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The Importance of Mechanical Transport, Rock Texture, and Mineral Chemistry in Chemical Weathering of Granites: The Melechov Massif, Czech Republic

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Abstract

Data of 41 or more elements in superficial as well as drill-core samples of the peraluminous Lipnice and Melechov granites, located several kilometers apart in northern Moldanubian Batholith, are evaluated. Weathering of both granite types proceeded in virtually identical time and environment, but it shows very different patterns. In the weathered Lipnice granite, Al_2O_3 slightly increased, loss on ignition (LOI) increased strongly, and contents of all other major elements except for Fe are lower (however, reconcentration of K, Mg, and Ti in secondary phases is possible). In the relatively coarse-grained and more acidic Melechov granite, the depleted major elements are Si, Fe, Ti, Mn, and Mg. Strongly increased Al in half of weathered samples is independent on the moderate increase of LOI and relatively small changes of Na, Ca, K, and P contents. These samples are relatively poor in quartz, which is the result of fossil weathering, mechanical mineral separation, and erosion processes. In the Lipnice granite, however, chemical weathering dominated over mechanical fractionation due to a more compact character of the rock (as well as of biotite and plagioclase). Regarding trace elements, enrichment in Ga and loss of U are the only changes documented in both granite types (in different proportions however). The rare-earth element (REE) fractionation is generally weak, but in the Lipnice granite, two processes are proven: (i) dissolution of apatite which has an M-type lanthanide tetrad effect in the fresh rock and (ii) formation of positive Ce anomaly.

Keywords: granite weathering, temperate climate, trace elements, apatite, lanthanide tetrad effect, grain size

1. Introduction

Knowledge of chemical weathering processes is important for pedology, sedimentology, hydrogeochemistry, environmental chemistry, and petrology. Chemical weathering is most frequently studied in magmatic and high-grade metamorphic

rocks which are, by their nature, thermodynamically unstable in superficial conditions. At the same time, chemical composition of the fresh rock is an important fingerprint of magma origin and differentiation. Several elements relatively conservative at weathering, like Sc, Th, and rare-earth elements (REEs), have been also used to assess the source composition of ancient sediments [1].

Chemical weathering of rocks is a complicated interplay of alteration and decomposition of primary minerals including removal of ions in solution, formation of secondary minerals, and removal of the solid weathering products. Ideal conditions for bedrock decomposition differ from ideal conditions for erosion. Therefore, in geological time, environmental changes may lead to the formation of complex profiles, where fossil weathering can be documented [2].

While the research of weathering crusts in the Bohemian Massif was mainly dedicated to economic clay deposits, fossil weathering and small-scale clay formation have been independently documented in various rocks [3]. Pivec [4] described kaolinization in the Říčany granite which probably took place in a warm and humid climate in the Cretaceous. The study of low-temperature fracture fillings in a 100-m-deep borehole in the Kouty granite of the Melechov Massif (MM) [5, 6] documented an intense downward transport of supergene clay enriched in fine-grained resistant accessory minerals prevalently in the lower Cretaceous. In this way, also clay minerals of hydrothermal origin could be concentrated. Štemprok [7] showed that hydrothermal kaolinite in granites and greisens occurs in the whole profile of a 1.5-km-deep borehole at Cínovec.

The Melechov Massif is a good representative of the granite body in highland areas of the Bohemian Massif, with thin soil cover and low rate of recent chemical weathering. However, influence of weathering was documented down to ca. 50 m of depth [6, 8]. In this chapter we will focus on the comparison of chemical weathering of Lipnice and Melechov granites, which proceeds in nearly the same time and space but shows very different patterns due to differences not only in rock and mineral chemistries but also in properties relevant for hydrology, mechanical transport, and mineral separation.

2. Geological setting

The study area is located in the northwestern part of the Bohemian-Moravian Highlands in the Czech Republic (**Figure 1a**). The granites of MM represent the northernmost surface body of Moldanubian Batholith. The massif was formed during the Variscan orogeny (330–300 Ma) in high-grade metamorphic rocks of Moldanubian Unit (prevalently biotite paragneisses and migmatites). The relatively older granites of Lipnice and Kouty types outcrop in the outer part of MM, prevalently on SE (see **Figure 1b**). The central part is formed by the younger Melechov granite type and its derivative, the Stvořidla type. For additional geological and geochemical information, see [9–14].

Similar to other crystalline units of Bohemian Massif, the area was largely peneplenized during the Mesozoic and then uplifted as late as during Pliocene and Pleistocene [15]. Thus, the rocks may have been affected by supergene alterations more than 100 million years ago (even in warmer and more humid climate), as also indicated by Pb isotope ages of fracture fillings [5, 6]. The present climate is temperate with a mean annual temperature of 7 °C and humid, with maximum rainfall in summer; the annual precipitation is roughly 750 mm. Erosion base represented by rivers Sázava and Želivka is located in altitudes 350–380 m. The region has been little industrialized and belongs to the relatively unpolluted ones within central Europe. However, acidification also influenced the area at the end of the twentieth century [16].
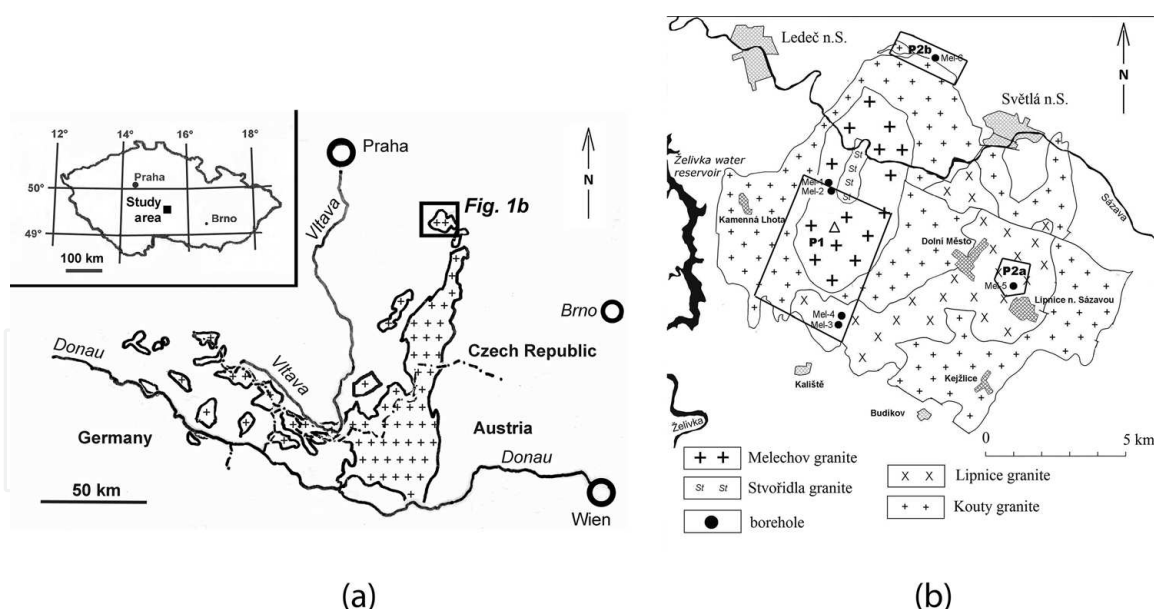
Figure 1.
(a) Situation of the Melechov Massif in the Czech Republic and in the Moldanubian Batholith (delimitation of the batholith from Mísař et al. [15]). (b) Granites of the Melechov Massif [10] with localization of boreholes and polygons of geochemical mapping. Triangle indicates the top of Melechov (715 m).

The Lipnice granite is fine-grained, with a grain size mostly below 2–2.5 mm. U-Th-Pb monazite ages of this granite range according to the electron microprobe dating from 308 ± 13 to 315 ± 23 Ma [17]. The major minerals are represented by quartz, oligoclase (locally albitized), K-feldspar (mainly microcline), biotite (with dominant annite or siderophyllite component [18, 19]), and muscovite (less abundant than biotite). K-feldspar partly replaces plagioclase, and domains unusually rich in K-feldspar are common, possibly formed by recrystallization of poikilitic microcline observed in some gneisses nearby. In addition, nodules rich in sillimanite and both micas are also abundant, representing probably restite from a material similar to paragneisses present within the area. The significant accessory minerals are ilmenite, fluorapatite (in the following "apatite" only), monazite (Ce), zircon, rutile/anatase, and locally secondary fluorite or pyrrhotite [19–21].

The delimitation of the Lipnice granite boundary in the south and east is difficult and controversial. Also more acidic intrusive and vein rocks appear frequently in the southwest of the granite body [13, 14]. Nevertheless between Lipnice nad Sázavou and Dolní Město, the granite is remarkably homogeneous [18, 21, 22], regardless of the ubiquitous presence of small restite nodules. Microscopic alterations of biotite (with formation of chlorite, muscovite/illite, TiO_2 phase, and K-feldspar) and of plagioclase, i.e., mainly formation of sericite (illite), together with rock fracturation and porosity were recently investigated in detail in the Mel-5 borehole in the Lipnice granite [8].

The Melechov granite to alkali-feldspar granite is relatively coarse-grained (with typical grain size ∼5 mm) and more fractionated than the Lipnice type. The major minerals are quartz, K-feldspar (prevalently microcline), albite (prevalently in perthite with An < 5, however magmatic albite and oligoclase also occur), muscovite and biotite (siderophyllite; less abundant than muscovite). Abundant apatite is the dominant accessory mineral. Zircon and monazite are less abundant, whereas primary ilmenite and rutile are scarce [20]. Tourmaline (schorl) is distributed irregularly; xenotime occurs rarely [19].

Chemically the differentiation of Melechov granite is manifested by higher content of SiO_2 and P_2O_5 and lower content of elements which are compatible in peraluminous granites (mainly Mg, Ti, Fe, Ca, Zr, LREE, Th). In addition the

(a) Major elements												
Samples		SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$t.	MgO	MnO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	LOI
Lipnice granite												
Fresh, Mel-5 (16.5–150 m), n = 18	Mean	69.87	0.54	14.93	2.49	0.78	0.044	1.06	2.91	5.46	0.301	1.21
	St. dev.	0.24	0.03	0.12	0.05	0.05	0.004	0.12	0.06	0.15	0.017	0.05
Weathered, P2a low-Al group, n = 20	Mean	70.76	0.44	15.15	2.33	0.67	0.027	0.79	2.65	5.09	0.290	1.72
	St. dev.	0.70	0.05	0.27	0.33	0.12	0.007	0.21	0.22	0.16	0.033	0.49
Weathered, P2a high-Al group, n = 26	Mean	67.82	0.49	17.36	2.69	0.74	0.028	0.70	2.35	5.06	0.271	2.38
	St. dev.	1.46	0.08	0.52	0.55	0.13	0.006	0.14	0.34	0.26	0.040	0.93
Fresh, Mel-3 (36.4–106.5, 175–175.5 m), Mel-4 (22–168.4 m), n = 30	Mean	69.79	0.48	14.99	2.53	0.83	0.039	1.10	2.95	5.43	0.256	1.35
	St. dev.	0.41	0.04	0.13	0.12	0.05	0.003	0.07	0.09	0.17	0.010	0.17
Weathered, P1, n = 16	Mean	67.21	0.47	17.14	2.65	0.76	0.034	0.77	2.54	5.12	0.280	2.99
	St. dev.	2.97	0.08	1.83	0.54	0.15	0.010	0.25	0.48	0.33	0.075	1.38
Melechov granite												
Fresh, Mel-1 (37–199.5 m), Mel-2 (22–193 m), n = 44	Mean	72.98	0.14	14.66	1.26	0.25	0.045	0.74	3.51	4.54	0.41	1.20
	St. dev.	0.71	0.01	0.43	0.19	0.08	0.011	0.14	0.52	0.26	0.02	0.43
Weathered, P1 low-Al group, n = 25	Mean	70.44	0.09	16.49	1.00	0.20	0.032	0.71	4.03	4.68	0.48	1.81
	St. dev.	1.16	0.02	0.62	0.14	0.03	0.006	0.12	0.29	0.20	0.08	0.53
Weathered, P1 high-Al group, n = 29	Mean	65.32	0.10	21.51	1.04	0.20	0.030	0.68	3.97	4.62	0.47	1.95
	St. dev.	1.06	0.02	0.89	0.13	0.03	0.007	0.11	0.30	0.28	0.07	0.52

(b) Trace elements and element ratios (average)						
		Lipnice granite			Melechov granite	
Samples Element	Mel-5 fresh	P2a weathered —low Al	P2a weathered —high Al	Mel-1, Mel-2 fresh	P1 weathered —low Al	P1 weathered —high Al
Ba	528.4	514.4	486.6	168.1	174.7	172.3
Be	3.8	4.2	4.2	3.8	4.3	4.1
Co	3.9	3.6	4.5	1.0	1.0	0.9
Cs	8.0	7.4	8.6	24.5	25.2	24.9
Ga	23.0	23.9	27.1	21.4	22.3	25.1
Hf	6.5	6.5	6.4	2.0	2.3	2.2
Nb	9.1	8.5	9.2	14.6	13.0	13.7
Rb	322.3	327.9	333.4	296.7	313.6	314.6
Sn	5.2	6.4	7.4	19.1	24.1	25.8

(b) Trace elements and element ratios (average)					
	Lipnice granite			Melechov granite		
Samples	Mel-5 fresh	P2a weathered —low Al	P2a weathered —high Al	Mel-1, Mel-2 fresh	P1 weathered —low Al	P1 weathered —high Al
Element						
Sr	109.0	103.8	96.7	92.9	98.0	94.6
Ta	0.81	0.75	0.82	3.5	2.96	3.12
Th	42.9	46.1	43.9	3.9	4.1	4.5
U	9.9	6.6	6.1	13.5	5.0	5.3
V	24	24	30	5.5	4	4
W	1.4	1.9	1.6	48	4.3	4.6
Zr	224.5	213.5	210.6	54	55.6	53.7
Y	15.7	15.5	15.7	11.4	13.1	12.7
La	56.7	52.3	52.6	9.1	9.9	9.7
Gd	5.45	5.03	5.19	2.10	2.22	2.16
Lu	0.17	0.16	0.15	0.09	0.10	0.09
REE total	297	281	271	51.6	53.2	51.9
K/Rb	141	130	127	128	125	123
Ca/Sr	70.1	53.6	50.8	60	51.8	52.1
Al/Ga	3437	3367	3512	3638	3930	4573
Th/U	4.37	7.37	7.21	0.31	0.87	0.88
Zr/Hf	34.4	32.9	33.1	26.6	24.2	24.8
Nb/Ta	11.4	11.8	11.3	4.23	4.5	4.4
Eu/Eu*	0.247	0.235	0.239	0.43	0.443	0.43
Ce/Ce*	1.06	1.09	1.09	1.05	0.99	1.00
Pr/Pr*	1.11	1.01	1.00	1.02	0.97	0.97
Y/Ho	32.6	34.0	33.9	32.8	35.5	34.6

Primary data are from [13, 21]. Note that borehole samples of "fresh" Melechov granite include also hydrothermally altered rock which is relatively common. Weathered samples from boreholes were excluded.
$Eu/Eu^* = 2Eu_N/(Sm_N + Gd_N)$.
$Ce/Ce^* = 3Ce_N/(2La_N + Nd_N)$.
$Pr/Pr^* = 3Pr_N/(2Nd_N + La_N)$.

Table 1.
Statistics of elements in boreholes (Mel-1 to Mel-5) and in soil base samples of polygons (P1, P2a).

Melechov type has significantly lower fluorine content (0.08–0.14 wt.%) than the Lipnice type (usually 0.20–0.25 wt.%) and somewhat lower content of K (see also **Table 1a**; **Figure 2**).

In comparison with the Lipnice type, the Melechov granite is generally more affected by subsolidus alterations [13, 14]: chloritization; baueritization with formation of secondary Ti, Fe, and Zn oxides [23]; sericitization of plagioclase (with formation of secondary apatite); probably kaolinization of feldspars; and locally carbonatization. Samples affected by such alteration processes (except for carbonatization) exhibit weaker chemical and mineralogical changes (including coloration by ferric pigments) during supergene weathering, whose influence is sometimes difficult to be distinguished from alteration at higher temperature [24].
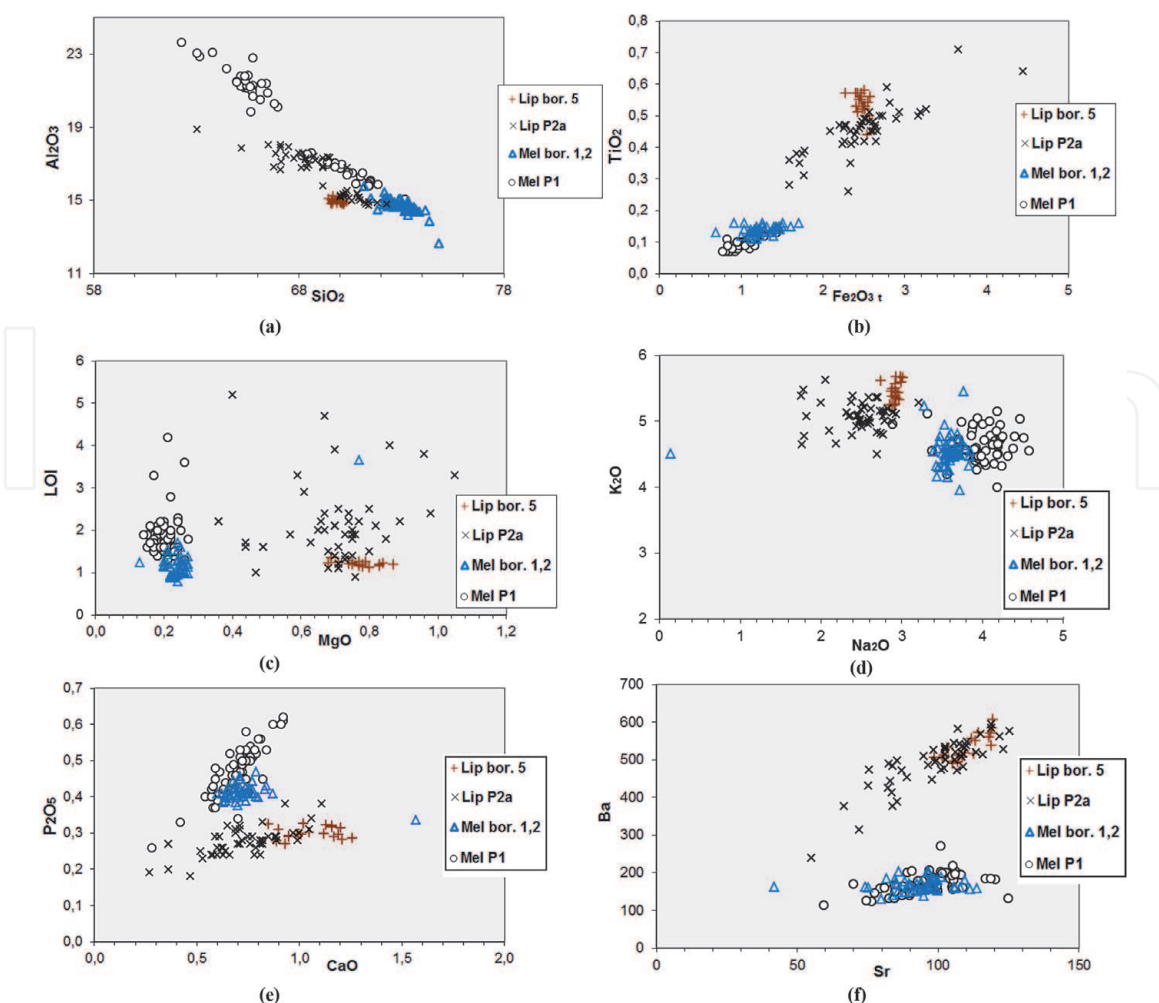
Figure 2.
(a–f) Plots of selected pairs of chemical parameters (major components in wt. %, Sr and Ba in ppm) in Lipnice and Melechov granites from boreholes Mel-5, Mel-1, and Mel-2 (including fresh, altered, and weathered samples) and from soil cap in polygons P2a and P1.

3. Material and methods

Since the 1990s, the Melechov Massif has been the subject of intensive investigation, leaded by the Radioactive Waste Repository Authority of the Czech Republic (RAWRA = SÚRAO). The results include numerous whole-rock analyses of granites from cores of boreholes 100–200 m deep and from shallow drill holes. These data are completed in unpublished reports [13, 21] and with respect to weathering partly discussed in [25–27].

The fresh granites are represented by core samples taken in intervals of 5–10 m from boreholes Mel-1 and Mel-2 (Melechov type) and Mel-3 to Mel-5 (Lipnice type). However, due to complicated geology and petrology in boreholes Mel-3 and Mel-4, which were intentionally drilled in inhomogeneous environment [13, 14], we present results from these two boreholes only marginally. Borehole samples displaying visible indices of weathering have been included in graphs (**Figure 2**) but not in the statistical processing (**Table 1**). We also used nine analyses of generally very slightly weathered Lipnice granite from outcrops in polygon P2a, analyzed under the same conditions [22]. The major elements were analyzed in the labs of the Czech Geological Survey (ČGS) in Prague and trace elements in the ACME Laboratories, Vancouver, Canada (by ICP-OES and ICP-MS).

As for weathered granite, analyses of samples taken from the lower part of shallow drill holes (soil cap) in the polygons P1 (which also includes the boreholes

Mel-1 to Mel-4) and P2a (which includes borehole Mel-5) were used. These samples were collected in profile grid making a regular network (interval between profiles is ca. 750–900 m, sampling step on profile 150 m). Samples for chemical analyses were collected from the maximum attainable depth, this varying from 0.6 to 2.8 m (mostly close to 2 m in Lipnice granite and 1.5 m in Melechov granite)—see [21] for details. Analyses of saprolites containing pegmatite or quartz veins were excluded from the data processing in the presented study.

The polygon P1 extends from contact of the Melechov and Stvořidla granites to exocontact of the Lipnice granite with paragneisses (the gneisses/migmatites sampled in this area seem to be chemically very similar to the Lipnice granite [21]). Between the Lipnice and Melechov granites outcrops Kouty granite, compositionally and texturally largely transitional between the Lipnice and Melechov types; this rock, however, is represented by relatively few samples and so is not considered here. The area is dominated by the Melechov hill (715 m) and covered prevalently by a managed spruce forest. The major soil type in the forest is dystric cambisol, locally podzolic [28]. Especially in the southern part of P1 (i.e., mainly on Lipnice and Kouty granites), there are also agricultural fields and meadows.

The polygon P2a north of Lipnice nad Sázavou represents Lipnice granite (only locally with acidic vein intrusions) and is dominated by the Holý vrch hill (620 m). Almost all samples were taken in the forest (prevailing spruce) and only few samples in abandoned quarries. The dominant soil type is lithic cambisol, in places also pseudogleys occur [28].

Samples from soil cap were analyzed in the ACME Laboratories for both major and trace elements, the methods applied for the presented trace elements being the same as in case of samples from boreholes. The fact that major elements have not been determined under the same conditions in samples of boreholes and of soil cap implies that subtle differences between fresh and weathered rocks have to be treated carefully; however it plays no role in comparison of behavior of the Lipnice and Melechov granite types.

Regarding the distribution of trace elements in rock-forming minerals of the fresh granite, mainly data from the previous studies [19, 20] are considered. In addition, new trace element analyses of apatite are presented. REE, Y, Sr, Th, and U in apatite have been determined by LA-ICP-MS spot analyses in polished sections of rocks at the Department of Chemistry of Faculty of Science, Masaryk University, Brno.

Instrumentation for the LA-ICP-MS consists of a laser ablation system UP 213 (New Wave, USA) and an ICP-MS spectrometer Agilent 7500 CE (Agilent, Japan). A commercial Q-switched Nd:YAG laser ablation device works at the wavelength of 213 nm. Helium was used as the carrier gas. For measurements we used hole drilling mode for the duration of 40 seconds for each spot. Laser ablation was performed with a spot diameter of 25 μm, laser fluence 4.5 J cm^{-2}, and repetition rate 10 Hz. The isotopes were measured with integration time 0.1 s / isotope. Optimization of LA-ICP-MS parameters (gas flow rates, sampling depth, electrostatic lens voltages of the MS) was performed with the glass reference material NIST SRM 612 with respect to maximum S/N ratio and minimum oxide formation (ThO^+/Th^+ count ratio 0.2%, U^+/Th^+ count ratio 1.1%).

4. Results

4.1 Composition of fresh and weathered rocks

Several interesting facts not related to weathering, especially some vertical compositional gradients of fresh rocks, have been also found. Here, we present this

information only to distinguish the influence of weathering processes from original granite inhomogeneity. The chemical contrasts between Lipnice and Melechov granite types (including the ratios of isovalent elements Zr/Hf and Nb/Ta and the Eu/Eu* ratio) are mostly not significantly affected by weathering; however in case of few elements, they were enhanced (Na, P) or smoothened up to reversed (Si, K, U).

4.1.1 Major elements

Core samples of Lipnice granite from the borehole Mel-5 have very low variability regarding major as well as trace elements (see also **Table 1**), and the results show no relation to rock pigmentation and microscopic alteration patterns (chloritization, sericitization) which were investigated in detail [8] in this borehole (except for the uppermost weathered sample, representing the "brown granite"). In Mel-3 and Mel-4, the situation is more complicated: in addition to the typical Lipnice granite, also magmatic vein rocks and a relatively bright, more acidic variety of Lipnice granite were found [13]. In addition, hydrothermally altered granites occur (in contrast to Mel-5). We excluded such samples from the data processing; however it is obvious that even the "fresh" Lipnice granite from boreholes Mel-3 and Mel-4 is less representative than that from Mel-5.

Similarly, the polygon P1 is very inhomogeneous in comparison with P2a [21], and in addition redistribution and contamination of weathered material have been more intensive there [27]. For these reasons and due to the fact that the Lipnice granite is represented by relatively few samples in P1, we evaluated the weathering of Lipnice granite mainly by comparison of borehole Mel-5 and polygon P2a.

Comparing borehole samples taken from various depths, iron oxidation is observed near the surface [25], which is also supported by several slightly weathered samples taken from outcrops in P2a [22]. However, Fe_2O_3 and FeO were not determined in samples from soil cap singly, what precludes the application of Fe_2O_3/FeO ratio as otherwise a powerful indicator of chemical weathering in our study.

The weathered Lipnice as well as Melechov granites are enriched in Al_2O_3 and H_2O (which due to low C and S content represents the majority of loss of ignition), especially at the expense of SiO_2. Two distinct groups of weathered granite can be distinguished according to Al content, most notably in the Melechov type: $Al_2O_3 \leq 17.6\%$ and $Al_2O_3 \geq 19.8\%$ (**Figure 2a**). As shown by [24, 26, 27], the second group is enriched in small particles, which include secondary minerals, detrite of plagioclase, micas and chlorite, and accessory minerals, and is relatively depleted in quartz (the original overlying quartz-rich eluvia were mostly eroded; nevertheless in places, sandy eluvium was preserved and locally used as a building material). Such mineral fractionation was most effective in the coarse-grained Melechov granite, where plagioclase had been already intensively affected by subsolidus alteration and small particles could be transported through a skeleton formed by quartz and K-feldspar [27].

In the Lipnice granite, two groups with different enrichment in Al can be observed in polygon P2a, but they are not so contrasting (Al_2O_3 = 14.57–15.82 wt. % and 16.66–19.11 wt. %, respectively; in the first group, SiO_2 is not lower than in borehole). The most contrasting single parameter of chemical weathering intensity is hydration (expressed as LOI), reaching higher values than in the Melechov type (**Figure 2c**).

The behavior of K is complicated: its content seems to be slightly decreased in weathered Lipnice granite. However, there is no trend of ongoing K removal

with weathering intensity (**Table 1**; **Figure 2d**). One of the possible explanations is formation of illite. In weathered Melechov granite, no systematic shift of K content is observed.

Both Ca and Na exhibit very different behaviour in the two granites. In weathered Melechov type, Ca is comparable and Na even higher than in the fresh rock (**Figure 2d** and **e**). In contrast, in the Lipnice type, Ca and Na are strongly depleted during weathering. Mg is slightly depleted in weathered granites of both types; however note that in the Melechov granite, this could be related rather to the original magma inhomogeneity than to the weathering (see **Figure 3d**). As for Mn, it is removed by weathering in both granites (**Table 1**).
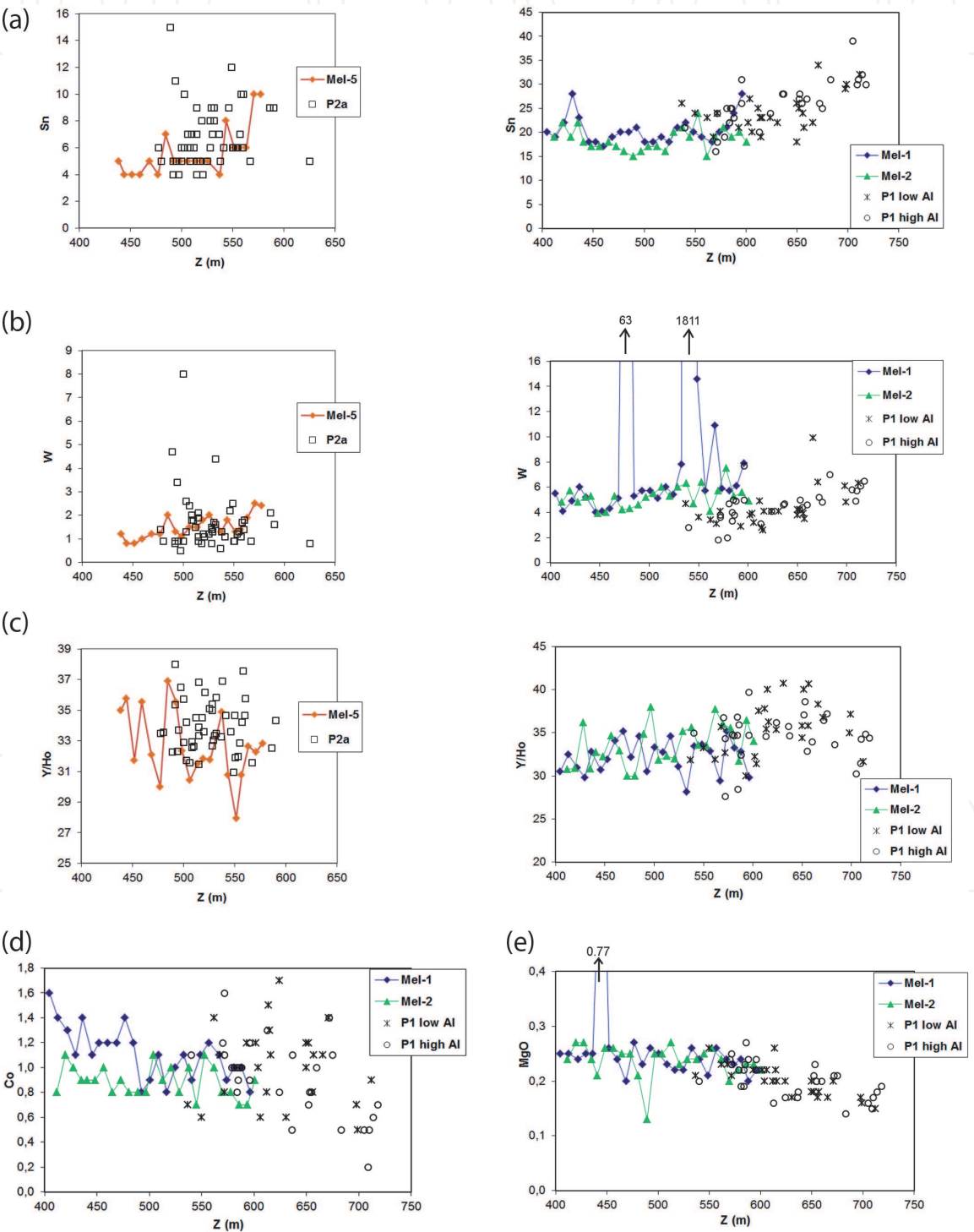

Figure 3.
Relationships of selected element concentrations and ratios in granites of boreholes and polygons (soil cap) to altitude. (a)–(c) Sn (ppm), W (ppm), and Y/Ho ratio in Lipnice and Melechov granites. (d) Co (ppm), (e) MgO (wt. %) in Melechov granite.

Phosphorus, slightly depleted in Lipnice granite in P2a only and possibly enriched in weathered Melechov granite, has in all weathered granites positive correlation with calcium (**Figure 2e**), missing in the fresh rock. This indicates importance of apatite. Negative correlation of P and LOI especially in weathered Lipnice type is an indication for apatite dissolution. Another indirect evidence for apatite dissolution and phosphorus mobility is the common occurrence of P-rich limonite in eluvia and low-temperature fracture fillings ([6] and unpublished data of V. Procházka).

Iron content decreased in the weathered Melechov granite but not in Lipnice granite (**Figure 2b**), where the correlation of Fe and LOI (R = 0.68) indicates the possibility of passive (re)concentration of Fe in weathered rock. Note that Fe content (especially Fe_2O_3) is also significantly lower in borehole Mel-2 than in Mel-1 [13], perhaps as a result of subsolidus alterations of Melechov granite. The behavior of Ti is similar to that of Fe; however weathered Lipnice granite in polygon P2a is mostly significantly depleted in Ti relatively to the fresh rock (**Figure 2b**).

The total carbon content was not measured in boreholes; in soil cap samples, it is usually smaller than 0.2 wt. %, the peak value being 0.36% in P1 and 0.95% in P2a.

It follows that mainly elements concentrated in plagioclase are depleted in the Lipnice granite whereas elements originally concentrated mainly in biotite (or its alteration products) are depleted in both granite types, except for Fe in Lipnice granite.

4.1.2 Trace elements

Only elements showing significant fractionation during weathering at least in one granite type are presented here.

Sr, Ba. Strontium and barium are significantly depleted in weathered Lipnice granite but not in weathered Melechov granite (**Figure 2f**). Despite the removal of Sr, the mean Ca/Sr ratio of weathered Lipnice granite is significantly lower than that of fresh rock (**Table 1b**).

Co. There is no systematic trend of Co content in Lipnice granite. In Melechov type, however, Co has a decreasing trend with altitude (as a compatible element), and it cannot be excluded that weathering leads to enrichment in Co (**Figure 3e**). The Co content in borehole Mel-2 is mostly lower than in Mel-1.

Ga. Gallium was passively concentrated in chemically weathered rocks similarly to Al. However, the Al/Ga ratio in weathered Melechov granite is significantly higher than in fresh rock. In weathered Lipnice granite, such a systematic trend is not observed; only the variability of Al/Ga ratio is much higher.

Sn. Tin content is at average higher in weathered Melechov granite than in the fresh rock (**Figure 3a**; **Table 1b**). This may reflect vertical differentiation trend only, which however is not apparent in boreholes Mel-1 and Mel-2. Possible explanation is stronger chemical fractionation in apical part of the Melechov granite intrusion (according to [29], the original contact was not far above the present top of Melechov hill). Interestingly, Mg in the Melechov granite exhibits opposite behavior to Sn (**Figure 3d**). In the Lipnice granite, Sn also has an increasing trend with altitude, complicating the evaluation of possible weathering influence (**Figure 3a**).

V. In weathered Lipnice granite, V content is higher than in boreholes. The concentration of V by Fe-oxyhydroxides is one of the possible explanations. In Melechov granite, vanadium was mostly below detection limit (<5 ppm), the exception being borehole Mel-1. It follows that weathering led rather to removal of V from the Melechov type; however the effect of older alterations could be similar.
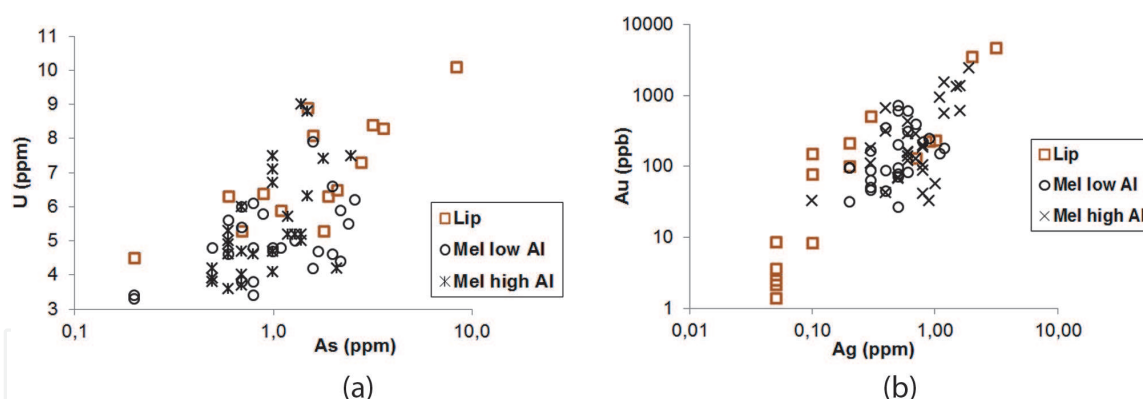
Figure 4.
(a) Relation of As and U content (in ppm) in Lipnice and Melechov granites in polygon P1 (samples of Melechov granite divided into groups with lower and higher Al content). (b) Gold and silver in granite eluvia of Lipnice and Melechov types in P1.

W. Of the elements analyzed, W is the most differentiated one by vertical fractionation. Its content increases with altitude in boreholes and even in P1, probably reflecting fluid-dominated upward transport of incompatible elements. After distinguishing this vertical trend, it is obvious that weathered Melechov granite is significantly depleted in W and weathered Lipnice granite possibly too (**Figure 3b**); in both cases, however, mean values are biased by outliers.

U. In Lipnice granite, the U contents both in the samples from shallow pits and even from outcrops are significantly lower than in the borehole samples. The removal of U from Melechov granite was yet more intensive than from the Lipnice type. As shown by mineral chemistry data and mass balance calculations [19, 30], the rock-forming accessory minerals (monazite, zircon, apatite; in the Melechov type also xenotime) contain at most 70% of U in the Lipnice granite and < 50% U in Melechov granite (in fresh rocks), the rest being obviously in an unstable phase. One possibility is uraninite which was found scarcely [20]; perhaps more important is uranium bound to Fe-oxyhydroxides (see also [5]) and along grain boundaries [31].

In the soil cap, there is correlation of U and As, missing in boreholes and suggesting formation of secondary uranium arsenate, in both granite types in polygon P1 (**Figure 4a**; in P2a, As was not analyzed).

Unlike U, no systematic shift of Th concentration was observed. Therefore, Th/U ratio increased during weathering of both granites (**Table 1b**). Thorium is concentrated predominantly in monazite whose Th/U ratio is higher than that of respective whole rock [19, 20, 30].

Au, Ag. Both elements have been systematically determined only in eluvia of P1 polygon. Nevertheless the high concentrations, especially of Au in Al-rich eluvia, cannot be explained by their high content in the original granite, and probably not only passive concentration during weathering but also supergene contamination was important [27]. In six samples from boreholes Mel-1 and Mel-2, the peak Au content (measured by ET-INAA) is 4.5 ppb (V. Procházka & J. Mizera, unpublished data), i.e., by 1–3 orders of magnitude lower than in eluvia of Melechov granite (**Figure 4b**).

REE, Y. REEs are generally little affected by weathering. However, the most weathered (high-Al) group of Lipnice granite shows some depletion in total REE, and evaluation of their mutual ratios revealed several trends. The comparison of variability of individual REEs in boreholes and in eluvia shows that the variation coefficient (the mean/standard deviation ratio) in weathered Melechov granite has a distinct minimum at Eu (**Table 2**). It follows that in weathered Melechov granite, the content of feldspars (the major reservoir of Eu^{2+}) in individual samples is more

stable than that of the main carriers of trivalent REEs, including Sm and Gd—monazite and apatite. The fact that similar situation is not observed in the Lipnice granite could be related to more intense weathering of feldspars and to more homogeneous distribution of monazite in the Lipnice type (in Melechov granite, the most of monazite is bound to large apatite crystals [19]).

In "fresh" Melechov granite of borehole Mel-2, the REE distribution including elevated Eu/Eu* ratio is very similar to weathered Melechov granite, the weathered granite having only somewhat higher total REE (**Figure 5b**). This shows that the effect of surface weathering on REE distribution of Melechov granite was very similar to the effect of former alteration processes, which were more intensive in Mel-2 than Mel-1. Note that the lower REE content in Melechov granite is associated with relatively greater analytical uncertainty.

To display subtle changes at a relatively low degree of weathering, we normalized REE in weathered samples by the average value of REE in boreholes (**Figure 5**).

The Y/Ho ratios of weathered granites seem to be somewhat elevated, which is however partly masked by vertical fractionation (**Figure 3c**).

In the Lipnice granite of outcrops (in P2a), there are relative minima of Ce and Pr, resembling the W type of tetrad effect. The appearance of only first tetrad can be related to REE distribution in apatite (see Section 4.2.). In more weathered samples (soil cap) of P2a, the minimum at Ce gradually disappears, and rather a positive cerium anomaly is formed. The W-type tetrad effect and positive Ce anomaly partially mask one another. It can be summarized that some portion of REE controlled by apatite (with M-type tetrad effect) was removed from weathered rocks, but Ce was partly immobilized by oxidation to Ce^{IV}.

The fact that fractionation of La, Ce, Pr, and Nd does not reflect the original granite inhomogeneity is documented by **Figure 6**.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
Lip bor. 5	0.05	0.04	0.04	0.05	0.05	0.06	0.07	0.09	0.07	0.06	0.08	0.09	0.13	0.11	0.10
Lip P2a	0.16	0.15	0.15	0.15	0.15	0.14	0.13	0.14	0.13	0.14	0.16	0.17	0.15	0.17	0.17
Mel bor. 1,2	0.12	0.11	0.10	0.13	0.12	0.10	0.13	0.12	0.13	0.10	0.13	0.12	0.28	0.13	0.20
Mel P1	0.20	0.20	0.20	0.21	0.21	0.14	0.22	0.22	0.22	0.20	0.19	0.19	0.22	0.19	0.22

Table 2.
Variation coefficients for individual REE and Y in fresh and weathered granites (bor. = borehole Mel-5 or Mel-1 and Mel-2).
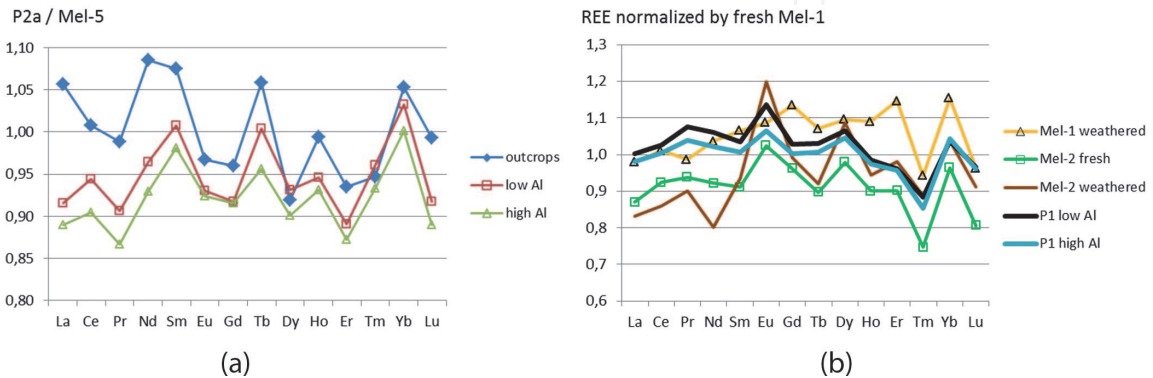

(a)

(b)

Figure 5.
(a) REE in Lipnice granite of soil base (divided into low-Al and high-Al groups) and small rock outcrops in polygon P2a, normalized by the mean of the borehole Mel-5. (b) REE in various groups of samples of Melechov granite normalized by the mean of fresh Melechov granite from borehole Mel-1.
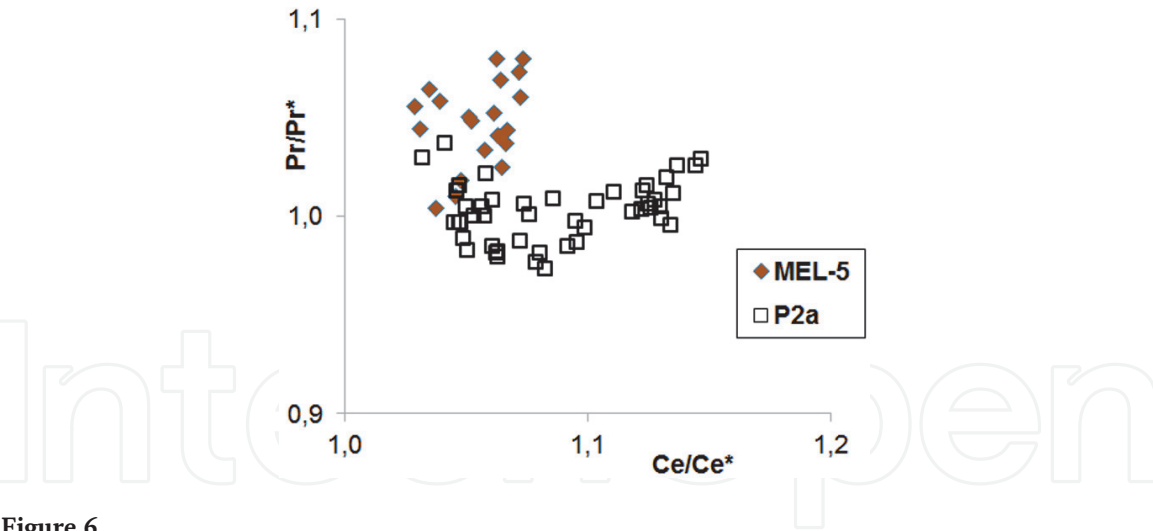
Figure 6.
Plot of cerium anomaly and Pr/Pr* (as a manifestation of the first tetrad) in the Lipnice granite in borehole Mel-5 and polygon P2a (soil cap). $Ce/Ce = 3Ce_N/(2La_N + Nd_N)$; $Pr/Pr* = 3Pr_N/(2Nd_N + La_N)$. Normalizing values from [32].*

Out of other REEs, the only systematic fractionation in weathered granites is a relative maximum of Yb (**Figure 5a** and **b**).

Other elements concentrated in monazite (Th), zircon (Zr, Hf), and (Fe-)Ti oxides (Nb, Ta) are not significantly affected by weathering, which is also true for Zr/Hf and Nb/Ta ratios. Therefore, it seems that dissolution of primary accessory minerals except for apatite was not significant for REE behavior during weathering. The locally observed alteration of monazite can be attributed to Ca-rich hydrothermal fluids [20].

	(a) Lipnice granite, Kopaniny (standardized to assumed Ca content 38 wt. %)												
An. no.	**1**	**2**	**3**	**4**	**5**	**8**	**9**	**10**	**14**	**15**	**16**	**Mean**	**St. dev.**
Sr	128	153	140	122	121	102	129	118	105	124	151	**127**	15
Y	2101	2755	2477	2182	2040	1979	2124	1959	2031	2470	1171	**2117**	367
La	384	486	473	431	330	378	373	399	405	484	222	**397**	70
Ce	1182	1633	1762	1661	1128	1363	1304	1500	1511	1461	842	**1395**	245
Pr	180	267	287	271	166	226	226	209	221	212	142	**219**	41
Nd	970	1353	1203	1352	815	1039	1132	890	956	1033	743	**1044**	183
Sm	376	475	391	475	318	367	417	350	347	386	233	**376**	63
Eu	9	10	9	10	9	8	10	7	7	9	12	**9**	1,5
Gd	310	525	372	502	368	440	420	316	345	396	262	**387**	74
Tb	48	89	66	65	58	70	63	47	61	58	41	**60**	12
Dy	351	605	516	412	378	475	393	330	422	449	294	**421**	81
Ho	67	98	103	79	73	82	74	64	74	80	61	**78**	12
Er	207	271	272	247	212	213	196	188	197	193	145	**213**	34
Tm	32	36	38	34	32	27	26	29	31	26	28	**31**	3,6
Yb	204	241	216	188	198	172	174	187	184	167	138	**188**	25
Lu	27	38	30	27	27	22	30	26	25	25	21	**27**	4,1
Th	21	16	9	9	23	20	25	10	15	10	19	**16**	5,3

(a) Lipnice granite, Kopaniny (standardized to assumed Ca content 38 wt. %)												
An. no.	1	2	3	4	5	8	9	10	14	15	16	Mean	St. dev.
U	39	63	72	79	54	52	41	43	64	54	34	**54**	13
Ca/Sr	2974	2489	2707	3117	3143	3720	2936	3220	3628	3055	2514	**3046**	361
Eu/Eu*	0.083	0.061	0.070	0.065	0.079	0.057	0.070	0.063	0.058	0.073	0.150	**0.075**	0.024
Ce/Ce*	1.08	1.08	1.13	1.14	1.15	1.10	1.06	1.24	1.20	1.09	1.11	**1.12**	0.05
Pr/Pr*	1.26	1.38	1.43	1.44	1.26	1.44	1.48	1.24	1.30	1.20	1.48	**1.36**	0.10
Y/Ho	31.1	28.0	24.0	27.6	28.1	24.2	28.9	30.8	27.6	30.8	19.2	**27**	3

(b) Melechov granite, Leštinka (standardized to assumed Ca content 35 wt. %)										
An. no.	1	2	3	4	5	6	7[**]	8	9	Mean	St. dev.
Sr	186	257	257	153	116	98	143	134	212	**177**	58
Y	252	202	207	1573	946	1740	1686	1876	747	**943**	662
La	201	345	271	242	236	220	536	195	283	**249**	46
Ce	385	766	594	655	603	738	1597	616	730	**636**	113
Pr	46	87	78	86	79	109	205	103	94	**85**	18
Nd	138	247	271	370	302	406	863	469	334	**317**	96
Sm	32	46	54	170	91	154	247	195	95	**105**	58
Eu	12.0	13.7	10.4	12.0	7.3	7.2	6.7	6.6	15.7	**11**	3.1
Gd	28	62	60	178	134	249	361	334	100	**143**	98
Tb	11	9	10	33	40	74	77	73	24	**34**	25
Dy	52	42	49	238	204	409	422	422	152	**196**	144
Ho	7	6	8	43	33	59	69	70	28	**32**	23
Er	13	16	13	94	81	143	142	131	62	**69**	49
Tm	1.7	2.5	1.5	13.4	11.1	17.3	15.6	14.3	7.4	**9**	5.8
Yb	16	19	6	68	65	119	104	82	51	**53**	36
Lu	1.2	0.6	1.2	9.7	7.2	11.4	12.6	8.7	6.2	**6**	4.0
Th	6.8	0.7	2.2	4.3	2.3	4.1	201	25.6	7.6	**7**	7.5
U	19	26	26	205	138	236	333	148	105	**113**	79
Ca/Sr	1881	1363	1363	2290	3020	3571	2447	2620	1648	**2220**	753
Eu/Eu*	1.208	0.786	0.553	0.211	0.202	0.113	0.068	0.079	0.492	**0.455**	0.366
Ce/Ce*	0.92	1.03	0.97	1.09	1.06	1.14	1.16	1.03	1.07	**1.04**	0.06
Pr/Pr*	1.03	1.10	1.07	1.05	1.10	1.30	1.09	1.16	1.14	**1.12**	0.08
Y/Ho	34.1	33.5	25.7	36.9	28.7	29.4	24.5	26.8	27.1	**30.3**	3.8

[**]*Analyzed spot influenced by monazite (not included in the statistics).*
$Eu/Eu^* = 2Eu_N/(Sm_N + Gd_N)$.
$Ce/Ce^* = 3Ce_N/(2La_N + Nd_N)$.
$Pr/Pr^* = 3Pr_N/(2Nd_N + La_N)$.
Normalizing bulk Earth values from [32].

Table 3.
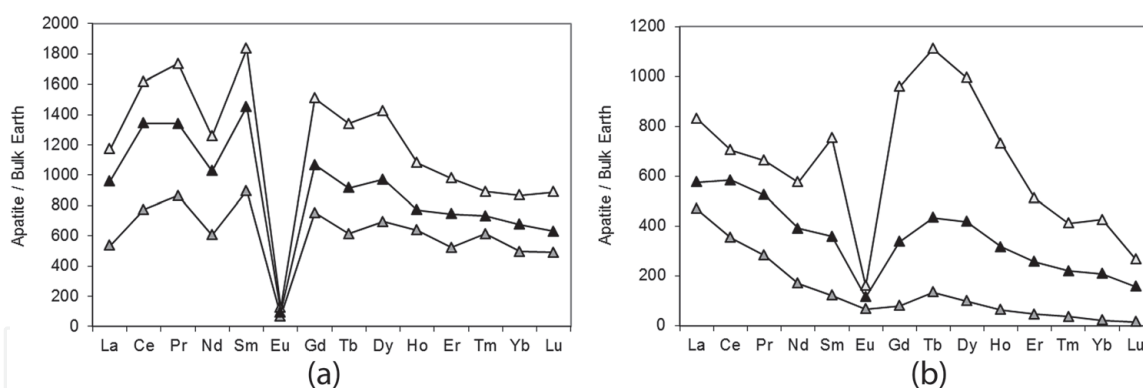*LA-ICP-MS spot analyses of apatite (elements in ppm).*

Figure 7.
Bulk Earth normalized [32] REE in apatite (minimum, maximum, and median) as determined by LA-ICP-MS in polished sections of rocks: (a) Lipnice granite, Dolní Město—Kopaniny. (b) Melechov granite, Leštinka.

4.2 REE distribution in apatite

The analyzed trace elements indicate that apatite is a relevant carrier of Y and HREE; however its contribution to whole-rock LREE budget cannot be neglected as well. Results of apatite LA-ICP-MS analyses in polished sections (**Table 3**) are consistent with ICP-MS solution analyses (see [20, 30]). The negative europium anomaly in apatite is deeper than that one in the whole rock. The apatite of Lipnice granite is characterized by strong M-type tetrad effect, forming the first tetrad (whose magnitude is proportional to Pr/Pr* and, in the absence of cerium anomaly, also to Ce/Ce* values) and probably second tetrad (**Table 3a**, **Figure 7a**).

In apatite of Melechov granite (as well as of Kouty and Stvořidla granites), the tetrad effect was already documented before [20]. However, the first tetrad from solution analyses is weak and incomparable to that of apatite in Lipnice type. This is partly due to greater portion of altered and secondary apatite, which does not show tetrad effect (e.g., spot 1 in **Table 3b**). The most spot analyses of apatite in Melechov granite (**Table 3b**, **Figure 7b**) show probably the first three tetrads which, however, are weak.

5. Discussion

5.1 Alteration of primary minerals by chemical weathering

The overall rate of Ca release from the rock is higher than that one of Na, because a large part of the Na budget is relatively better fixed as albite lamellae in perthitic K-feldspar, which is more resistant to weathering than plagioclase; a minor influence of apatite (and perhaps calcite) is possible as well.

Strontium is probably—in contrast to calcium—concentrated in K-feldspar too (see also [33]). This would explain why Ca/Sr ratio decreases at weathering (**Table 1b**). Also note that the Ca/Sr ratio in springwater (~130 at Lipnice granite and ~200 at Melechov granite; **Table 4a**) is significantly higher than in the rocks. White [34] suggested that at the initial stages of weathering, Ca and Sr are released mainly from accessory calcite. According to [35], both calcite and apatite are important sources of Sr in the very early stages of weathering. The loss of Ba and Na shows that the simplest explanation—leaching of Ca and Sr from plagioclase and K-feldspar—is the most likely. Nevertheless the decrease of P_2O_5 in the most weathered samples suggests that apatite contributes to the release of Ca, too. The Sr abundance in apatite is in the range ca. 100–250 ppm (**Table 3**), and so the Ca/Sr ratio of apatite

(a) Statistics of major ions and pH in springs on Melechov and Lipnice granites sampled within the frame of the PADAMOT project [36]; if values below detection limit represented less than half of analyses, they were replaced by 1/2 detection limit						
Substrate rock type		Melechov in the forest (n = 17)		Melechov others (n = 8)		Lipnice (n = 4)
	Unit	Mean	Median	Mean	Median	Mean	Median
Na^+	mg/l	8.86	9.16	11.41	10.57	8.01	7.67
Mg^{2+}	mg/l	2.97	2.87	4.44	4.81	3.15	2.87
Al	mg/l	0.22	0.2	0.04	0.1	0.1	0.1
K^+	mg/l	1.39	1.38	11.24	5.72	1.63	1.55
Ca^{2+}	mg/l	14.9	13.5	24.9	26	11.9	10.4
Mn^{2+}	μg/l	89.3	25	34.8	9.5	4.4	5
Zn^{2+}	μg/l	41.3	35	18.5	17	9	10
Sr	μg/l	77.8	72.4	117.7	134.6	92.3	81.2
$(NO_3)^-$	mg/l	5.68	2.04	24.8	22.9	20	11.3
F^-	mg/l	0.28	0.19	0.1	0.08	0.08	0.08
$(SO_4)^{2-}$	mg/l	57.6	57.4	47.6	49.8	21.5	22.7
Cl^-	mg/l	2.43	2.21	13	12.5	6.39	4.74
pH		5.32	6.08	6.98	7.04	7.04	7.14
Ca/Sr		192	186	212	193	129	128

(b) Chemistry of springs (all components in mg/l) sampled by L. Rukavičková and co-workers in 2004 within the frame of the RAWRA project; for comparison the discharge of catchment Loukov [16, 44]; values in italics represent 1/2 of detection limit

Object, date	Method	Na$^+$	Mg^{2+}	Al	K$^+$	Ca^{2+}	(NO$_3$)$^-$	F$^-$	(SO$_4$)$^{2-}$	Cl$^-$	SiO$_2$	pH
		FAAS	FAAS	FAAS	FAAS	FAAS	HPLC	ISE	HPLC	HPLC	FAAS	ISE
Springs on Lipnice granite (n = 5) 27.5. / 22.6.2004	Mean	10.0	4.5	0.20	1.8	17.0	23.2	0.18	48.6	7.1	19.3	6.3
	Median	9.7	4.3	0.20	1.7	18.0	21.0	0.15	40.6	6.6	19.4	6.2
Springs on Melechov granite (n = 24) 27.5. / 22.6.2004	Mean	8.1	2.8	0.42	1.6	14.0	3.4	0.25	56.7	2.7	17.9	5.43
	Median	8.4	2.9	0.27	1.4	14.3	2.3	0.21	57.9	2.3	18.1	5.86
Catchment discharge 1.6.2004		9.8	3.2	0.24	0.5	13.9	*0.15*	0.26	62.7	2.0		5.11
Catchment discharge X.1994–X.2014 (weighed average, monthly sampling)		8.9	3.2	0.36	0.82	13.1	0.29	0.21	59.4	2.1	21.1	5.06

FAAS, flame atomic absorption spectrometry; PMT, photometry; HPLC, high-performance liquid chromatography; ISE, ion-selective electrode.

Table 4.
Springs on Melechov and Lipnice granites sampled within the frame of the (a) PADAMOT project and (b) RAWRA project.

is by 2–3 orders of magnitude higher than that of the whole rock. Thus, apatite weathering can contribute to the lower Ca/Sr ratio in the eluvium as well.

The slight depletion of Lipnice granite in K also indicates some weathering of K-feldspar, because Rb and Cs, concentrated in micas relatively stronger than K (see also analyses of separated micas [37]), are not depleted. However the possibility of selective Rb and Cs concentration (including adsorption) by secondary phases like vermiculite has to be also kept in mind [38–40]. Note that a considerable amount of vermiculite (with minor chlorite) has been proven in concentrates of biotite from eluvia of Lipnice granite [25].

Weathering of feldspars and biotite could also explain the Al/Ga fractionation. It seems that Ga was preferentially removed (in comparison with Al), as documented in the literature [41, 42], but in some places especially in Lipnice granite, it reconcentrated in the eluvium. Ga can be scavenged by Fe-oxyhydroxides [43], as indicated by positive correlation with Fe in P2a.

5.2 Stream water chemistry

Chemical composition of surface water has been systematically monitored in a small catchment Loukov starting with hydrological year 1995. This catchment drains Melechov granite at the eastern slope of Melechov hill. More than 95% is covered by spruce forest [44]. It has been shown [26] that recent mass balance of the catchment explains very poorly the chemical differences between fresh and weathered Melechov granites (especially the behavior of sodium, which is significantly removed in the discharge but not depleted in weathered rock).

Occasionally springs were analyzed at various granite types. The data show that differences between waters draining Lipnice and Melechov granite types are mainly in anions (usually higher sulfate and lower nitrate and chloride in springs on Melechov type), and they can be largely explained by different land use. Sampled springs on Lipnice granite are prevalently in agricultural area, whereas Melechov granite is largely covered by forest, which also enhances atmospheric deposition of sulfur (peaking in the last quarter of the twentieth century). The surface water draining Melechov granite is usually more acidic, and from that reason (as evidenced by negative correlation with pH), it has higher content of Mn, Al, and Zn than springs on Lipnice granite. Obviously the differences in water chemistry cannot explain the different behavior of Ca, Na, and Sr during weathering of Lipnice and Melechov granites because in such case, the content of these cations should be higher in water draining the Lipnice granite. Similarly, concentration of SiO_2 which is depleted mainly in weathered Melechov granite is comparable in discharge from both granite types. On the other hand, the water chemistry data indicate that removal of elements in discharge could explain quite well the observed weathering of Lipnice granite.

Recent accumulation of P and K in the catchment was documented [16]. While some enrichment of the weathered Melechov granite in P is possible (see **Table 1**, **Figure 2**), we should keep in mind that strong retention of both elements can be a short-time phenomenon caused by deposition of dust from agricultural areas and by accumulation of nutrients in biomass (see also [26]) whose volume was increasing during the monitoring period (F. Oulehle, pers.commun.).

For a representative composition of surface water, see **Table 4a** and **b**.

5.3 Erosion and mechanical transport

It was concluded that erosion of a quartz-rich skeleton in the upper part of the weathering profile influenced significantly the present mineral and chemical

composition [26, 27]. The Al-rich and Si-poor eluvia represent original lower horizon or domains, relatively depleted in quartz due to enrichment in small grains of weathered and secondary minerals. As indicated by Pb isotope evolution of fracture fillings in granite from borehole PDM-1 (close to Mel-3 and Mel-4), as early as in the Early Cretaceous, there was significant supergene redistribution of U and/or Pb [5, 6]. This event corresponds to the erosion of rocks immediately overlying the granites of Melechov Massif.

Solid-phase physical separation may also explain the question why elements contained in the most chemically resistant minerals (Zr, Hf, Nb, Ta, Th, partly REE; see also [45]) were not passively concentrated in weathered rocks (in case of Nb and Ta even slight depletion cannot be excluded). Also Zr/Hf and Nb/Ta ratios are unaffected. Observations of the relevant accessory minerals (zircon, monazite, rutile, ilmenite) in heavy-mineral concentrates from eluvia showed very weak influence of chemical weathering [21, 25]. However, a significant portion of these minerals in the rock forms very small grains—down to a few μm (zircon and monazite in Melechov type). These very small grains, unless included in other minerals, were easily transported by gravity and water flow away and partly to open fractures deeper in the granite [5, 6].

5.4 Origin of the REE fractionation

The lanthanide tetrad effect in granites and other felsic melts, including experimental ones, has been documented and discussed in numerous publications (e.g., [46–48]). Regarding the tetrad effect in apatite, one possibility is fractionation of monazite (± xenotime), which would produce a pattern similar to M-type tetrad effect in the coexisting melt [49, 50]; see also [51]. In monazite within granites of Melechov massif, no fractionation similar to tetrad effect is apparent in EMP data [17, 19]. Nevertheless if monazite crystallized close to apatite, which is true especially in the Melechov granite but partly in the Lipnice granite as well [19], the light REE in apatite would be modified even in the case of only weak tetrad effect in monazite. The difference between apatite composition of Lipnice and Melechov types can be related to the several times higher abundance of monazite in the Lipnice granite. As documented by [48, 52], another important factor can be fluorine content, which is higher in the Lipnice granite as well.

REE fractionation seems to support a hypothesis of formation of P-rich domains in the melt, where monazite and apatite could have influenced one another much more than the remaining melt. Formation of such domains is also supported by conclusions of [19].

As shown by [49], the tetrad effect-like pattern of trivalent REE produced by monazite and xenotime fractionation is more complex. Another important feature is the peak of Yb in the residual melt. Similar Yb peak is observed in weathered Lipnice and Melechov granites (and in altered Melechov granite), when normalized by fresh rocks (**Figure 5**).

Despite the fact that many details of REE fractionation are unanswered, we can sum up that magmatic crystallization of phosphates, possibly with an important role of fluorine, produced complicated REE fractionation among rock-forming minerals, which can be insignificant in whole-rock chondrite-normalized patterns, but it can be enhanced by weathering processes.

Dissolution of apatite whose Y/Ho ratio (**Table 3**) is generally slightly lower than that of whole rock (**Table 1b**) could also lead to slightly elevated Y/Ho ratios of weathered granites (see **Figure 3c**).

6. Conclusions

A unique dataset from the Lipnice and Melechov granites showed that whole-rock analyses of the fresh rock and eluvium combined with the knowledge of element's abundance in primary minerals are a very effective tool for the reconstruction of granite weathering. Combination with borehole data helps to interpret large medium- to small-scale inhomogeneity of weathering processes.

Both granites are depleted in several elements concentrated mainly in biotite: Mg, Ti, Mn (mainly the Lipnice type), and the Melechov type in Fe and V, too. Content of elements concentrated in plagioclase, apatite, and partly K-feldspar (Ca, Na, Sr, P, Ba) decreased in weathered Lipnice granite, but not in Melechov granite. The main factor causing these differences is that superficial chemical weathering of the relatively coarse-grained and permeable Melechov granite was weaker than in Lipnice granite. In addition, the influence of chemical weathering (e.g., on Fe content and REE distribution) could be similar to subsolidus alterations, which had been more intense in the Melechov type. However, in some cases, like carbonatization or U enrichment, the effect of subsolidus alteration is opposite to weathering. In the Lipnice type, especially in the homogeneous P2a polygon (with borehole Mel-5), we were also able to distinguish formation of positive cerium anomaly at weathering and trace the role of secondary phases (Fe-oxyhydroxides, vermiculite) in retention of some elements (Ga). The first stage of Lipnice granite weathering in P2a is characterized mainly by alteration of biotite, not lowering SiO_2 content.

The natural solid-phase separation led to relative depletion of the sampled eluvia in quartz (especially in the Melechov granite) and prevented the most resistant accessory minerals (e.g., zircon) to be passively concentrated in the eluvia. The petrologically important Zr/Hf and Nb/Ta ratios are not significantly affected. Contamination of eluvia by material from quartz veins and other sources led to their enrichment in Au and Ag. A thorough examination of mutual ratios of REE and Y revealed also some influence of apatite dissolution.

The loss of U was significant in both granite types, but more intense in the Melechov type where larger portion of U was allocated to unstable phases or only adsorbed. Gallium was passively concentrated in eluvia of both granites, however stronger in the Lipnice type, possibly thanks to better retention of Fe-oxyhydroxides.

Assessment of weathering behavior of several elements (W, Sn, Co, partly Mg) is complicated by their spatial inhomogeneity in the intrusions, indicated by vertical differentiation in boreholes. In case of strongly incompatible W, we are able to distinguish this vertical trend from obvious removal of W by weathering of the Melechov granite.

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