous rocks and have been used as building stones since XVII century (Rajchel, 2012). In other regions, they are covered by the Late Ediacaran clastic sediments and younger deposits.

The Volyn-Brest trap region is a continental flood basalt province, analogous to the well-known Columbia River, Deccan, Paraná, or Siberian traps (Kuzmenkova et al., 2010). It is considered a product of the supercontinent Rodinia rifting, which detached Amazonia from Baltica by opening of the Tornquist Ocean in the Late Ediacaran (Poprawa et al., 1999; Nawrocki and Poprawa, 2006). Deep root bodies of the basalt province were identified recently by geophysical methods in the Teisseyre-Tornquist Zone, SE of Brest (Mazur et al., 2018a).

Volyn basalts have been studied since the mid-19th century, and particular interest was generated by finding a native copper mineralization (Małkowski, 1929). These early studies (conf. Białowolska et al., 2002 for references) were carried out on rocks from the Volyn outcrops, later also on the core materials from Belarus, Poland and Ukraine (Ushakova, 1962; Juskowiak and Ryka, 1967; Makhnach and Veretennikov, 1970; Juskowiakowa, 1971; Compston et al., 1995; Białowolska et al., 2002; Bakun-Czubarow et al., 2002; Emetz et al., 2004; Kuzmenkova, 2007; Nosova et al., 2008; Kuzmenkova, 2011; and many others). Recent investigations, summarized in a monograph (Shumlyanskyy, ed., 2006), were centered on the genesis of native copper mineralization. All of these studies were devoted mainly to geochronology, geochemistry, and petrographic observations of mineral successions.

Shumlyanskyy et al. (2016) reviewed the geochronological literature. Early K-Ar measurements of the whole rock gave a broad range of 690-540 Ma. The  $^{40}\text{Ar}/^{39}\text{Ar}$  whole rock method yielded two age groups: 590-560 Ma (magma crystallization) and 393-369 Ma (potassic alteration). The Rb-Sr isochron method applied to four whole rock samples gave an imprecise age of  $552\pm 59$  Ma, while U-Pb zircon ages range from  $551\pm 4$  Ma to  $573\pm 14$  Ma.

Geochemical studies identified the trap rocks as within plate continental basalts and documented vertical zonation of the trap: picrobasalts and subalkaline olivine basalts in the lower basalt flows are covered locally (Figure 1) by felsic rocks (andesite, dacite, rhyodacite,

trachyandesite), and tholeiites dominate the upper flows, all accompanied by more or less abundant tuffs (Bakun-Czubarow et al., 2002; Kuzmenkova et al., 2008; Nosova et al., 2008). The Ediacaran paleosols are developed both on the lower (Kuzmenkova et al., 2011) and on the upper basalts (Levykh, 1999; Liivamägi et al., 2018), documenting the continental, subaerial origin of the volcanic sequence.

Since the findings of native copper (Małkowski, 1929) and celadonite (Kamieński, 1929), later confirmed by Lazarenko (1956), it was realized that Volyn basalts underwent widespread hydrothermal alteration of variable intensity. Shumlyanskyy and Tsymbal (2006) recognized this variable degree of alteration and characterized geochemically the alteration sequence: oxidation of iron; increase of MgO, K<sub>2</sub>O, LOI, Rb, Ba, Zr, Nb, Ta, Th, U; decrease of CaO and Sr. They observed more intense alteration of tuffs compared to the flood basalts, but they interpreted the exceptionally high MgO content of some tuffs as reflecting the primary volcanic composition. Melnychuk (2006) documented carbonate, zeolite, and prehnite-pumpellyite zones of hydrothermal alteration in the flood basalts and volcanic tuffs.

In Volyn and Belarus, i.e. outside the Teisseyre-Tornquist Zone, the basalts have never been deeply buried, as indicated by regional organic geochemistry data for overlying sediments (Nehring-Lefeld et al., 1977) and confirmed recently by studying the Ediacaran paleosols developed on basalts (Liivamägi et al., 2018) and hopane biomarkers in the overlying Ediacaran sediments (Goryl et al., 2018). Initially, a "fresh" appearance of the unaltered sections was used as evidence of the lack of regional metamorphic or advanced diagenetic changes (Ushakova, 1962; Juskowiak and Ryka, 1967; Makhnach and Veretennikov, 1970). Juskowiakowa (1974) observed that the alteration develops from the upper and lower surfaces of the lava flows, it may be complete in thin flows and tuffs or tectonic zones, and it involves the development of chlorite, illite and celadonite. The alteration sequence was characterized by the microscopic studies of Volyn native Cu deposits

(Derevska et al., 2006; Emetz et al., 2006; Skakun et al., 2006). Plagioclase (andesine-anorthite), clinopyroxene, magnetite, ilmenite, titanomagnetite, volcanic glass, and rare olivine (often recognized only as prehnite pseudomorphs) were identified as primary basaltic components. Clinocllore, hematite, albite, and pumpellyite were identified as pre-ore minerals; prehnite, laumontite, wairakite, quartz, and K-spar as syn-ore minerals; and quartz, stilbite, mordenite, heulandite, thomsonite, tri- and dioctahedral smectite, chlorite, vermiculite, calcite, analcime, barite, and kaolinite as post-ore minerals. Similar composition, including a wider range of zeolite minerals, was reported by Kuzmenkova (2005). Kuzmenkova et al. (2006) characterized in detail glassy-looking accumulations of dark material, described from various basalts under the name "chlorophaeite" and present even in very fresh-looking basalts – the equivalent of palagonite (conf. review by Stroncik and Schmincke, 2002), of the late-magmatic lithogel of Simanovich et al. (1986), and probably of glass of Emetz et al. (2006). Smectite, chlorite and analcime were identified in chlorophaeite accumulations. Mysiak et al. (2016) reported native Cu and Ag occurring along with hydrothermal minerals, while native Fe, Sn, Al, chlorides of Sn and Fe, and a FeCrNiTi alloy in pneumatolytic veins cutting the hydrothermal alteration zones. Native Fe was reported also by Kvasnytsya et al. (2006).

Kuzmenkova (2007) investigated the felsic rocks (rhyodacites) and found large amounts of quartz, K-spar, albitized plagioclase, and chlorite+biotite pseudomorphs after pyroxene. The chemical composition of tuffs is also much more variable than flood basalts, demonstrating higher K and Na and lower Ca. Saponite, mixed-layer chlorite-smectite, hydromica, analcime, other zeolites, and hematite were identified as alteration minerals in the tuffs.

To summarize: the Volyn flood basalt mineral and chemical composition, and their alteration processes have been well recognized by numerous studies. This study aims at



quantifying the alteration process, investigating its relationship to the conditions on the Ediacaran land, and investigating in more detail the iron-rich smectite, which is the main alteration product.

## **Materials**

All investigated samples (locations in Figure 1) are core materials, except for the Tashki samples, collected from a quarry. Present depth, macroscopic characteristics, and location of a sample in the trap profile (lower, middle, and upper volcanogenic strata) are given if available in Inline Supplementary Tables 1 and 2, listing separately flood basalts, clays from veins and cavities in basalts, felsic rocks, and tuffs, according to the macroscopic identification. Several chlorophaeite accumulations, studied earlier by Kuzmenkova et al. (2006) were also investigated, some of them only by FTIR because of small amount of the available material, along with the reference montmorillonite samples 4529-2 and 4517-1 from the paleosol, developed on the Volynian basalt (Liivamägi et al., 2018). In three cases (Mokrany-1, 2, and 3), both basalt sample and a chlorophaeite accumulation separated from this basalt sample were available. Additional paleosol samples were used in the organic geochemistry study.

## **Methods**

The main techniques used in this study are: quantitative X-ray diffraction of the bulk rock (QXRD) using in-house Q-Min software (by Dr. M. Szczerba, Institute of Geological Sciences PAS), XRD of the clay fractions separated from the bulk rock, chemical analysis (major elements by X-Ray Fluorescence (XRF) and trace elements (including REE) by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) on the same lithium

borate fused disc), Mössbauer spectroscopy and iron isotope composition of the bulk rock and of the clay fractions, and the K-Ar dating of clay fractions. These methods are identical to those used by Liivamägi et al. (2018) in the study of paleosols developed on these basalts, and their descriptions are reproduced with some modifications in the Supplementary Materials, along with additional techniques applied in this study: oxygen isotope and FTIR measurements of the bulk rock and the clay fraction, organic geochemistry, and petrographic observations of the basalt alteration products.

## **Results**

### ***XRD of the bulk rock***

#### ***Flood basalts and chlorophaeites***

Quantitative XRD data for basalts (in wt%) are given in Inline Supplementary Table 1, and representative XRD patterns, illustrating the encountered variability of mineral composition, are presented in Figure 2. Most common major components are calcic plagioclase, pyroxene, magnetite, dioctahedral smectite, trioctahedral smectite and chlorite or mixed-layer chlorite-smectite. Quantities of these major components vary broadly. Both di- and trioctahedral smectites are present in most samples, as evidenced by separate 02 and 06 peaks (Figure 2). Common minor components are: quartz, potassium feldspar of orthoclase/sanidine/sanidine group (most often more abundant than quartz), and hematite. Orthoclase cannot be distinguished from sanidine in the bulk rock XRD, so they are reported as a group. Rare minor components are ilmenite, anatase, analcime, pseudobrookite, clinoptilolite, laumontite, calcite, and siderite. Olivine, reported in published petrographic studies, was not detected. The mineral compositions of two available gabbro samples fall within the limits characteristic of basalts (Inline Supplementary Table 1). Three chlorophaeite accumulations were

investigated by XRD along with the host basalts, but only qualitatively in glass capillaries, because of the small amount of sample available. Di- and trioctahedral smectites, quartz and traces of calcic plagioclase, calcite and dolomite were detected in these samples. The smectitic clays are identified as separate di- and trioctahedral phases based on well resolved 02 reflections, by analogy to the bulk basalt XRD patterns, where the 06 reflections could also be recorded (compare Figures 2 and 3).

### **Felsic rocks**

Three rhyodacite samples were available. Their mineral composition is totally different from basalts: quartz, orthoclase/sanidine/sanidine, dioctahedral clay (illite-smectite), trioctahedral mica, hematite, chlorite, and a trace of kaolinite in one sample (Inline Supplementary Table 1, Inline Supplementary Figure 1).

### **Tuffs**

Only purevolcanic materials were considered (Inline Supplementary Table 2, Inline Supplementary Figure 1). The presence of minerals absent from pyroclastic materials: microcline and muscovite was regarded as evidence of non-volcanic contamination (tuffites) and such samples were not included in the analysis. Mineral composition of tuffs is extremely variable. Most common components are: quartz, orthoclase/sanidine, Ca-plagioclase, dioctahedral expandable clay (illite-smectite or smectite), aluminoceladonite (identified by  $1M_{IV}$  polytype and  $d_{001}$  close to  $9.88 \text{ \AA}$ , characteristic of this mineral, and distinguishing it from celadonite of  $d_{001}=9.97 \text{ \AA}$ ), and chlorite or mixed-layer chlorite-smectite. Less abundant are trioctahedral smectite, albite, anatase, hematite, analcime, minor and rare are pyroxene and amphibole. Locally, tuffs contain dolomite, Mn-Fe dolomite and calcite (Pinsk-26), or only calcite (Tashki).

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276 **Tuff-basalt alternation**

277 The contrasting characteristics of flood basalts and tuffs, emerging from the entire data set,  
278 can be observed also in a single vertical profile (Kobryn), composed of three basalt flows  
279 interbedded with four tuff layers free of non-volcanic contamination (Inline Supplementary  
280 Table 2). Flood basalts contain trace of quartz and hematite, abundant Ca-plagioclase,  
281 pyroxene, and trioctahedral smectite, and occasional minor chlorite or chlorite-smectite. Clay  
282 abundances increase towards the top surfaces of the basalt flows. Tuffs contain abundant  
283 quartz, orthoclase/sanidine, Ca-plagioclase and hematite, chlorite plus minor chlorite-  
284 smectite, dioctahedral illite-smectite, and aluminoceladonite. Top samples from two tuff  
285 layers contain kaolinite.

286

287 **XRD identification of clay fractions**

288

289 Mineral composition of  $<0.2\ \mu\text{m}$  clay fractions, including percent smectite (%S) in mixed-  
290 layer illite-smectite, measured from the diagnostic peak positions on the glycolated patterns,  
291 using the regressions based on data of Środoń et al. (2009), is presented in Inline  
292 Supplementary Table 3.

293

294 **Flood basalts**

295 Attempts to separate pure clay fractions were unsuccessful for basalts with  $>60\%$  of primary  
296 minerals, despite long grinding in McCrone mill and sonification. The  $<0.2\ \mu\text{m}$  separates  
297 contain abundant plagioclase and exhibit poor orientation (Mokrany-1B in Inline  
298 Supplementary Figure 2), indicating intimate intergrowth of smectite with host plagioclase  
299 crystals. More altered samples allow clean separation of clay fractions (e.g. 4504-1A in Inline

Supplementary Figure 2), which contain mixtures of di- and trioctahedral smectites (Inline Supplementary Figure 3), as evidenced by separate 02 and 06 reflections. Sample 4417-1 (Inline Supplementary Figure 2) contains corrensite, chlorite and illite-smectite with ca. 40% S. Among clays filling cavities in basalts, pure trioctahedral minerals were identified: saponite (4600-1), and chlorite with minor corrensite (Kob-23: both shown in Inline Supplementary Figure 2). Sample 4600-1 contains a minor admixture of corrensite in 2-0.2  $\mu\text{m}$  fraction.

### **Tuffs**

Clay fractions of tuffs differ from flood basalts by the presence of aluminoceladonite in many samples: from a trace to the dominant component. The trace amounts are associated with illite-smectite of >70%S (Inline Supplementary Figure 4: Pinsk-40), sometimes also with small amounts of chlorite-smectite close to corrensite (Inline Supplementary Figure 4: Tashki-10), and characterize rocks with low quartz content (<10%). In one sample a chlorite-smectite close to chlorite was dominant (Inline Supplementary Figure 4: Pinsk-40C).

Samples with more abundant aluminoceladonite contain illite-smectite of <50 %S, chlorite-smectite close to corrensite, discrete chlorite, and represent rocks with higher quartz content (>10%, Inline Supplementary Figure 4: Pinsk-46). Such samples contain abundant chlorite in 0.2-2  $\mu\text{m}$  fraction. Most commonly, the 005 reflection of aluminoceladonite is at 1.978 $\text{\AA}$  ( $d_{001}=9.90 \text{ \AA}$ ). In the extreme case, aluminoceladonite is the dominant component, (Inline Supplementary Figure 4: Kob-9B). In this sample, aluminoceladonite is accompanied by a regular illite, as 005 and 003 reflections are split into two peaks.

### ***Chemical data***

The chemical data were obtained for selected bulk samples and clay fractions (Inline Supplementary Table 4). The bulk rock data are grouped according to lithology into five categories: flood basalts, rhyodacites, tuffs, chlorophaeite, and vein and cavity clays. When average values are compared, tuffs are intermediate between flood basalts and rhyodacites, except Mg is similar to that of basalt and tuffs have elevated LOI, B, Cr, Cs, Cu, Ni, and Pb. The chlorophaeite sample (Mokrany-3A), when compared to its host basalt (Mokrany-3B), is depleted in most elements, including HREE and Fe, Na, Ca, Ba, Sr, Nb, Sc, Y, Zn, U, V, and Zr, but is strongly elevated in Si and moderately elevated in Mg, LOI, Cr, Cs, Cu, Ni, Rb, and LREE. The vein clays, when compared to average basalt, have strongly elevated Mg, LOI, and Co, elevated Fe, Ga and Ni, but most of the elements are depleted. REE are depleted particularly strongly and several times stronger in chlorite (Kob-23) than in the trioctahedral smectite sample (4600-1). The clay fraction of the latter is depleted even stronger. When clay fractions separated from basalts are compared to their host rocks, the common characteristics are the clay enrichment in Mg, LOI, Be, Co, Cr, Mo, and Ni, and depletion in B, K, Ca, Sr, Ba, Ti, Cu, Nb, and V. REE contents of the basalt clay fractions do not differ significantly from the bulk rock contents.

#### ***Mössbauer data***

The Mössbauer data (Table 1) were collected for a range of bulk rock basalt, vein clay, and tuff samples, selected clay fractions <0.2 µm, and two pyroxenes separated from the basalts. The spectra of pure minerals separated from basalts were used as starting parameters for fitting polymineral spectra of rocks (Table 1, Figure 4) and include: trioctahedral smectite (Inline Supplementary Figure 5, 4600-1), dioctahedral smectite (4529-2, cf. Liivamägi et al.,

2018), chlorite (Figure 4, Kob-23), and pyroxenes (4519-0 and 4603-1). Where applicable, the well known sextet of hematite and two sextets of magnetite were included in the fit.

Chlorite was found to contain only  $\text{Fe}^{2+}$ , dioctahedral smectite only  $\text{Fe}^{3+}$ , and trioctahedral smectite both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Two pyroxenes contained  $\text{Fe}^{2+}$  distributed over two possible crystallographic positions in different proportions, visible in the Mössbauer spectra as two well resolved quadrupole doublets. Finally, the rocks were analyzed assuming up to 7 different components with 9 subspectra (Table 1, Figure 4). In sample Mokraný-1B one additional component was detected with parameters characteristic of the amorphous wüstite,  $\text{FeO}$ .

The measured bulk rock percent  $\text{Fe}^{2+}$  in the total Fe vary from 65 to 23% for flood basalts and from 49 to 11% for tuffs. The corresponding  $\text{Fe}^{2+}$  values, calculated for the clay fraction from the bulk rock data, are lower than the bulk rock values for less altered flood basalts but higher than the bulk rock values for more altered basalts and tuffs. The %  $\text{Fe}^{2+}$  values of clays, measured for the  $<0.2\ \mu\text{m}$  fractions and calculated from the bulk rock analysis are essentially identical, if no chlorite or chlorite-smectite is present (Mokraný-3B and 4504-1 in Table 1), indicating that the separation procedure did not affect the oxidation status of Fe in smectites. The %  $\text{Fe}^{2+}$  values are lower in the bulk rock in other cases (4417-1 and 4600-1), which is explained by relative concentration of smectite with respect to chlorite in the  $<0.2\ \mu\text{m}$  fraction.

#### ***FTIR data***

#### ***Identification of clay fractions***

The mid-infrared (MIR) spectra of the  $<0.2\ \mu\text{m}$  fractions of XRD-identified end-member components (dioctahedral smectite from paleosol 4517-1, trioctahedral smectite from 4600-1,

and chlorite from Kob-23) were measured to serve as references (Figure 5). Spectra appear similar in the  $\nu\text{OH}$  region, exhibiting two broad bands centered at  $3624\text{ cm}^{-1}$  due to smectite or chlorite structural OH, and at  $3434\text{ cm}^{-1}$ , mainly due to water. For chlorite, the band at  $3624\text{ cm}^{-1}$  is characteristically broader than for the other samples and is typical of trioctahedral chlorite (clinochlore type). For the dioctahedral smectite, the  $3624\text{ cm}^{-1}$  is characteristically narrower than for the other samples and is typical of montmorillonite (e.g. Madejová et al., 2017). For the trioctahedral smectite (4600-1), a shoulder at about  $3670\text{ cm}^{-1}$  is observed in addition to the  $3624\text{ cm}^{-1}$  band. Such bands are found in griffithite (Madejová et al., 2017), which was previously identified as a trioctahedral iron-rich saponite (Komadel et al., 2000). Note that for saponite depleted in iron, the  $\nu\text{OH}$  is narrow and centered at  $3678\text{ cm}^{-1}$ . The spectra of the two other samples Mokraný-3B and 4504-1A are similar to 4600-1.

The  $1200\text{-}400\text{ cm}^{-1}$  region was more discriminant for sample characterization. The dioctahedral smectite could be unambiguously identified as montmorillonite through the occurrence of  $\delta\text{Al}_2\text{OH}$  and  $\delta\text{AlMgOH}$  specific vibration bands at  $920$  and  $837\text{ cm}^{-1}$ , respectively (e.g. Madejová et al., 2017). A shoulder at  $878\text{ cm}^{-1}$  due to  $\delta\text{AlFe}^{3+}\text{OH}$  indicated that the montmorillonite contains some octahedral trivalent iron. The spectra of the 4600-1 and 4504-1A samples corresponded clearly to griffithite with the characteristic bands at  $1016$ ,  $678$  and  $452\text{ cm}^{-1}$  and shoulders at  $740$  and  $520\text{ cm}^{-1}$  (Madejová et al., 2017). The two strong bands at  $1016$  and  $452\text{ cm}^{-1}$  are respectively due to  $\delta\text{Si-O}$  and  $\delta\text{Si-O}$ , whereas the  $678\text{ cm}^{-1}$  band is mainly due to  $\delta(\text{Fe}^{2+},\text{Mg})_3\text{OH}$  and indicates clearly the trioctahedral nature of the smectite. The Mokraný-3B spectrum revealed quartz in mixture with griffithite. The small shoulders at  $876$  and  $912\text{ cm}^{-1}$  indicated the occurrence of octahedral aluminium and trivalent iron in dioctahedral configuration.

#### **Comparison between clay component in chlorophaeite and the surrounding basalt**



As seen in Figure 6, the clay components in chlorophaeite are the same as those in the surrounding basalt. Indeed, for Mokrany-3A and Mokrany-4A, the spectra revealed the same features as for Mokrany-3B described above. The clay component is then griffithite (see above). The slightly more pronounced dioctahedral features (shoulders at 878 and 912  $\text{cm}^{-1}$  due to of  $\delta\text{Al}_2\text{OH}$  and  $\delta\text{AlFe}^{3+}\text{OH}$ ) in Mokrany-4A indicated a higher content of octahedral aluminium and trivalent iron in dioctahedral configuration than in Mokrany-3A. For Mokrany-1A, the difference between the two spectra was the occurrence of feldspars in the surrounding basalt that hide the clay component features. However, in both samples griffithite could be identified and no dioctahedral features could be observed. The variability of chlorophaeite composition detected in MIR was also well expressed in NIR (near infrared), where the clay features could be observed without overlapping by quartz or feldspars.

#### ***Organic geochemistry data***

All the rock samples investigated in this study contain organic matter (OM), but total organic carbon (TOC) content did not exceed 0.2%. The main constituents of OM in silylated total extracts (Figure 7A) were *n*-alkanes and fatty acids (FAs). The distribution of these biomarkers in the basalt sample 4600-3B differs significantly from other samples (Figure 7B): long-chain *n*-alkanes and *n*-alkanoic acids with the maxima between  $\text{C}_{23}$  and  $\text{C}_{29}$ , and  $\text{C}_{22}$  and  $\text{C}_{30}$  carbon atoms, respectively, are present in relatively high concentrations. The values of short-chain to long-chain ratio (SCh/LCh) for *n*-alkanes and FAs for 4600-3B are 2.64 and 1.27, respectively, whereas they are 9.12 and 29.81 for 4600-3A. Moreover, OM in sample 4600-3B is characterized by the predominance of high molecular weight odd-carbon-numbered *n*-alkanes and even-carbon-numbered FAs, with the carbon preference index (CPI) values of 1.70 ( $\text{CPI}_{(25-31)}$ ) and 1.30 ( $\text{CPI}_{\text{total}}$ ) for *n*-alkanes, and 7.43 ( $\text{CPI}_{\text{f.a.}(20-30)}$ ) for FAs (for

CPI formulas see Rybicki et al., 2016). In the clay sample 4600-3A such predominance is not evident ( $CPI_{(25-31)}=1.01$  and  $CPI_{total}=0.83$ ).

### *Alteration petrography of chlorophaeite-bearing flood basalts*

The primary components of basaltic rocks identified by the petrographic observations are pyroxenes (ortho- and clinopyroxene), Ca-Na plagioclases, Fe,Ti oxides (titanomagnetite and ilmenite) and a homogeneous orange-brown isotropic substance presenting all the characteristics of chlorophaeite, as identified in several basaltic fields (Peacock and Fuller, 1928). Such isotropic material occurs in several petrographic settings: (1) areas of intersertal mesostasis through the body of the basaltic rocks (Figure 8A), (2) filling or lining of circular cavities (Figure 8B), (3) veinlets and associated infilling of dicitaxitic voids in the basaltic rock (Figure 8C), (4) pseudomorphs after orthopyroxene (Figure 8D).

In the least altered basalts (sample 4522-1), chlorophaeite is totally isotropic at a microscopic scale and it contains fine networks of minute cracks, which tend to be more developed when observed under vacuum (evidence of water content). In the cavities, chlorophaeite occurs as irregular films showing frequently collomorphous texture typical of precipitation of a gel material (Figure 8B).

Chemical microanalysis of the isotropic material observed in thin sections confirms its chemical homogeneity (Table 2). The sum of oxide weight percent, which does not exceed 85%, indicates a high water content of this isotropic material. Silicon and iron (oxidation state not determined from EDS) are dominant, with subordinate Mg, Al and Ca, and minor amounts of alkali elements (Na, K). Such a composition reasonably agrees with the formula given by Peacock and Fuller (1928) for chlorophaeite:  $(Fe,Al)_2O_3 \cdot 2(Mg,Fe,Ca)O \cdot 4SiO_2 + 10H_2O$ .

Observation of secondary mineral infillings indicates that chlorophaeite was deposited after the crystallization of quartz on the walls of vesicles and before the crystallization of chlorite, which cements the central parts of the vesicles. In the absence of phyllosilicates, minerals of the zeolite group are commonly observed as the late mineral cement of the residual open spaces of the basaltic rocks.

Smectitic clays were observed systematically as alteration products of the chlorophaeite bearing basaltic rocks. In the less altered basalts (sample 4522-1), the occurrences of smectitic clays are limited to minute spherules replacing chlorophaeite close to the contacts with the primary minerals of basalt (Figure 8E). Detailed observations with SEM indicate that such spherules are alteration features of chlorophaeite with a typical concentric structure. Smectitic clays, rimmed by a thin iron rich layer, were observed in the inner part of the spherule. The transition to unaltered chlorophaeite is marked by an external alteration halo, due to increasing microporosity and/or hydration of the initial isotropic material (Figure 8F).

Chemical microanalysis of smectitic clays formed in the spherules indicates a close chemical similarity with that of the chlorophaeite starting material, except for lower iron and higher Mg and Al in the smectite (Table 2). The thin iron rich layer of the spherules likely accommodates the excess iron released during the alteration process of chlorophaeite.

In moderately altered samples (sample 4519-0), most of chlorophaeite lost its isotropic optical characteristics because of replacement by spherulitic and ribbon-like smectitic clays. Furthermore, primary or the previously formed hydrothermal minerals present features of partial dissolution. This is particularly the case for the iron rich phyllosilicates such as Fe-chlorite (Figure 8G). It should be noted that quartz presents also some evidence of dissolution at the contact with the smectitic clays (Figure 8H). In strongly argillized samples (4603-1, and

4603-4), chlorophaeite is totally replaced by smectitic clays and the basaltic primary minerals are partially replaced by smectitic clays and minerals of the zeolite group.

#### ***O and Fe isotope data***

Oxygen isotope data were collected for a range of bulk basalts showing variable alteration intensity, for a few clay vein and tuff samples, and for selected clay fractions  $<0.2\ \mu\text{m}$  (Table 1). The least altered basaltic rocks have oxygen isotope values of 5.6 to 8.4 ‰. Basalts with increasing amount of alteration as well as tuffs have elevated  $\delta^{18}\text{O}$  values ranging from 10.1 to 20.0 ‰, similar to the isotope range of clay separates (17.8 to 21.0 ‰), and green clays from veins and cavities (10.1 to 17.0 ‰). The paleosol samples have elevated oxygen isotope values of 21.3 to 21.7 ‰ and the chlorophaeite sample has the highest measured value of 23.0 ‰.

A few of these  $<0.2\ \mu\text{m}$  clay fractions were also analyzed for iron isotope compositions (Table 1). In moderately altered basalts, the measured  $\delta^{56}\text{Fe}$  values are positive (0.028 for Mokraný-3B), but become negative with increasing alteration (down to -0.574 for Kob-23).

#### ***K-Ar dating of aluminoceladonite and illite-smectite***

Selected 2-0.2 and  $<0.2\ \mu\text{m}$  fractions of tuffs containing aluminoceladonite and illite-smectite were dated, at least twice, in order to establish the age of potassic alteration (Table 3). The  $\text{K}_2\text{O}$  contents vary from 1.785 % for the sample Tashki-10, with minor amounts of aluminoceladonite and illite-smectite, to 6.71% for Kob-9B, dominated by aluminoceladonite

(comp. Inline Supplementary Figure 4). The measured ages range from  $447.5 \pm 2.5$  to  $296.0 \pm 5$  Ma.

## **Interpretation**

### ***Alteration of flood basalts***

#### **Mineral changes**

No single sample was identified by XRD to be composed exclusively of primary basalt minerals: Ca-plagioclase, pyroxene, magnetite, ilmenite, and pseudobrookite. All samples contain hydrated components (mostly clays), but in variable quantities. If the sum of primary basalt minerals is accepted as an inverse index of basalt alteration, and if the degree of alteration is interpreted as a chronosequence (stronger alteration considered as a subsequent step of the process), a clear pattern of basalt alteration emerges, which can be described by five steps (Inline Supplementary Table 1), leading from almost fresh basalt to completely altered rock, though still preserving the basalt texture.

In the investigated samples, the earliest alteration products are quartz with trioctahedral smectite, or with a mixture of di- and trioctahedral smectite, all together < 10 wt%. This is also the mineral composition identified in chlorophaeite accumulations, found in basalts with more advanced alteration (compare Mokrany samples in Inline Supplementary Table 1). Based on this identity and on the microscope observations, we assume that the early quartz did not crystallize from melt but it is a product of basalt alteration (mostly of volcanic glass), deposited in crystal interstices or in larger chlorophaeite accumulations. Thus, step I can be identified tentatively as predominantly the alteration of volcanic glass. Emetz et al. (2006) also identified quartz as an alteration mineral based on petrographic observations.

In step II (90-80 % primary minerals), orthoclase/sanidine and hematite appear and the amount of smectites increases compared to step I. In step III (80-60 % primary minerals), chlorite appears, hematite, quartz and smectite abundances increase, pyroxene decreases, and ilmenite is absent. In step IV (60-25% primary minerals), anatase, analcime, zeolites and calcite appear, smectite, quartz and orthoclase/sanidine increase further, plagioclase starts decreasing, and pyroxene and pseudobrookite disappear. In step V (<25% primary minerals), plagioclase and magnetite disappear, and dioctahedral smectite plus chlorite prevail over trioctahedral smectite. The mineral composition of green clay veins and cavities in basalts is similar to the most altered basalts of step V. Ubiquitous hematite indicates an oxidizing alteration environment. In general, the lower basalts appear more altered than the upper basalts. Petrographic study confirmed the crystallization of smectite both before and after chlorite.

#### **Chemical changes**

The mineral alteration of basalt is paralleled by characteristic chemical changes, which are surprisingly limited (Inline Supplementary Table 4) considering the extent of alteration observed in some samples. The most pronounced is the decrease of CaO from 10% almost to 0% (except of samples with abundant calcite). The progressing dissolution of Ca-plagioclase results in the removal of Ca from the system (Inline Supplementary Figure 6). Sr decreases along with Ca. In steps IV and V, when plagioclase decreases strongly and analcime and other zeolites appear, Na seems to undergo redistribution: it is depleted from rocks without zeolites and enriched in remaining rocks.

The most pronounced gain during basalt alteration is the sum of OH and H<sub>2</sub>O in clays, represented by the loss on ignition (LOI), which increases from almost 0% to 6.5% in samples free of calcite. The correlation of sum of clay with LOI is very high and extrapolates to 0 for

unaltered basalt and to 9% for completely altered basalt. The trend line runs between values characterizing smectitic and chloritic green clay veins in basalt (Figure 9), in agreement with the intermediate, smectite+chlorite composition of clays in strongly altered basalt. LOI can serve as a simple measure of the degree of basalt alteration.

In the course of alteration, basalts also gain MgO, which increases about two times: from 5 to 10% and is positively correlated with the sum of clays (Figure 9), except of the samples with carbonates (not shown in the figure). Boron increases even more, in particular in steps IV and V, and good positive correlation indicates that B is located in the dioctahedral clay (Inline Supplementary Figure 7). Some increase in K, Cs, and Rb is also observed, and these trends can be best explained by combined contributions from K-spar and dioctahedral clay (Inline Supplementary Figure 8), which is partially illitized during much younger Paleozoic events (see below), particularly in highly altered basalts (Inline Supplementary Table 3).

The remaining elements vary, but no trends related to the degree of alteration can be observed (Inline Supplementary Table 4). The mass of basalt during alteration essentially does not change, because the additions and subtractions of elements quantitatively compensate. This mass stability is best expressed by very stable SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents. The collected data do not indicate measurable chemical changes between the lower and upper flood basalts.

REE patterns of most basalt samples are very similar and characteristic of the continental flood basalts (Farmer, 2003): enriched in LREE and without an Eu anomaly (Figure 10). REE do not differentiate the lower from the upper basalts. LREE seem slightly depleted at the final alteration step, particularly in the rock with high chlorite content (Kob-22), but otherwise basalt alteration does not affect the REE pattern, despite sometimes total destruction of major primary minerals. Inline Supplementary Figure 9 indicates that LREE in

basalts seem mostly contained in phosphates, of too low content to be detectable mineralogically (Inline Supplementary Table 1).

In chlorophaeite, LREE are strongly concentrated, compared to regular basalts, while HREE are depleted, and a strong negative Eu anomaly is present (Mokrany-3A in Figure 10 and Inline Supplementary Figure 9). This composition confirms the origin of chlorophaeite from the volcanic glass, enriched in incompatible LREE, while depleted in Eu contained in plagioclase (Weill and Drake, 1973) and depleted in HREE, which form isomorphic substitutions in pyroxene (Rollinson, 1994; Kuzmenkova, 2009). The basalt sample hosting chlorophaeite concentrations (Mokrany 3B in Figure 10 and Inline Supplementary Figure 9) displays analogous characteristics. Both have much higher LREE/P<sub>2</sub>O<sub>5</sub> ratio compared to regular basalts (Inline Supplementary Figure 9). These characteristics are similar to rhyodacite samples, which also differ from basalts by elevated LREE, negative Eu anomaly (Figure 10), and much higher LREE/P<sub>2</sub>O<sub>5</sub> ratio (Inline Supplementary Figure 9).

#### **Oxygen isotopes and $Fe^{2+}/Fe^{3+}$ ratio**

The progress of basalt alteration can be traced also by oxygen isotope compositions of the bulk rock samples (Table 1, Figure 11). They evolve linearly and extrapolate to a value close to 5‰ for the unaltered protolith, consistent with the oxygen isotope composition of unaltered continental flood basalts that show little to no contamination by continental crustal material (e.g. Harmon and Hoefs, 1995; Eiler 2001), and to the value of about 22‰ for complete alteration, similar to the isotopic compositions of smectite from the weathering zone (4529-2 and 4517-1) developed on basalts. A similar value of 23‰ characterizes the measured chlorophaeite sample, composed exclusively of secondary minerals (Mokrany-3A) and the clay fraction separated from the host basalt (Mokrany-3B<0.2). In Figure 12, the equilibrium relationships between oxygen isotope composition of smectite, of water, and temperature,



based on the fractionation equation of Sheppard and Gilg (1996) are depicted. The smectite-rich paleosol samples are in equilibrium with waters of about -5 ‰ at ambient temperatures. Using this isotope value of meteoric water, temperatures of dioctahedral smectite alteration in the basalts is estimated at less than 40°C. On the other extreme, if only magmatic water with a heavy oxygen isotope composition of +5‰ is assumed as the clay-forming fluid, then temperatures of about 100 to 130°C are indicated for the dioctahedral smectite formation.

Another parameter correlating well with the applied index of basalt alteration is % Fe<sup>2+</sup> of the bulk rock measured by Mössbauer spectroscopy (Table 1, Figure 13). The only measured chlorophaeite sample also fits this trend (Mokrany-3A). The linear trend extrapolates to ca. 67% for pure basalts and falls to 30% at ca. 40% of primary minerals, where those containing Fe almost disappear. Fe<sup>2+</sup> was lost due to oxidation, and not removal under anoxic conditions, as Fe content of the rock remained stable (Inline Supplementary Table 4). This trend implies that basalt alteration from the very beginning involved water carrying oxygen, in agreement with the increasing content of hematite.

The most altered samples (Kob-15 and 4417-1) and green clays from veins and cavities (4600-1 and Kob-23) fall off the general trend, as their % Fe<sup>2+</sup> is much higher (Table 1, Figure 13). This implies higher % Fe<sup>2+</sup> of clays at this stage of alteration, which agrees well with the Mössbauer estimates of % Fe<sup>2+</sup> in clay fractions of rocks (Figure 13), the Mössbauer data for tuffs, and the abundance of chlorite in these rocks. These data lead to the conclusion that at the most advanced stage of alteration, the conditions became more reducing.

#### **Alteration of organic compounds**

The primary distribution of particular organic compounds depends on the source of OM and can be modified by a wide range of post-depositional processes. Algae and bacteria generate short-chain *n*-alkanes with preponderance of C<sub>17</sub> and C<sub>19</sub> carbon atoms in the molecule, while

terrestrial higher plants (especially their leaf epicuticular waxes) are characterized by the occurrence of long-chain *n*-alkanes and *n*-fatty acids (*n*-FAs). Our studies evidenced a clear predominance of long-chain *n*-alkanes and *n*-FAs (excluding C<sub>16</sub> and C<sub>18</sub>) with majority of an odd and even number carbon atoms in the molecules, respectively, in most of the Ediacaran sedimentary rocks from the EEC (Goryl and Marynowski, 2016). Bobrovskiy et al. (2018) suggested that a possible source of long-chain *n*-alkanes in the Ediacaran rocks are spherical cyanobacterial colonies. The level of thermal maturity of the Ediacaran OM from the EEC is unusually low (the estimated equivalent of vitrinite reflectance did not exceed 0.57% R<sub>r</sub>) which promoted preservation of the primary character of distribution of organic compounds (Pehr et al., 2018; Goryl et al., 2018).

We believe that OM from the basalt sample 4600-3B is the most primary, non-oxidized or only slightly oxidized remnant of the Ediacaran cyanobacteria (and other microorganisms?) activity in the basalt hydrothermal system. Decay of long-chain *n*-alkanes and *n*-FAs and decreasing value of CPI in all other samples indicate more intense oxidation of OM in paleosols and in clays from cavities. Similar effect of OM alteration was presented by Elie et al. (2000, 2004): gradual degradation of long-chain *n*-alkanes and *n*-alkanoic acids during artificial oxidation of argillaceous rocks. Also Marynowski and Wyszomirski (2008) presented significant influence of early diagenetic oxidation on *n*-alkanes and other organic compounds distribution on an example of green and red Triassic clays. It seems that in the basaltic rock, primary OM was better protected against oxidation by the Ediacaran hydrothermal processes and further Caledonian and/or Variscan alterations. Such cyanobacteria activity offers a feasible explanation of more reducing conditions observed at the final stages of basalt alteration.

#### **Characteristics of the basaltic smectite**

For three available pure smectitic samples (<0.2  $\mu\text{m}$  fractions) with variable ratios of di- and trioctahedral components, the chemical data (Inline Supplementary Table 4), including  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio from the Mössbauer spectroscopy (Table 1), were cast into structural formulae (Table 4). The amount of potassium is very low, consistent with the XRD characteristics (Inline Supplementary Table 3, Inline Supplementary Figure 2).

The chemical compositions of the three smectitic samples evolve in a regular manner, consistent with the XRD evaluation of di/tri-smectite ratio (Table 4). The calculated numbers of octahedral cations are between 2 and 3 per half unit cell and they can be used as a measure of di/tri-smectite ratio. Plots of other data with respect to these numbers are linear ( $R^2 = 0.92$ - $0.99$ ) and allow extrapolating compositions of the end member components (Table 5). The dioctahedral smectite end member is a perfect montmorillonite without tetrahedral substitution, high Fe and Mg contents, and no divalent iron, as confirmed by Mössbauer spectra of the dioctahedral smectite component (Table 1) and dioctahedral smectite identified from basalt weathering zones by Liivamägi et al. (2018). Its oxygen isotope characteristics and its positive  $\delta^{56}\text{Fe}$  are also similar to the montmorillonites from paleosols, which are however much more rich in Al (op. cit.). The dioctahedral smectite has been partially illitized during the Paleozoic thermal events (see below).

Almost all REE is contained in the dioctahedral clay, which is consistent with their trivalent character (the dioctahedral sheet accepts mostly trivalent cations). Exceptionally low REE content of chlorite Kob-23 (Figure 10), which contains 95% of divalent iron (Table 1) is consistent with this interpretation of REE segregation. Thus dioctahedral clays are partially responsible, along with phosphates, for the REE budget of the investigated rocks. This conclusion is confirmed by  $\text{P}_2\text{O}_5$  depletion in clay fractions compared to the bulk rock (Inline Supplementary Table 4), parallel to the LREE enrichment in the clay fraction with dominant dioctahedral component (Mokrany-3B). REE seem to be incorporated in the dioctahedral clay

structure and not adsorbed like in weathering clays (Bau, 1991), as the clay fractions were analyzed after Na-exchange. The location of REE in clay structure indicates that they became available at the time of clay crystallization and not later. Otherwise they would occupy the exchange sites.

The trioctahedral smectite end member is almost ideal iron-rich saponite, with 0.84 Al<sup>IV</sup>, no Al<sup>VI</sup>, very high Mg, and Fe not much higher than in the dioctahedral clay, but ferrous in 42%. Its  $\delta^{18}\text{O}$  value is much lower than in di-smectite and its  $\delta^{56}\text{Fe}$  is negative, like in chloritic trioctahedral clays (Table 1).

XRD, chemistry and FTIR data are consistent and detect variable di/tri ratio of the investigated basaltic smectites. Based on the XRD evidence (separate 02 and 06 reflections) and very different REE contents and oxygen and iron isotope ratios, the smectitic clay component of Volyn basalts is interpreted here not as a mineral but as a mixture of iron-rich montmorillonite and iron-rich saponite. This mineral mixture occurs both in basalts and in the chlorophaeite accumulations (Figure 3 and Inline Supplementary Figure 3). A similar material was identified by Faust (1955), Ross (1960), and Komadel et al. (2000) as iron di-trioctahedral saponite, and named griffithite. Formulae of griffithite calculated from Ross (1960) and Komadel et al. (2000) data (Table 4) and the XRD data, obtained for Komadel et al. (2000) sample (Inline Supplementary Figure 3), suggest that it is also a mineral mixture, close to our sample 4600-1. The reported griffithite formulae differ strongly in the degree of iron oxidation, which may reflect sample heterogeneity and/or the measurement technique. Both samples come from the same original griffithite locality at Griffith Park in California, but may represent slightly different material. Other samples from this area are end-member Fe-saponites with high Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios (Treiman et al., 2014).

Very similar materials, named oxysmectites, were described by Dainyak et al. (1981) and Simanovich et al. (2010) from continental flood basalts of Siberia (Table 4) and from an

oceanic basalt sample. The continental sample has di/tri ratio close to our 4504-1 but it has more Fe than Mg. A pure trioctahedral analogue of our sample 4600-1, but with Fe dominant over Mg (Table 4), was identified in a Siberian hydrothermal deposit and called ferrosaponite (Chukanov et al., 2004), the name accepted by IMA (Jambor and Roberts, 2004). Numerous occurrences of similar materials were reviewed by Sarkar et al. (2016), who identified ferrosaponite in continental basalts.

The relative enrichment of montmorillonite in the heavy Fe isotope compared to Fe-saponite is consistent with the general rule that the oxidized form of Fe is enriched in heavy isotopes (Teutsch et al., 2009 and literature cited). Negative  $\delta^{56}\text{Fe}$  values of chloritic samples (Table 1), which contain only  $\text{Fe}^{2+}$ , support this interpretation. Comparable or even higher fractionations of iron have been observed during oceanic basalt alteration and interpreted as abiotic (Rouxel et al., 2003), though a biotic involvement cannot be excluded in our case, as the dissimilatory iron reduction is regarded as the most efficient mechanism for generating isotopically light  $\text{Fe}^{2+}$  (Wu et al., 2010), and the presence of unaltered organic matter in basalt has been documented in previous sections.

Major differences in  $\delta^{18}\text{O}$  values between di- and trioctahedral smectite could be related to formation from the same fluid at different temperatures with trioctahedral smectite forming at ca. 50°C higher temperatures if fractionation factors are similar (Figure 12). However, theoretical considerations (Savin and Lee, 1988; Kohn and Valley, 1998) and empirical data (Craw et al., 1995) suggest that oxygen isotope fractionation between smectite and water is about 5 ‰ smaller for Mg-rich smectite than for Al-rich smectite. Thus, di- and trioctahedral smectites may have formed at similar temperatures and from the same fluid. On the other hand, the temperature difference may have been higher, if trioctahedral smectites formed from a fluid with magmatic component (isotopically heavier).

Petrographic observations document the appearance of early smectite as the alteration product of isotropic material, which was described earlier in many publications under the name “chlorophaeite”. It was deposited during hydrothermal processes, cementing successively the residual open spaces of the basaltic rocks. Under the microscope chlorophaeite appears isotropic only in the least altered rocks, and during progressing alteration it gradually evolves into birefringent smectite. This alteration is almost isochemical, but some iron is lost (Table 2). In XRD, smectite from the chlorophaeite accumulation in least altered basalt differs from others by more trioctahedral character and much smaller crystal thickness, evidenced by more diffuse 001 reflection (Figure 3). NIR spectra indicate that it is richer in Fe, without detectable Al contribution. Combining these observations, we suggest that the isotropic substance is a trioctahedral smectite close to ferrosaponite, with extremely fine crystal size, which results in the isotropic characteristics. It may have been deposited originally as an amorphous material, but no clear evidence of such material was found in the investigated samples. Smectite crystallizing from an amorphous material is known to form originally extremely thin, even monolayer crystals (Derkowski et al., 2015 and references therein). In the course of further alteration, ferrosaponite alters into a mixture of Fe-montmorillonite and Fe-saponite with well-developed multi-layer crystallites. At early stages, the quantities of both smectites grow in parallel in the course of progressing alteration, but trioctahedral smectites grow at twice higher rate (Inline Supplementary Figure 10). Latter, the content of dioctahedral smectites continue to grow steadily, while the content of trioctahedral smectites levels off and starts decreasing, when the hematite content starts increasing. We interpret these relationships as indicative of the redox control over the process: as long as the conditions are relatively reducing, crystallization of trioctahedral smectite is favored, both by abundant  $Mg^{2+}$  and  $Fe^{2+}$ : the major constituents of the trioctahedral sheet. When  $Fe^{3+}$  becomes dominant, the crystallization of dioctahedral smectite is favored (trivalent ions dominant in

the dioctahedral sheet), and the decrease of trioctahedral smectite indicates that it is altered into chlorite and/or dioctahedral smectite at these advanced stages of basalt alteration.

## *Alteration of tuffs*

### *Mineral changes*

Mineralogically, tuffs (volcano-clastic rocks) differ strongly from flood basalts by their much broader range of quartz content, which, if elevated above basalt values, is always higher than K-feldspar content. The opposite relation, characteristic of flood basalts, is common in low quartz tuffs. If % quartz is plotted against % Kspar for all tuff samples (Inline Supplementary Figure 11) it becomes clear that the tuffs have a broad range of intermediate compositions, extending from basalts to the felsic rocks. Quartz content was used then as a proxy for this primary tuff mineral variability (Inline Supplementary Table 2), and tuffs were divided into samples close to basaltic composition (quartz <14%) and more felsic samples. In general, tuffs with >20% quartz are competent rocks and with lower content of quartz are friable.

The basaltic tuffs resemble by mineral composition the most altered flood basalts: some plagioclase still present in some samples, pyroxene and other primary minerals are absent, anatase is present, hematite, di- and trioctahedral smectite plus chlorite are abundant, and analcime is occasionally present. The apparent differences are the presence of albite and aluminoceladonite.

The felsic tuffs seem less altered because their calcic plagioclase content is much higher. They contain less anatase, hematite, trioctahedral smectite and chlorite. Only dioctahedral clay is as abundant as in basaltic tuffs, but more illitized. They also contain aluminoceladonite, but no albite or analcime. Kaolinite detected in the top samples of two

Kobryn tuffs are indicative of subaerial weathering and soil development before deposition of subsequent lava flows.

### Chemical changes

The arrangement of tuff samples by % quartz reveals very clear trends in their chemical composition (Inline Supplementary Table 4). Towards the basaltic end, Si and K contents decrease to a level typical of basalt, while Fe, Al, Mn, Mg, Ti and LOI increase. Mg and LOI increase to the level characteristic for the most altered basalts, which is consistent with the mineralogical evidence. Among trace elements REE, Be, Ba, Cs, Nb, Rb, Sr, Ta, Th, U, Y, and Zr decrease, while Co, Cr, Cu, Ni, Sc, V and Zn increase. No measurable control of the trap stratigraphy (lower vs. upper basalts) over chemistry can be observed.

In accordance with these trends, average contents of most elements for tuffs are intermediate between values for flood basalts and rhyodacites, indicating that, like flood basalts, also tuffs were altered without a major change of mass. For a few elements, the averages for tuffs are higher than the end member values: B, Mg, LOI, Cr, Cs, Cu, Ni, and Pb. Such elevated values imply the import of these elements during alteration, similar to the detected in basalts (B, Mg, LOI, Cs) but including metals. Also in basalts metals are mobile, as recorded by the metals enrichment in chlorophaeite and clay fractions, as compared to their bulk basalt samples (Inline Supplementary Table 4). This conclusion is consistent with the observation of native copper and silver occurrences in association with chlorophaeite (Kuzmenkova et al., 2006a).

Elements commonly most immobile in rocks: Hf, Nb, Pr, and Zr, used as the mass balance references in weathering studies (e.g. Liivamägi et al., 2018) are much less abundant in basalts than in felsic rocks. They differentiate the studied rocks similarly to quartz content (compare Inline Supplementary Figure 11 and 12), confirming the classification of tuffs based



on mineralogy into more basaltic and more felsic. In general, also this approach does not differentiate lower from upper volcanics. Locally, subsequent levels of flood basalts and tuffs can be differentiated, as illustrated in Inline Supplementary Figure 13 for Kobryn profile, where three levels of tuffs and two levels of flood basalts have been sampled over ca. 150 m of depth. The tuff composition is clearly more felsic. On the other hand, four tuff samples from Tashki plot in Inline Supplementary Figure 9 outside the basalt field, indicating an even more basic composition than the available basalt samples. They represent bottom part of the volcanic sequence, where picrites and microbasalts were identified (Kuzmenkova et al., 2011; Shumlyanskyy et al., 2016).

The tuffs vary in color in most profiles, alternating from green to brown and even red. Green color is more common among more felsic tuffs. When compared with other tuffs of similar quartz content, green tuffs differ from brown tuffs only by less hematite and more U, which is consistent with more reducing local environment (evacuation of Fe, enrichment in U) but does not allow us to conclude whether this is a hydrothermal alteration feature or the result of a younger process. The lack of systematic difference in clay composition favors the latter explanation.

#### **Oxygen isotopes and $Fe^{2+}/Fe^{3+}$ ratio**

Both sets of data collected for tuffs of basaltic composition do not follow trends characteristic of flood basalts and resemble data obtained for clay veins in basalts:  $d^{18}O$  values are lower (Figure 11) and %  $Fe^{2+}$  values are higher than extrapolations of basaltic trends to the zone of complete alteration (comp. Table 1 with Figure 13). These relations can be explained by higher abundance of chlorite in the analyzed tuff samples compared to the flood basalts (Supplementary Table 1 and 2), based on the %  $Fe^{2+}$  and the oxygen isotope data for Kob-23 chlorite (Table 1).

813

814 **K-Ar dating of clay fractions**

815 Dates of replicate analyses and dates of two fractions all are within the error range for a given  
816 sample, thus they can be regarded as representing unique illitization episodes (Środoń et al.,  
817 2002). In the south (Tashki), the Carboniferous date of ca. 300 Ma was obtained, while in the  
818 north, dates range from 417 to 447 Ma. A very similar geographical distribution of ages was  
819 detected by dating aluminoceladonite and illite-smectite in paleosols developed on basalts  
820 (Liivamägi et al., 2018). Clearly, the potassic alteration episode affected tuffs and paleosols  
821 developed on flood basalts long after the formation of these rocks. Basalts were also affected,  
822 though to a lesser extent: aluminoceladonite was not formed, but smectite was slightly  
823 illitized (Supplementary Table 3).

824

825 **Discussion and conclusions**

826

827 Flood basalts and tuffs of the Volyn-Brest province were affected to a very different extent by  
828 two subsequent alteration episodes, the first pre-dating and the second post-dating the  
829 Ediacaran weathering of top surface.

830 The first alteration episode involved sequential destruction of volcanic glass and  
831 primary basaltic minerals and crystallization of secondary phases: tri- and dioctahedral  
832 smectite, chlorite and/or mixed-layer chlorite-smectite, hematite, quartz, anatase, and zeolites.  
833 Basalts which underwent Ediacaran weathering studied by Liivamägi et al. (2018) contained  
834 such secondary mineral assemblage.

835 The basaltic smectites are of unique composition: montmorillonite with high  $\text{Fe}^{3+}$  and  
836 saponite also high in Fe, but with significant  $\text{Fe}^{2+}$  content. Similar clays have been described

earlier from various basalt provinces under the names “chlorophaeite”, "griffithite" or "oxysmectite", and "ferrosaponite" if  $\text{Fe} > \text{Mg}$ .

The term “chlorophaeite” is used also in macroscopic descriptions to name accumulations of dark glassy matter in basalts. Such chlorophaeite accumulations do not contain primary basaltic minerals, but mainly secondary minerals characteristic of the first step of basalt alteration (quartz, tri- and dioctahedral smectite), also if chlorophaeite accumulations are contained in basalts of higher alteration step (Supplementary Table 1). In particular, they do not contain hematite, they are strongly enriched in Si and enriched in Mg and metals compared to the host basalt. These observations, along with the REE pattern, suggest that chlorophaeite accumulations are products of alteration of the amorphous material (solidified leftover melt, i.e. volcanic glass), in agreement with conclusions of many earlier researchers (Kuzmenkova et al., 2006b and the references cited), and that the alteration took place at the earliest stage, in non-oxidizing environment, but it is related to the same solutions that altered flood basalts and tuffs.

The subaerial location, the evolution of bulk rock  $\text{Fe}^{2+}/\text{Fe}^{3+}$  measured by Mössbauer spectroscopy, the evolution of bulk rock oxygen isotope composition, the presence of hematite, and the lack of depletion in Fe and Mn indicate that the basalt alteration involved oxygenated meteoric waters, probably heated and put in motion by the cooling basalt flows. Such heat-driven convection of meteoric water is a very effective mechanism of alteration of cooling volcanic bodies (e.g. Eberl et al., 1987). A similar mechanism of alteration of Volyn flood basalts was proposed by Melnychuk (2006), who envisioned the Ediacaran dolerite sills intruding basalts and the underlying sandstones as the source of heat. The heat-driven convection mechanism explains well the observed major enrichment in Mg, brought by upflow from deeper parts of the basalt body, where olivine and pyroxene are early subjects to alteration. The alteration sequence is analogous to these reported from other hydrothermal

subaerial, hydrothermal submarine, and burial metamorphic alterations of basalts, including the difference in Si/(Si+Al) and Fe/(Mg+Fe) ratios between the smectitic and chloritic clays (Table 4). The alteration conditions were more oxidizing, which is manifested by the presence of hematite from early stages of the alteration process. A rare feature for the basalt alteration series is the abundant development of dioctahedral smectite, which continued later during the weathering stage, as documented by Liivamägi et al. (2018). The alteration proceeded from outside into the basalt layers, as observed also earlier (Juskowiakowa, 1974), and in extreme cases it was complete: all basaltic minerals were altered but the basalt texture was preserved. Our data indicate that microbial organisms participated in the hydrothermal alteration process, which is consistent with earlier evidence of the microbial life on the Ediacaran land in this area (Kremer et al., 2018; Liivamägi et al., 2018).

Compared to flood basalts, the alteration of tuffs of basaltic composition is much more advanced, which seems related to their high porosity and permeability. Mineralogically, they differ by much more abundant chloritization, and albitization not noted in basalts. The alteration of rhyodacites and tuffs of felsic composition seems less advanced than basaltic tuffs but more advanced than of the neighboring flood basalts, as best illustrated by the Kobryn profile (Supplementary Table 2). The abundance of felsic tuffs in the entire profile of the volcanic province indicates that felsic volcanism was active during much longer period than indicated by the known felsic lavas of the middle volcanogenic series (e.g. Kuzmenkova et al., 2011).

The detected mineral assemblage: from smectite to chlorite with zeolites, but without major albitization, epidote, actinolite, or amphibole puts the upper temperature limit of post-magmatic, pre-weathering alteration at ca. 220°C and lower at 50°C, based on the calibration in the Icelandic active hydrothermal systems (Franzson et al., 2008: cf. Introduction) and many other smectite-to-chlorite transformation series reviewed by Robinson et al. (2002). The

evidence of such maximum temperature conditions comes from most tuffs and the most altered flood basalts. Low  $\delta^{18}\text{O}$  of chlorite (10.1‰ for Kob-23 sample) is consistent with a temperature of 190°C if a magmatic fluid with ca. 6‰ is assumed (Cole and Ripley, 1998). In this scenario, chlorite is considered as an indicator of a higher temperature overprint, which altered older iron saponite, formed by the interaction of basalt with the heated meteoric waters. Locally, the temperatures of Ediacaran alteration may have been even higher, as albite, prehnite, and pumpellyite were reported (Emetz et al., 2006; Melnychuk, 2006), and epidote was identified in the olivine pseudomorphs in samples from west Belarus (Skveriki well: Kuzmenkova, 2009.). On the other hand, most flood basalts were altered by much cooler fluids, as evidenced by the lack of chlorite and by the preservation of fresh organic material. Our data confirm earlier observations that the extent of basalt alteration is controlled by the temperature and permeability. Figure 14 presents a synthetic model of the basalt alteration during the hydrothermal episode.

The second alteration episode, evidenced by K-Ar dating (Table 1 and Liivamägi et al., 2018) and detected earlier by Ar-Ar of the whole rock samples (Elming et al., 2007), involved the crystallization of aluminoceladonite and potassium feldspar (Liivamägi et al., 2018) and alteration of dioctahedral smectite into illite-smectite. K-Ar identifies two thermal events on the cratonic foreland of neighboring orogenic systems: in more northern locations (Belarus and Poland) related to the Caledonian orogeny, and in Volyn – to the Variscan.

This late diagenetic alteration affected porous tuffs to a greater extent than flood basalts, and within the flood basalts, it preferentially affected samples more intensely altered by the first alteration episode, i.e. with higher secondary porosity. The temperature of this late alteration was not higher than 85°C, according to illite-smectite data from the overlying sediments (Liivamägi et al., 2018) or even lower, according to the organic geochemistry data

(Goryl et al., 2018). Apparently, in a high-Mg environment, aluminoceladonite can crystallize at relatively low temperatures.

Inline Supplementary Figure 7 demonstrates that potassium was imported into basalt during the diagenetic alteration. In addition to potassium, enrichments in Cs, Rb, and B in basalts can be also explained by this diagenetic event, based on their observed positive correlations with %  $K_2O$  and % dioctahedral clay, and established knowledge of their behavior (cf. Derkowski and McCarty, 2017 for Rb and Cs, and Środoń, 2010 for B). For tuffs, such reasoning cannot be made, as their original  $K_2O$  content is variable. Thus it remains unclear whether  $K_2O$ , Cs, Rb, and B imported into flood basalts were derived locally from felsic tuffs, or if these elements result from a more long-range transport.

Hydrothermal alteration of the Volyn-Brest basalt trap, in continental settings and driven by heat of the cooling traps, can be considered as a good Earth analogue of the Noachian basalt alteration on Mars. The Noachian alteration also produced Fe-rich smectites and hematite (e.g. Ehlmann et al., 2011; Carter et al., 2103; Chemtob et al., 2015), which are also interpreted as a result of subsurface basalt interaction with heated ground waters (Ehlmann et al., 2011b), and are investigated with the techniques used in this study (XRD: e.g. Blake et al., 2012, Downs et al. (2015); Mössbauer: e.g. Klingelhöfer et al., 2004; NIR: e.g. Carter et al., 2013; Bishop et al., 2017). Particularly useful for Martian studies should be (1) detail characterization of the Fe-smectite alteration products, which are also dominant on Mars and in particular the role of redox in controlling the di/tri-smectite ratio; (2) detecting Mg enrichment during the alteration, considered indicative for the proposed alteration mechanism, and inconsistent with weathering models (e.g. Le Deit et al., 2012); (3) limited chemical changes despite radical changes in mineralogy, indicative for the proposed alteration mechanism and analogous to the observations of Martian basaltic sediments (e.g., Bristow et al., 2018); and (4) the location of elevated boron contents in illitized dioctahedral smectitic

clays, which may explain Martian observations (e.g., Gasda et al., 2017). The analogy may not be perfect, as the involvement of microorganisms in the alteration process of the Ediacaran Volynian flood basalts is indicated by our data, which provide another piece of evidence for the Ediacaran life on land.

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1341

## 1342 **Tables**

1343 Table 1. Decomposition of Mössbauer spectra of rocks and selected clay fractions, % Fe<sup>2+</sup> in  
1344 total Fe calculated from the decomposition data for bulk rock and clay fraction, oxygen and  
1345 iron isotope data, along with % primary minerals from Supplementary Table 1.

1346

1347 Table 2. Chemical composition (wt% SEM/EDS microchemical analyses) of isotropic  
1348 chlorophaeite and replacing birefringent smectitic clays in different sites of the basaltic rock  
1349 affected by incipient alteration (sample 4522-1). Ferrous state has been assigned to iron in all  
1350 analyses.

1351

1352 Table 3. K-Ar data for selected clay fractions containing aluminoceladonite and/or illite-  
1353 smectite (cf. Supplementary Table 3).

1354

1355 Table 4. Structural formulae of smectites from Volynian basalts, presented along with  
1356 formulae derived from published chemical data of similar materials: griffithite from Ross  
1357 (1960) and Komadel et al. (2000), oxysmectites from Dainyak et al. (1981), and ferrosaponite  
1358 from Jambor et al. (2004). Formula of chlorite (Kob-23) added to show tendency in chemical  
1359 composition of clays.

1360



Table 5. Characteristics of end-member di- and trioctahedral smectite from Volynian basalts extrapolated using number of atoms in the octahedral sheet given in Table 4.

Supplementary Table 1. Quantitative XRD mineral composition data for basalts, green clays from veins and cavities in basalt, and rhyodacites, plus XRD estimates of chlorophaeite composition. Basalts arranged by alteration steps I-V, based on sum of primary minerals. If data available, basalts are assigned to lower or upper volcanic series.

Supplementary Table 2. Quantitative XRD mineral composition data for tuffs and for basalt-tuff alternation in section Kobryn. Tuffs arranged from felsic to basic, based on the content of quartz. If data available, samples are assigned to lower or upper volcanic series.

Supplementary Table 3. Mineral composition of  $<0.2\ \mu\text{m}$  fractions, separated from basalts, green clays in veins and cavities, and tuffs. The peak position data, used in the evaluation of percent smectite layers (%S) in illite-smectite are given along with calculated %S and the average %S value. tr: trace, i-s: illite-smectite, ch-s: chlorite-smectite,  $\delta 2$ : angular distance between i-s reflections in  $42\text{-}49^\circ 2\theta$  range.

Supplementary Table 4. Chemical composition of basalts, chlorophaeite, green clays from veins and cavities in basalt, rhyodacites, tuffs, and clay fractions. Major elements and loss on ignition (LOI) given in %, trace elements in ppm. Below average values for different lithologies and compositions of clay fractions along with their bulk rocks are listed.

## Figure captions

Figure 1. Map of the Volyn-Brest volcanic province with sampling sites indicated (modified from Kuzmenkova et al., 2010, TTZ after Mazur et al., 2018b).

Figure 2. Random powder XRD patterns of the bulk rock, with ZnO internal standard, illustrating the compositional variability of Volyn basalts, reflecting the degree of hydrothermal alteration.

Figure 3. Random powder XRD patterns of the chlorophaeite accumulations, registered in glass tubes because of the scarcity of the available material, and documenting coexistence of di and trioctahedral smectite (02 peaks at 4.48 and 4.58 Å, respectively).

Figure 4.  $^{57}\text{Fe}$  room temperature Mössbauer spectra of bulk rock basalts, chlorophaeite (Mokrany-3A), chloritic clay in basalt (Kob-23), and tuffs (B), illustrating the variability of compositions encountered, and presented along with calculated spectra of iron-bearing fractions used in the fitting procedure.

Figure 5. FTIR transmission KBr spectra (<0.2 µm fraction) of basaltic clays: Mokrany-3B and 4504-1A, with end-member components used as references: chlorite (Kob-23), trioctahedral smectite (4600-1), and dioctahedral smectite from paleosol (4517-1); Qz: quartz (distinctive bands).

Figure 6. FTIR transmission KBr spectra of chlorophaeite accumulations (a) and surrounding basalts (b); Qz: quartz (distinctive bands), Pl: feldspars (distinctive bands).

1411 Figure 7. Partial  $m/z$  71 mass chromatogram for TMS derivatized basalt extract showing the  
1412 odd-over-even long chain  $n$ -alkanes predominance (A) and partial  $m/z$  117 mass  
1413 chromatograms showing comparison of  $n$ -alkanoic acids for unaltered basalt (4600-3B) and  
1414 cavity clay (4600-3A). Note high-molecular-weight  $n$ -alkanoic acids (26 to 32) in the basalt  
1415 sample (B). Numbers denote carbon atoms in the molecule.

1416

1417 Figure 8. Photomicrographs (optical microscopy) and SEM images (BSE mode) of isotropic  
1418 chlorophaeite (A-D) and its smectitic alteration products (E-H). (A) Intersertal chlorophaeite  
1419 through the body of the basaltic rocks (sample 4522-1). (B) Chlorophaeite with collomorph  
1420 texture coating the wall of circular cavities (sample 4522-1). (C) chlorophaeite pseudomorphs  
1421 after orthopyroxene (sample 4603-1). (D) Chlorophaeite as veinlet and filling product of  
1422 diktytaxitic voids in the wall-rock (sample 4522-1). (E) Incipient alteration of chlorophaeite at  
1423 the contact of a plagioclase microlite (sample 4522-1). (F) Details of the clay-rich  
1424 microspherules related to incipient alteration of chlorophaeite (sample 4522-1). (G) Strong  
1425 replacement of chlorophaeite, partial replacement of chlorite and local dissolution of quartz  
1426 filling a vesicle in a moderately altered basalt (sample 4519-0). (H) Morphological aspects of  
1427 the smectitic clays as a function of alteration sites (sample 4519-0). Microspherules  
1428 predominate in both altered chlorophaeite and chlorite while ribbon like morphology is  
1429 observed when alteration is developed at the contact between quartz and chlorophaeite. Am:  
1430 fresh chlorophaeite; Ze: zeolite; OPXps: chlorophaeite pseudomorph after orthopyroxene;  
1431 CPX: clinopyroxene; Pl: plagioclase; Ma: magnetite; Amv: chlorophaeite veinlet; Sm  
1432 smectitic clays; IRL: iron-rich layer; AH: alteration halo; Ch: iron rich chlorite; Qz: quartz.

1433

1434 Figure 9.

1435 Relationship between % clay from XRD and % MgO (red triangles) and % LOI (loss on  
1436 ignition) in basalts of variable degree of alteration. The LOI trend (blue diamonds)  
1437 extrapolates to a value intermediate between rocks dominated by chlorite and smectite (pink  
1438 squares).

1439

1440

1441 Figure 10. Primitive mantle normalized REE spectra of basalts with variable degree of  
1442 alteration, chlorophaeite, vein clay (Fe-saponite), and rhyodacites.

1443

1444 Figure 11. Relationship between % primary minerals from XRD and  $\delta^{18}\text{O}_{\text{VSMOW}}$  in basalts of  
1445 variable degree of alteration, chlorophaeite accumulation, clay veins, and basaltic tuffs.

1446

1447 Figure 12. The oxygen isotope compositional ranges of smectites from paleosols, basalt, and  
1448 green clay veins in basalt from this study plotted onto the relationship of equilibrium oxygen  
1449 isotope fractionation between smectite and water as a function of temperature based the  
1450 equation of Sheppard and Gilg (1996).

1451

1452 Figure 13. Relationship between % primary minerals from XRD and percent divalent iron in  
1453 total iron of basalts with variable degree of alteration, of their clay fractions, and of the  
1454 chlorophaeite sample Mokraný-3A.

1455

1456 Figure 14. A synthetic model of basalt alteration during the hydrothermal episode, presenting  
1457 the most important changes in mineral and chemical composition (details in the text). Pl -  
1458 plagioclase, Py - pyroxene, M - magnetite+pseudobrookite+ilmenite, Z - zeolites, Ch -

1459 chlorite, A - anatase, H - hematite, Ksp - K-feldspar, Q -quartz, Tri-S - Fe-saponite, Di-S - Fe-  
1460 montmorillonite.

1461

1462

1463 Inline Supplementary Figure 1. Random powder XRD patterns of the bulk rock, with ZnO  
1464 internal standard, illustrating the compositional variability of Volyn tuffs, from felsic (top) to  
1465 basic (bottom), with rhyodacite Skv-0C as reference.

1466

1467 Inline Supplementary Figure 2. Oriented glycolated XRD patterns of <0.2  $\mu\text{m}$  clay fractions  
1468 (with  $\text{MoS}_2$  as internal standard), representative for the variability encountered in basalts and  
1469 green clays from veins and cavities in basalt.

1470

1471 Inline Supplementary Figure 3. Random powder XRD patterns of <0.2  $\mu\text{m}$  basalt clay  
1472 fractions and <2  $\mu\text{m}$  fraction of griffithite, documenting coexistence of di- and trioctahedral  
1473 smectite. The reference griffithite sample from Griffith Park, California, was provided by Dr.  
1474 Jana Madejova.

1475

1476 Inline Supplementary Figure 4. Oriented glycolated XRD patterns of <0.2  $\mu\text{m}$  clay fractions,  
1477 representative for the variability encountered in tuffs.

1478

1479 Inline Supplementary Figure 5.  $^{57}\text{Fe}$  room temperature Mössbauer spectra of minerals, used  
1480 for decomposing spectra of bulk rocks (results of decomposition in Table 1).

1481 Inline Supplementary Figure 6. Relationship between % plagioclase from XRD and % CaO in  
1482 basalts of variable degree of alteration. Three samples off the general trend (blue diamonds)  
1483 contain calcite veinlets.

1484

1485

1486   Inline Supplementary Figure 7. Relationship between % dioctahedral clays from XRD and  
1487   ppm boron in basalts of variable degree of alteration.

1488

1489   Inline Supplementary Figure 8. Relationship between % K<sub>2</sub>O calculated from XRD contents  
1490   of K-feldspar (assuming 12% K<sub>2</sub>O) and dioctahedral clay (6% K<sub>2</sub>O) and measured % K<sub>2</sub>O in  
1491   basalts of variable degree of alteration.

1492

1493   Inline Supplementary Figure 9. Relationship between % P<sub>2</sub>O<sub>5</sub> and ppm LREE in bulk rocks.

1494

1495   Inline Supplementary Figure 10. Quantitative evolution of secondary minerals in the course of  
1496   basalt hydrothermal alteration traced by percent of primary minerals.

1497

1498   Inline Supplementary Figure 11. Differentiation of tuffs into felsic (close to rhyodacite) and  
1499   basaltic, based on quartz and K-feldspar XRD contents.

1500

1501   Inline Supplementary Figure 12. Chemical variability of tuffs (felsic vs. basaltic) traced using  
1502   the most immobile trace elements.

1503

1504   Inline Supplementary Figure 13. Chemical differences between basalts and tuffs illustrated  
1505   for a single profile (Kobryn) using the most immobile trace elements.

1506

Sample	Hematite	Magnetite	Ill-sm	Saponite	Saponite	Chlorite	Pyroxene	%Fe <sup>2+</sup> in bulk rock Fe	%Fe <sup>2+</sup> in clay Fe	$\delta^{18}\text{O}$		Fe isotopes in <0.2 $\mu\text{m}$ fraction				% primary minerals
	3+	3+ & 2+	3+	3+	2+	2+	2+			Bulk rock	< 0.2	$\delta^{56}\text{Fe}$	2 SD	$\delta^{57/54}\text{Fe}$	2 SD	
<b>Basalts arranged by % primary minerals</b>																
4522-1	0	35	0	12*	0	0	53	65	0	8,1						93
Novosiolki-1	0	31	0	16	0	0	52	62	0	5,6						91
Skv-0A	0	24	5	18	0	0	44	52	0	8,4						85
Skv-0B	0	25	0	25*	3	0	47	58	11							85
Mokrany-1B	0	38	0	20*	0	0	33	46	0	6,8						79
Kob-13	0	27	0	28	8	0	38	55	22	10,8						74
Kob-14	6	21	0	28	11	16	19	53	49	9,9						66
4603-1	0	28	14	29	0	0	29	38	0	11,6						64
4504-1A	1	44	2	19	7	0	27	49	25	11,1						58
4504-1A < 0.2	0		34	41	25	0			25		17,8	-0,204	0,044	-0,305	0,055	
4466-1	9	56	12	6	0	0	18	37	50	12,6						53
Mokrany-3B	2	24	25	33	7	0	8	23	11	16,4						41
Mokrany-3B < 0.2	0		38	49	10	3			13		21	0,028	0,035	0,040	0,047	
Kob-15	11	21	0	24	44	0	0	51	65							31
4417-1	28	33	5	12	21	0	0	32	55							25
4417-1 < 0.2	20		29	20	19	12			39		18,3	-0,025	0,039	-0,072	0,059	
4600-1	15			39	46	0	0	46	54	17						7
4600-1 < 0.2	0		0	58	42	0			42		14,7	-0,459	0,060	-0,735	0,076	
Kob-23	0	0	0	5	0	95	0	95	95	10,1		-0,574	0,055	-0,843	0,066	0
<b>Chlorophaeite accumulations</b>																
Mokrany-3A	0	0	40	43	17	0	0	17	17	23						0
<b>Tuffs arranged by % quartz</b>																
Pinsk-50	15	0	40	0	44	0	0	44	52	15,2						
Pinsk-44	8	0	43	0	0	50	0	50	54	13,4						
Pinsk-47D	22	0	38	0	39	0	0	39	51	14,6						
Kob-16	30	9	34	0	28	0	0	31	45							
4600-2A	47	0	15	20	0	17	0	17	33	15						
Pinsk-47A	15	10	39	0	35	0	0	38	47	15,5						
Tashki-10	45		28	15	11	0		11	21	20	18,3					
<b>Paleosols</b>																
4529-2											21,3					
4517-1											21,7					

1507

1508 Table 1. Decomposition of Mössbauer spectra of rocks and selected clay fractions, % Fe<sup>2+</sup> in

1509 total Fe calculated from the decomposition data for bulk rock and clay fraction, oxygen and

1510 iron isotope data, along with % primary minerals from Supplementary Table 1.

1511

1512 Table 2. Chemical composition (wt% SEM/EDS microchemical analyses) of isotropic  
 1513 chlorophaeite and replacing birefringent smectitic clays in different sites of the basaltic rock  
 1514 affected by incipient alteration (sample 4522-1). Ferrous state has been assigned to iron in all  
 1515 analyses.

1516  
 1517

Petrographic entity	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	FeO	S
Isotropic chlorophaeite	0,49	2,96	5,61	48,41	0,56	1,75	0,06	0,14	22,63	8
	0,45	2,84	5,89	49,39	0,54	1,79	0,11	0,15	22,54	8
	0,3	3,31	6,05	50,17	0,54	2	0,07	0,19	23,65	8
Smectite	0,32	4,54	8,23	47,69	0,4	1,96	0,16	0,13	19,34	8
	0,09	4,25	9,73	46,23	0,87	1,81	0,34	0,13	16,45	7
	0,21	4,91	9,78	49,83	0,54	1,91	0,34	0,15	17,69	8

1518  
 1519



1520 Table 3. K-Ar data for selected clay fractions containing aluminoceladonite and/or illite-  
 1521 smectite (cf. Supplementary Table 3).

1522

1523

Sample and fraction	Mass [mg]	% K <sub>2</sub> O	% K	% 40Ar*	Age [Ma]	Error [Ma]	Ave. age [Ma]	Ave. error [Ma]
Kob-9B 2-0.2μm	10,50	7,395	6,139	95,7	446,7	11,7	448,5	8,3
	8,86			95,8	450,3	11,8		
Kob-9B <0.2μm	10,91	7,355	6,105	91,4	452,2	12,0	451,1	8,4
	8,93			97,1	449,9	11,8		
Vilch19 <0.2μm	10,91	4,115	3,416	93,6	442,7	13,1	439,4	9,3
	8,34			90,6	436,1	13,1		
Ochryny21 2-0.2μm	6,97	2,885	2,395	84,5	430,6	15,8	432,6	11,1
	7,71			94,3	434,6	15,6		
Ochryny-21 <0.2μm	8,45	3,74	3,105	96,3	420,2	13,1	419,2	9,4
	5,92			96,4	418,2	13,3		
Tashki1 2-0.2μm	8,66	1,785	1,482	89,2	298,2	19,9	297,1	14,1
	10,07			76,2	296,1	19,9		
Tashki-1 <0.2μm	10,81	2,07	1,718	92,9	310,9	16,3	309,0	11,4
	9,02			94,9	307,2	15,9		

1524

1525

Table 4. Structural formulae of smectites from Volynian basalts, presented along with formulae derived from published chemical data of similar materials: griffithite from Ross (1960) and Komadel et al. (2000), oxysmectites from Dainyak et al. (1981), and ferrosaponite from Jambor et al. (2004). Formula of chlorite (Kob-23) added to show tendency in chemical composition of clays.

Sample	Mokransky-3B < 0.2	4504-1A < 0.2	4600-1 < 0.2	Ross griffithite	Komadel griffithite	Oceanic oxysmectite	Continental oxysmectite	Ferrosaponite	Kob-23 bulk
Fraction Fe <sup>3+</sup>	0,87	0,75	0,56	0,46	0,91	0,54	0,83	0,25	0,00
Si	3,90	3,47	3,21	3,17	3,34	3,40	3,23	2,91	3,57
Al <sup>IV</sup>	0,10	0,53	0,75	0,83	0,66	0,59	0,47	1,03	0,43
Fe <sup>IV</sup>	0,00	0,00	0,04	0,00	0,00	0,01	0,30	0,06	0,00
Al <sup>VI</sup>	0,50	0,16	0,00	0,03	0,06	0,00	0,00	0,00	1,04
Fe <sup>3+</sup>	0,60	0,54	0,44	0,44	0,75	0,56	1,10	0,52	0,00
Fe <sup>2+</sup>	0,09	0,18	0,35	0,52	0,07	0,47	0,22	1,56	2,63
Mg	1,11	1,81	2,18	1,88	1,82	1,78	1,27	0,87	1,96
Layer charge	-0,38	-0,47	-0,42	-0,61	-0,46	-0,44	-0,50	-0,67	-0,13
No. oct. cat.	2,31	2,68	2,97	2,87	2,70	2,80	2,59	2,95	5,63
Ca	0,01	0,07	0,01	0,25	0,01	0,06	0,21	0,31	0,03
Na	0,32	0,32	0,38	0,11	0,43	0,31	0,05	0,04	0,08
K	0,04	0,01	0,02	0,00	0,01	0,02	0,03	0,01	0,01
Mg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
NH <sub>4</sub>	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Interlayer charge	0,38	0,47	0,42	0,61	0,46	0,44	0,50	0,67	0,15
Si/(Si+Al)	0,87	0,83	0,81	0,79	0,82	0,85	0,87	0,74	0,71
Fe/(Mg+Fe)	0,38	0,29	0,27	0,34	0,31	0,37	0,56	0,71	0,57

1535 Table 5. Characteristics of end-member di- and trioctahedral smectite from Volynian basalts  
1536 extrapolated using number of atoms in the octahedral sheet given in Table 4.

1537

1538

Smectite	di	tri
Si	4,00	3,16
Al <sup>VI</sup>	0,72	0,00
Fe <sup>3+</sup>	0,68	0,44
Fe <sup>2+</sup>	0,00	0,34
Mg	0,64	2,27
δ <sup>18</sup> O	24,0	14,5
δ <sup>56</sup> Fe	0,27	-0,47
ppm LREE	664,00	0,00
ppm HREE	27,00	4,00

1539

1540

## 1541 **Supplementary Materials**

### 1542 *Experimental methods*

#### 1543 *QXRD of the bulk rock*

1544       The mineral composition of whole rock samples was studied by means of quantitative  
1545 X-ray diffractometry (QXRD). A 3 g sample was spiked with 10% ZnO, ground in the  
1546 McCrone mill with methanol, and a randomly oriented preparation was made by side-loading  
1547 (Środoń et al., 2001). The XRD patterns were recorded in 2–65° 2θ CuKα range with  
1548 0.02°/sec step on Thermo X'tra diffractometer, the mineral phases were identified and then  
1549 quantified using QMIN software (by Dr. Marek Szczerba), which matches the sum of the  
1550 diffraction patterns of pure mineral standards with the pattern of a studied rock sample,  
1551 allowing for manual corrections. Dioctahedral and trioctahedral clays were quantified as  
1552 groups by careful 060 reflection fitting (Środoń et al., 2001) and split into species by fitting  
1553 the peaks in the 17–35° 2θ range. Chlorophaeite samples, available in quantities too small to  
1554 conduct regular QXRD, were analyzed only qualitatively in glass capillaries in 4–39°  
1555 2θ range, as random powders without the spike.

1556       QMIN software does not provide errors of mineral phase determination. Uncertainty  
1557 of the QXRD analysis can be however evaluated from the results of Reynolds Cup –  
1558 quantitative mineral analysis international round robin (Raven and Self, 2017). We got 4<sup>th</sup>  
1559 place in 2018 Reynolds Cup, with the absolute error per major components of 2.4%.  
1560 Considering much simpler mineralogy of the samples analyzed in this study than of the  
1561 samples of Reynolds Cup, the uncertainty of QXRD measurements should be even smaller.

1562

#### 1563 *Clay fraction separation*

1564       The clay fractions 2–0.2 and <0.2 μm were separated from ca. 50 g of the bulk rock after  
1565 ultrasonic dispersion of the crushed rock in deionized water. Standard chemical treatments  
1566 (Jackson, 1975) were used for samples prepared for K-Ar dating, but they were avoided in  
1567 case of the Mössbauer and FTIR studies, in order to minimize the oxidation of structural iron.

1568 The fractions were collected by centrifugation, coagulation by adding concentrated NaCl  
1569 solution, dialysis, and freeze-drying.

#### 1570 *XRD of clay fraction*

1571 Clay mineral identification in the bulk rock was verified and made more accurate by  
1572 studying 2-0.2 and <0.2  $\mu\text{m}$  fractions of selected samples. XRD patterns were recorded in air-  
1573 dried and glycolated state of the oriented slides, prepared by sedimentation of 10 mg clay/cm<sup>2</sup>  
1574 from a sonified water suspension, with 4% MoS<sub>2</sub> as the internal standard. The collected XRD  
1575 patterns were first analyzed using Mering rules for the identification of clay minerals (Moore  
1576 and Reynolds, 1997) and then percent smectite layers in mixed-layer illite-smectite (%S) was  
1577 measured from the selected peak positions on glycolated patterns, using the regressions based  
1578 on data of Środoń et al. (2009).

#### 1579 *K-Ar dating of illite*

1580 Na-exchanged, 2.0–0.2 and <0.2  $\mu\text{m}$  clay fractions containing illite-smectite and  
1581 aluminoceladonite were dated by K-Ar method to establish the age of crystallization of these  
1582 minerals. All the measurements were performed at the Institute of Geological Sciences, Polish  
1583 Academy of Sciences in Kraków using Nu Instruments Noblesse multicollector noble-gas  
1584 spectrometer. Four portions of samples: two 10 mg and two 50 mg, were weighted using  
1585 Sartorius mass balance with precision of 0.01 mg. A small quantity of CuO (approximately  
1586 0.1 mg) was added to the two lightest portions. These samples were then wrapped in an Al-  
1587 foil and proceeded to radiogenic argon measurements. Two heaviest portions were weighted  
1588 directly on platinum evaporators and proceeded to potassium measurements. All the samples  
1589 were equilibrated in the ambient atmosphere (air-dry state) and weighted one after another in  
1590 order to minimize the errors due to relative humidity affecting clay hydration.

1591 Radiogenic argon measurements were performed on Nu Instruments Noblesse  
1592 multicollector noble-gas spectrometer (NG039). The spectrometer is equipped with a Nier-  
1593 type ion-source, 75° magnetic sector, two quadrupole lenses and a collector block. The  
1594 collectors assembly consists of a Faraday detector (FAR) and three ETP ion-counting electron  
1595 multipliers (IC0, IC1, IC2). The high mass isotope (<sup>40</sup>Ar) is switchable between Faraday and  
1596 IC0 multiplier, depending on the height of the measured signal. Due to high mass resolving  
1597 power (MRP), which is ~5400, it is possible to resolve combined peaks of <sup>36</sup>Ar + H<sup>35</sup>Cl from

peaks of  $^{36}\text{Ar} + \text{H}^{35}\text{Cl} + ^{12}\text{C}_3$ . The signal of all argon isotopes was always calculated as a difference between measurement for sample and signal measured directly before, when ion pump was pumping the interior of the spectrometer. It was done to correct for background level of  $^{36}\text{Ar} + \text{H}^{35}\text{Cl}$ ,  $^{38}\text{Ar} + \text{H}^{37}\text{Cl}$  and also of  $^{40}\text{Ar}$  that is always leaking in very small quantities to the spectrometer through gaskets (background signal was at around 60, 40 and 400 cps, respectively; while e.g. for GL-O it is at: ~2000, ~30000, ~5000000 cps, respectively). Amount of  $^{35}\text{Cl}$  was also always monitored prior to the sample and when the sample was being measured: differences are maximally of few percent. This indirectly indicates that level of  $\text{H}^{35}\text{Cl}$  was constant prior and during measurements and, considering very low background level of  $^{36}\text{Ar} + \text{H}^{35}\text{Cl}$  peak, the used correction was reasonable.

Extraction-purification line with all-metal valves is attached to the Noblesse spectrometer. The Al-foil wrapped portions were loaded into a glass container, which is a part of the line. The aliquots were subsequently evacuated to approximately  $10^{-10}$  mbar pressure. The line was heated overnight at  $200^\circ\text{C}$  to remove all gases adsorbed on metal parts of the line. Samples were, however, not heated, to avoid any  $^{40}\text{Ar}_{\text{rad}}$  removal. The reactor was running several blank measurements to achieve signal of  $^{40}\text{Ar}$  lower than 0.01 V measured on FAR detector (corresponding to 650000 cps on multiplier). Then, each sample was melted in a double-vacuum resistant crucible at above  $1200^\circ\text{C}$  (assessed visually). CuO added to the samples enhances oxidation of organic matter during this step. Titanium sponge (>99.99% Ti) was always put to the place of the reactor (~0.5 g), where samples are heated. This was a first cleaning level of gases extracted from the samples. Most of the cleanup was achieved when temperature of the reactor was decreasing, which was monitored on Pirani gauge.

Pure  $^{38}\text{Ar}$  produced by the Institute for Inorganic and Physical Chemistry of Bern University was used as the spike. It was introduced to the extraction line after the sample extraction using a calibrated pipette, built at Heidelberg University. Impurities of  $^{40}\text{Ar}$  and  $^{36}\text{Ar}$  in spike are regularly monitored and the final results are corrected for these impurities. The final purification of argon was carried out in an isolated section of the line by a getter pump (D-100, SAES Getters), previously baked overnight to remove excess argon. The amount of gases poured to the spectrometer were optimized to keep  $^{40}\text{Ar}$  at level below 0.15 V, because otherwise fractionation on Nier ion source can occur (Kellett and Joyce, 2014). Gas aliquot released from the sample was measured three times or more by opening and closing valves of the line in a certain sequence.

The amount of the original aliquot of  $^{38}\text{Ar}$  spike was determined by measuring international standard GL-O (Odin, 1982:  $24.85 \pm 0.24 \cdot 10^{-6} \text{ cm}^3/\text{g STP } ^{40}\text{Ar}_{\text{rad}}$ ). This standard is measured at least two times with every batch of the samples. Standard deviation of received results for GL-O is  $\pm 0.09 (\pm 0.38\%) \cdot 10^{-6} \text{ cm}^3/\text{g STP } ^{40}\text{Ar}_{\text{rad}}$  for 19 measurements. Biotite LP-6 was also tested for comparison (Odin, 1982:  $43.26 \pm 0.44 \cdot 10^{-6} \text{ cm}^3/\text{g STP } ^{40}\text{Ar}_{\text{rad}}$ ) and have  $43.08 \pm 0.41 (\pm 0.96\%) \cdot 10^{-6} \text{ cm}^3/\text{g STP } ^{40}\text{Ar}_{\text{rad}}$ . Every day, the  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{38}\text{Ar}$  ratios are measured for air sample aliquots, delivered from a calibrated air pipette. Based on this results  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{38}\text{Ar}$  ratios were corrected for instrument mass fractionation and detector efficiencies assuming atmospheric ratios of  $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{air}} = 298.57$  and  $(^{40}\text{Ar}/^{38}\text{Ar})_{\text{air}} = 1583.5$  (Lee et al., 2006). The potassium contents were measured using Sherwood Model 420 flame photometer. The maximum error of this measurement was estimated to be equal 0.03% K. Based on 6 measurements, K content in GL-O glauconite was slightly higher:  $6.61 \pm 0.02\%$ , than that of standard:  $6.56 \pm 0.06\%$  (Odin, 1982). LP-6 biotite has slightly lower amount of K:  $8.27 \pm 0.022\%$  (4 measurements) comparing to reference value:  $8.33 \pm 0.03\%$  (Odin, 1982). Both measured standards are within reference ranges assuming 0.03% K error.

Age errors were calculated from the law of error propagation, taking into account uncertainties of:

- spectrometric measurement of argon isotopes determined by spectrometer's software delivered by Nu Instruments - sum of uncertainty for background and sample,
- weighting - assumed to be equal to  $\pm 0.03 \text{ mg}$ ,
- potassium measurements – equal to  $\pm 0.03 \%$  of absolute potassium content,
- normalization of amount of  $^{38}\text{Ar}$  in spike based on dating of GL-O standard – assumed to be equal to  $\pm 0.4 \%$ ,
- assessment of  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{38}\text{Ar}$  ratios, measured every day for air aliquots – equal to  $\pm 0.017 \%$  and  $\pm 0.013 \%$ , respectively.

### ***Chemistry of the bulk rock and clay separates***

Samples were ground in an agate mill and analyzed for the majority of elements at the Bureau Veritas Mineral Laboratories (ACME) in Perth, Australia using a combo package, which requires a single lithium borate fusion and provides major elements from X-Ray Fluorescence (XRF) and trace elements (including REE) from Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) on the same fused disc. Samples were pre oxidized using 66:34 flux containing 10%  $\text{LiNO}_3$  in order to convert sulfides into sulfates. All

elements were measured on the oven dry (105°C) weight basis. Loss on Ignition (LOI) was determined from a separate 1g split using a Thermo Gravimetric Analysis (TGA) system with furnaces set to 110 and 1000 °C. Boron content was measured by the Prompt-Gamma Neutron Activation Analysis (PGNAA) with 0.5 ppm detection limit at the Activation Laboratories, Canada.

#### *Mössbauer spectroscopy of the bulk rock and clay separates*

The Mössbauer spectroscopy was used in order to quantify the oxidation state of iron (recent review of the method applied to minerals in Murad, 2013). The Mössbauer spectra, both for the bulk rock and for mineral separates, were recorded in the transmission geometry at room temperature using a Wissel spectrometer. In addition, both fresh and hydrothermally altered basalts were studied as reference. The samples were prepared in form of pellets, 12 mm in diameter, containing 100 mg specimen mixed with 200 mg lucide powder. The velocity scale calibration was determined from  $\alpha$ -Fe foil standard.

The spectra were evaluated with the use of *WinNormos-for-Igor* program. The spectra were decomposed into sets of Zeeman sextets and quadrupole doublets. For each subspectrum the hyperfine field  $B$ , isomer shift  $IS$  and quadrupole splitting  $QS$  were determined and used for the identification of the iron bearing fractions. For natural mineralogical samples, due to the distribution of the hyperfine parameters and overlapping of the subspectra, such identification may be sometimes ambiguous. However, the distinction between  $Fe^{2+}$  and  $Fe^{3+}$  states is obvious, due the significant difference in  $IS$ . The  $Fe^{2+}/Fe^{3+}$  ratio was determined as the area ratio of the corresponding subspectra. The thickness saturation effects and differences in the recoil free fraction of Fe in different states were not included into analysis. The typical accuracy of the relative contribution of each component is 1%. The %  $Fe^{2+}$  values for clay fractions are less accurate, in particular if abundant pyroxene is present.

#### *Fe isotopes of the bulk rock and clay separates*

Fe isotope analyses ( $^{56}Fe/^{54}Fe$  and  $^{57}Fe/^{54}Fe$  ratios, reported as  $\delta^{56}Fe$  and  $\delta^{57/54}Fe$ ) were performed for bulk rock samples and clay separates to trace possible microbial influence (cf. Kappler et al., 2010). The measurements were conducted by ALS Scandinavia AB in Lulea, Sweden, by MC-ICP-MS technique of Malinovsky et al. (2003).

#### *Oxygen isotopes*



Oxygen isotopes were measured by Actlabs (Canada). Oxygen was extracted from 5 mg samples at 550-600°C according to the conventional  $\text{BrF}_5$  procedure of Clayton and Mayeda (1963) and analyzed via dual inlet on a Thermo-Finnigan DeltaPlusXP Isotope-Ratio Mass Spectrometer (IRMS). The  $\delta^{18}\text{O}$  values are reported in permil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW), with a precision of about 0.1‰.

#### ***FTIR measurements***

Middle infrared (MIR) investigations ( $4000 - 400 \text{ cm}^{-1}$ ) were performed in transmission mode using a KBr beam-splitter and a DTGS/KBr detector on a Nicolet 6700 FTIR spectrometer. The spectra were obtained using KBr pressed pellets, 13 mm in diameter. The pellets were prepared by mixing 1 mg of sample with 150 mg of well ground KBr. Then, the mixture was pressed for 5 min at 5 kbars and 4 min at 12 kbars. The pellets thus prepared were kept at 110 °C overnight in an oven before analyses. The spectra were recorded at  $4 \text{ cm}^{-1}$  resolution, from 100 co-added scans. Near infrared (NIR) spectra ( $7500 - 4000 \text{ cm}^{-1}$ ) were acquired with a Thermo-Scientific Integrating Sphere (diffuse reflectance) equipped with an internal InGaAs detector, set on a Thermo-Scientific Nicolet 6700 FTIR spectrometer. A white light source was used, associated with a  $\text{CaF}_2$  beam splitter. The resolution was set at  $4 \text{ cm}^{-1}$  with the co-additions of 100 scans. Samples were analyzed directly on the integrating sphere.

#### ***Organic geochemistry***

Seven bulk rock samples (basalts or clays in basalt cavities: 4600-1, 4600-3A, 4600-3B, and paleosols on basalts: 4504-3, 4504-4, 4504-5 and 4517-1) were used in the organic geochemistry study. Total carbon (TC), total inorganic carbon (TIC), and total sulphur (TS) contents were measured using an Eltra CS-500 IR-analyzer with a TIC module. TC was determined using an infrared cell detector in  $\text{CO}_2$  gas evolved by combustion in an oxygen atmosphere. TIC contents were derived from a reaction with hot 15% hydrochloric acid; the resulting  $\text{CO}_2$  was determined using an infrared detector. Total organic carbon (TOC) was calculated as the difference between TC and TIC. Calibration was made according to the Eltra standards. The samples crushed to ca. 100 mesh were extracted using a dichloromethane (DCM)-methanol mixture (1:1 v:v) with an accelerated Dionex ASE 350 solvent extractor. Elemental sulphur was removed using an activated copper mesh. Due to low TOC values and

low extract yields, samples were not separated into fractions. The *n*-hexane aliquots of the total extracts were converted to trimethylsilyl derivatives via a reaction with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine for 3 h at 70 °C. A blank sample (silica gel) was analysed using the same procedure. Only trace amounts of phthalates and fatty acids (FAs) were detected. All solvents were spectroscopically pure and the *n*-hexane for derivatization was of super-dehydrated grade. The GC-MS analyses were carried out using an Agilent Technologies 7890A gas chromatograph and an Agilent 5975C mass spectrometer with a Triple-Axis Detector at the Faculty of Earth Sciences, Sosnowiec, Poland. Helium (6.0 Grade) was used as the carrier gas at a constant flow of 2.6 ml/min. Separation was performed in either of two fused silica columns:

(i) J&W HP5-MS (60 m × 0.32 mm i.d., 0.25 µm film thickness) coated with a chemically 120 bonded phase (5% phenyl, 95% methylsiloxane). The GC oven temperature was programmed from 45 °C (1 min) to 100 °C at 20 °C/min, then to 300 °C (held for 60 min) at 3 °C/min. Solvent delay = 10 min.

(ii) J&W DB35-MS (60 m × 0.25 mm i.d., 0.25 µm film thickness) coated with a chemically bonded phase (35% phenyl, 65% methylsiloxane). The GC oven temperature was programmed from 50 °C (1 min) to 120 °C at 20 °C/min, then to 300 °C (held for 60 min) at 3 °C/min. Solvent delay = 15 min. The GC column outlet was connected directly to the ion source of the MSD. The GC-MS interface was at 280 °C, while the ion source and the quadrupole analyser were at 230 and 150 °C, respectively. Spectra were recorded from *m/z* 45–550 (0–40 min) and *m/z* 50–700 (> 40 min). The mass spectrometer was operated in the electron impact mode (ionisation energy 70 eV).

### ***Petrographic observations***

Petrographic studies were performed on thin sections and rock fragments using a polarizing optical microscope (Nikon Eclipse E600POL) and a JEOL IT 500 SEM equipped with an EDS (BRUKER XFlash 4030 Silicon drift detector). SEM observations were performed in secondary electron imaging mode (SEI) for morphological investigations and backscattering electron mode (BSE) on carbon-coated thin sections for imaging of chemical contrast and selection of local sites for punctual chemical analysis. Analytical conditions were 15 kV, 1 nA, a counting time of 60 s and a working distance of 16.5 mm. The standards used for EDS consisted of albite (Na, Al, Si), almandine (Mg, Fe), diopside (Ca), orthoclase (K) and spessartine (Mn). Matrix corrections were performed using integrated programs (a

1758 PhiRhoz correction). Reproducibility of the standard analyses was close to 1.5% for all of the  
1759 elements, except Na (3%).

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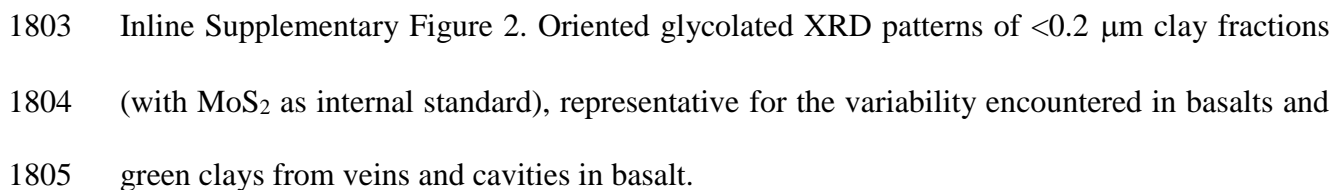
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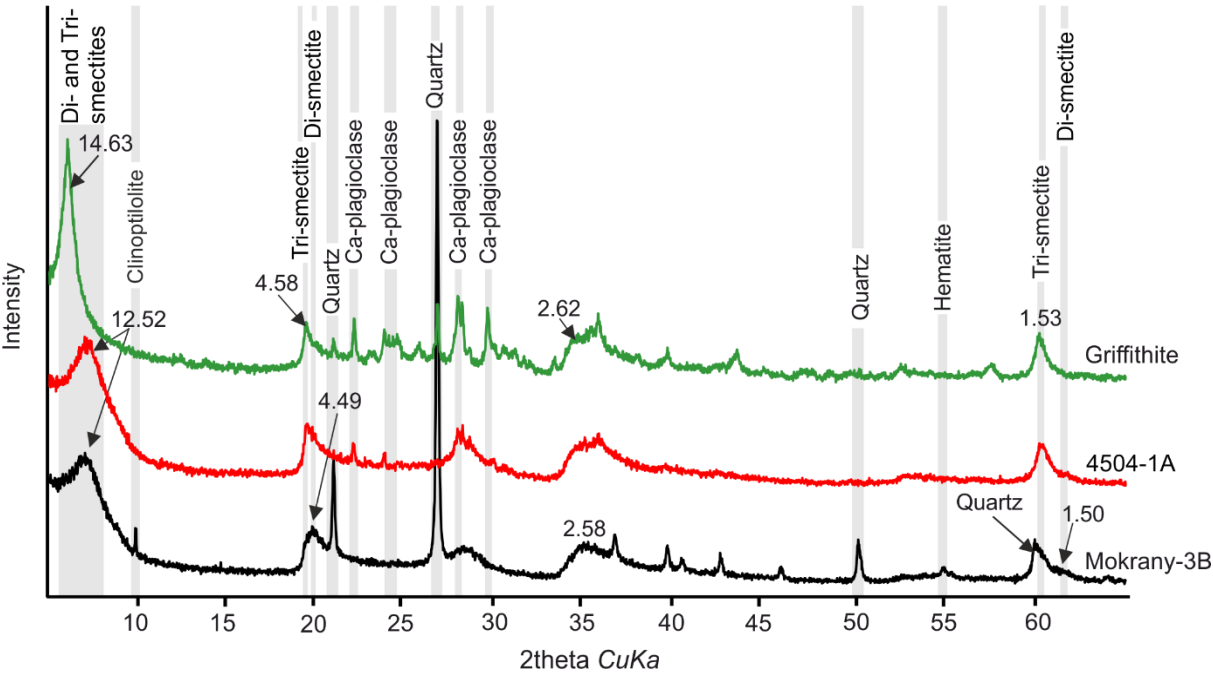
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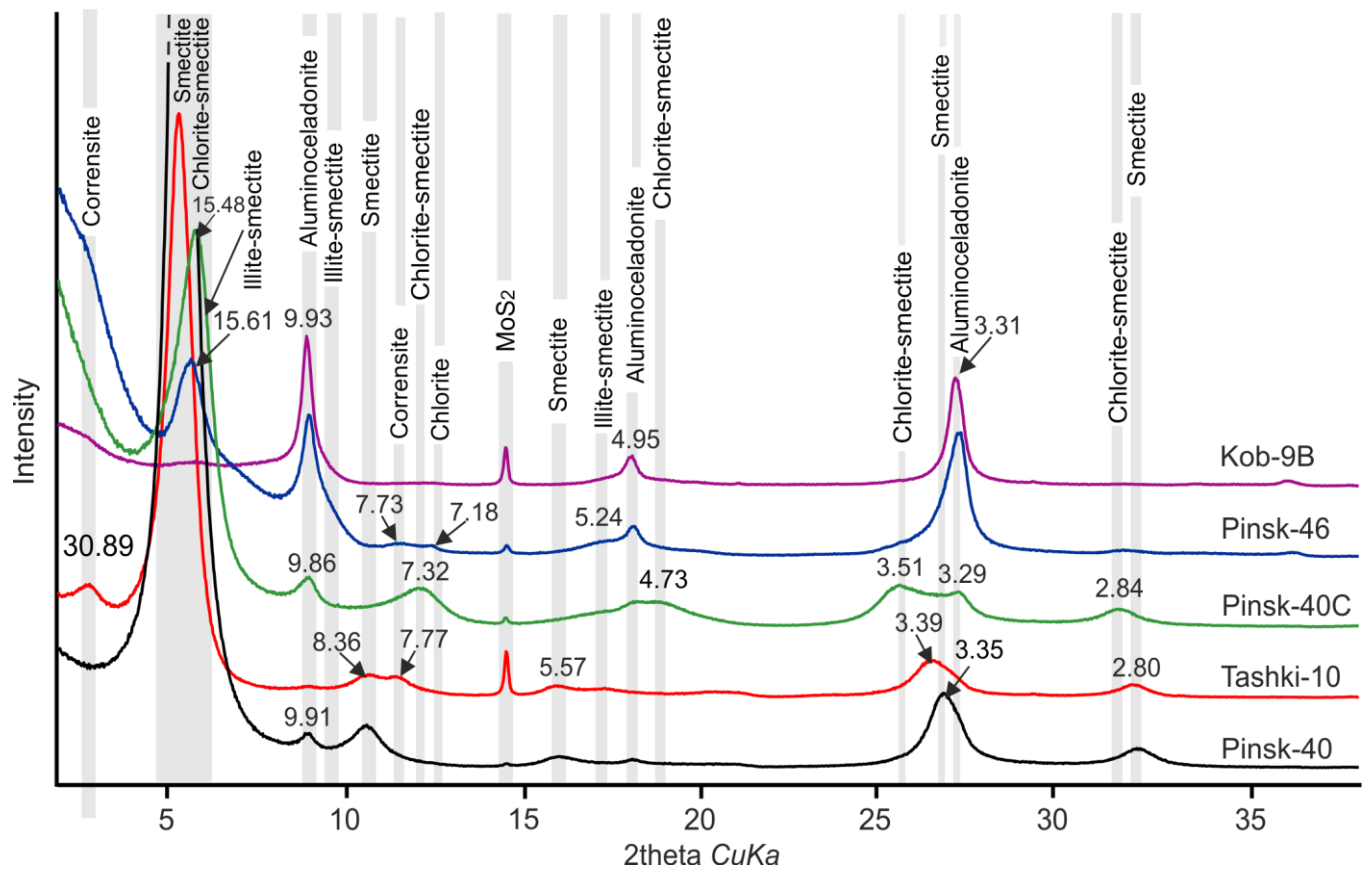
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 1793 diffraction analysis of clay-bearing rocks from random preparations. Clays and Clay Minerals  
 1794 49, 514–528.  
 1795  
 1796  
 1797 Inline Supplementary Figure 1. Random powder XRD patterns of the bulk rock, with ZnO  
 1798 internal standard, illustrating the compositional variability of Volyn tuffs, from felsic (top) to  
 1799 basic (bottom), with rhyodacite Skv-0C as reference.  
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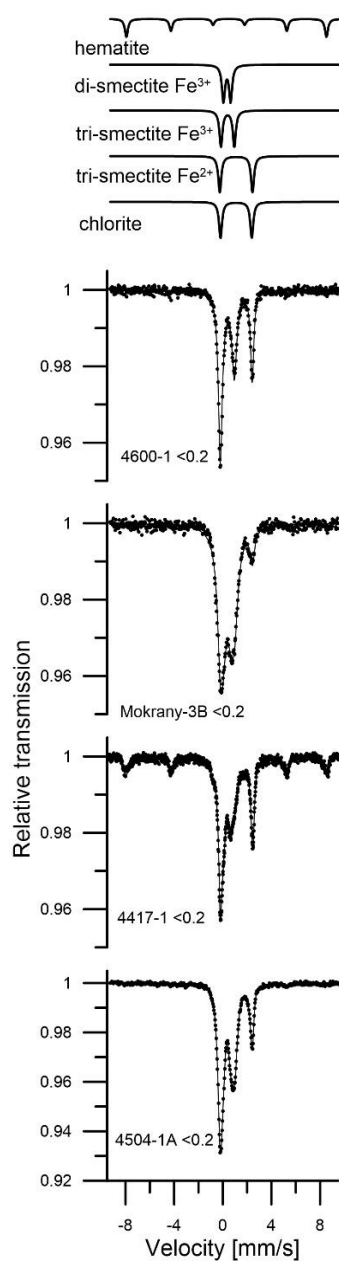
Inline Supplementary Figure 3. Random powder XRD patterns of <0.2  $\mu\text{m}$  basalt clay fractions and <2  $\mu\text{m}$  fraction of griffithite, documenting coexistence of di- and trioctahedral smectite. The reference griffithite sample from Griffith Park, California, was provided by Dr. Jana Madejova.



Inline Supplementary Figure 4. Oriented glycolated XRD patterns of <0.2  $\mu\text{m}$  clay fractions, representative for the variability encountered in tuffs.



Inline Supplementary Figure 5.  $^{57}\text{Fe}$  room temperature Mössbauer spectra of minerals, used for decomposing spectra of bulk rocks (results of decomposition in Table 1).



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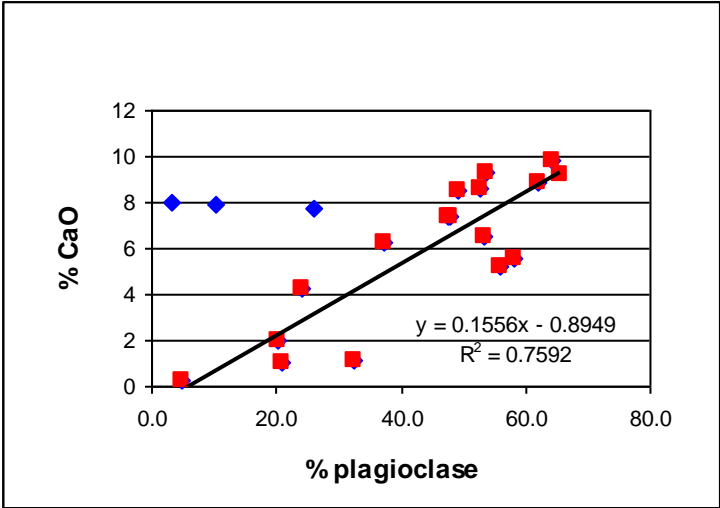
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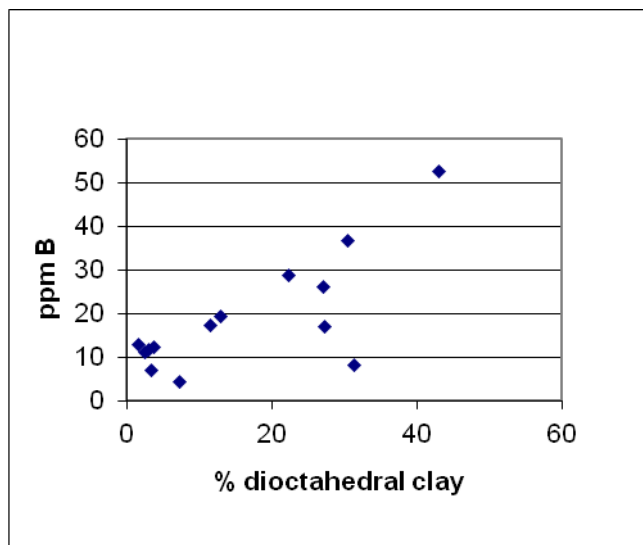
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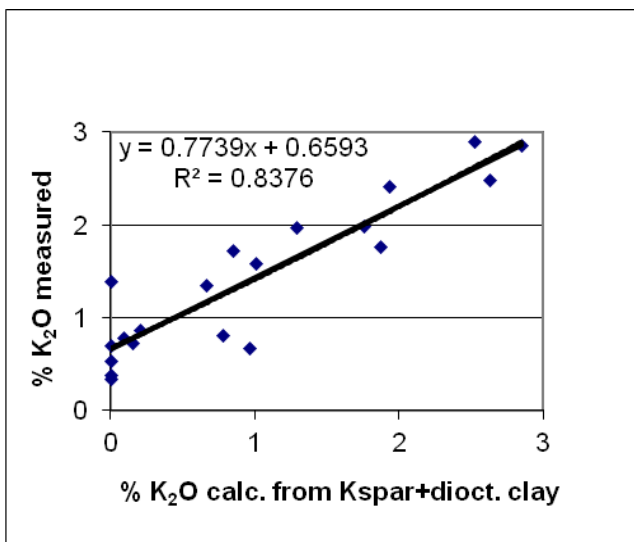
Inline Supplementary Figure 6. Relationship between % plagioclase from XRD and % CaO in basalts of variable degree of alteration. Three samples off the general trend (blue diamonds) contain calcite veinlets.



Inline Supplementary Figure 7. Relationship between % dioctahedral clays from XRD and ppm boron in basalts of variable degree of alteration.



Inline Supplementary Figure 8. Relationship between %  $K_2O$  calculated from XRD contents of K-feldspar (assuming 12%  $K_2O$ ) and dioctahedral clay (6%  $K_2O$ ) and measured %  $K_2O$  in basalts of variable degree of alteration.



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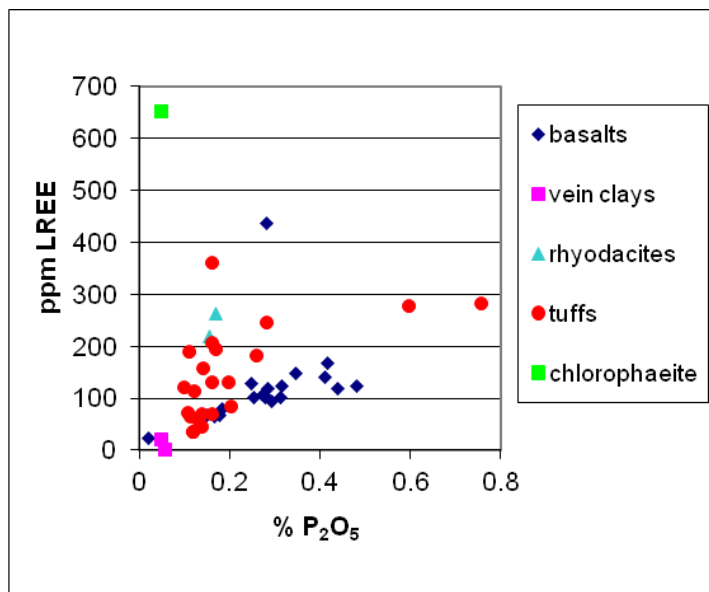
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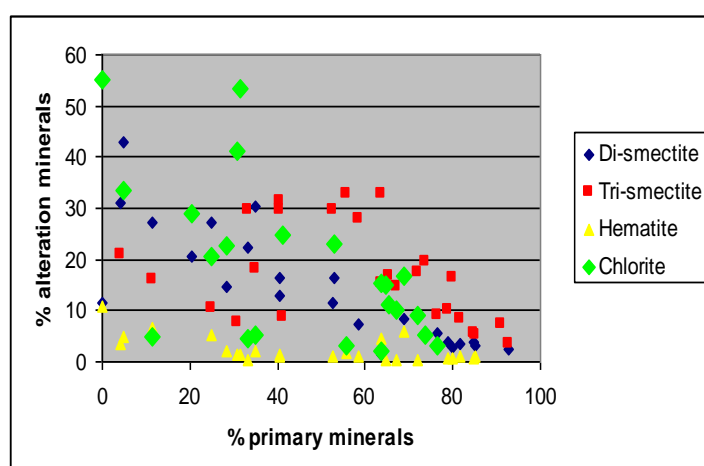
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1884 Inline Supplementary Figure 9. Relationship between % P<sub>2</sub>O<sub>5</sub> and ppm LREE in bulk rocks.

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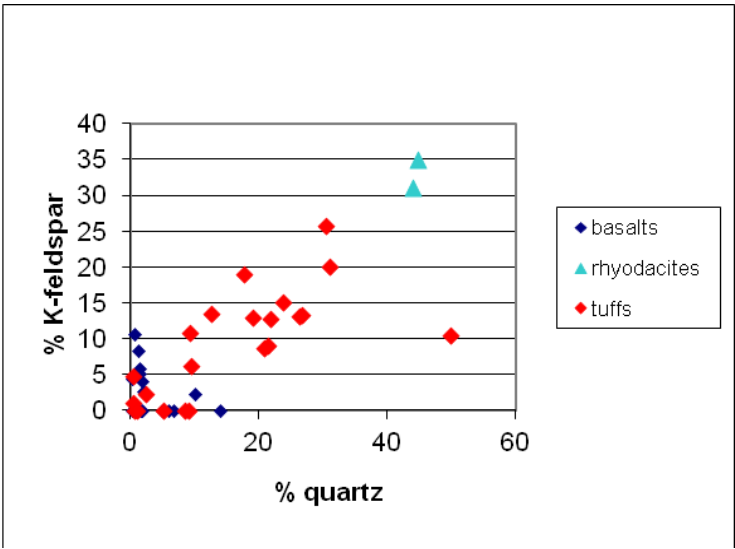


Inline Supplementary Figure 10. Quantitative evolution of secondary minerals in the course of basalt hydrothermal alteration(traced by percent of primary minerals).



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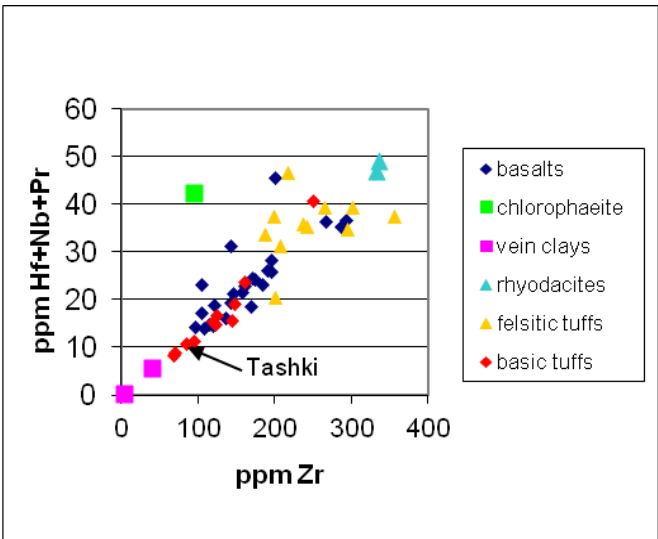
Inline Supplementary Figure 11. Differentiation of tuffs into felsic (close to rhyodacite) and basaltic, based on quartz and K-feldspar XRD contents.



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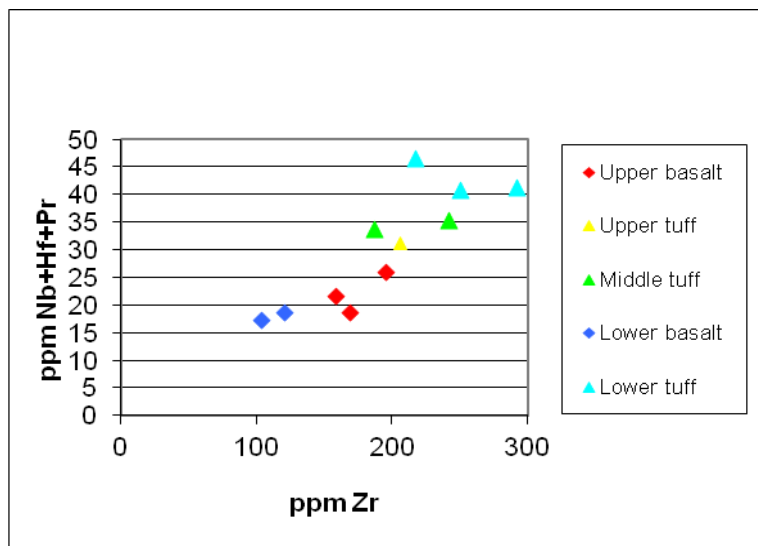
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Inline Supplementary Figure 12. Chemical variability of tuffs (felsic vs. basaltic) traced using the most immobile trace elements.



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Inline Supplementary Figure 13. Chemical differences between basalts and tuffs illustrated for a single profile (Kobryn) using the most immobile trace elements.



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