

Lithium and trace-element concentrations in trioctahedral micas from granites of different geochemical types measured via laser ablation ICP-MS

KAREL BREITER^{1,*}, MICHAELA VAŇKOVÁ², MICHAELA VAŠINOVÁ GALIOVÁ^{2,3}, ZUZANA KORBELOVÁ¹ AND VIKTOR KANICKÝ^{2,3}

¹ Institute of Geology of the Czech Academy of Science, Rozvojová 269, Praha 5 CZ-165 00, Czech Republic

² Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno CZ-611 37, Czech Republic

³ Central European Institute of Technology (CEITEC), Masaryk University, Kamenice 5, Brno CZ-625 00, Czech Republic

[Received 22 October 2015; Accepted 14 July 2016; Associate Editor: Linda Campbell]

ABSTRACT

The compositions of trioctahedral micas from 51 samples of granitoids with different geochemical affiliations and grades of differentiation from the Bohemian Massif, Central Europe, were analysed using electron microprobe (major elements) and laser ablation inductively coupled plasma mass spectrometry (Li, Sc, Ga, Ge, Nb, In, Sn, Cs, Ta, W, Tl). The micas form a continuous evolutionary series from phlogopite to zinnwaldite. The phlogopites and biotites from the I-type rocks are characterized by 5.5–5.7 Si, 2.4–2.6 Al, <0.1 Li atoms per formula unit [apfu] and $Mg/(Mg + Fe) = 0.4–0.8$. The biotites from the S-type granites usually contain 5.3–5.7 Si, 3.2–3.6 Al, 0.1–0.3 Li apfu and $Mg/(Mg + Fe) = 0.15–0.4$. The annites and zinnwaldites from the rare-metal granites contain 5.7–6.8 Si, 3.2–3.8 Al, 0.6–2.6 Li apfu and $Mg/(Mg + Fe) < 0.1$. The concentrations of F, Rb, Cs and Tl increase from the phlogopites and biotites to zinnwaldites: F 0.1 → 8 wt.%, Rb_2O 0.05 → 1.7 wt.%, Tl 2 → 50 ppm and Cs 40 → 2000 ppm. The concentrations of Sn, Nb, Ta and W in phlogopites and biotites from the I- and S-type granitoids generally correlate with those of the parent rocks and reach values of (in ppm) 20–100 Sn, 20–250 Nb, 1–20 Ta and <5 W. The highest concentrations were found in the Li-annites in the relatively early facies of rare-metal granites (in ppm): 250–600 Sn, 400–600 Nb, 60–120 Ta and 50–120 W. The zinnwaldites in the late rare-metal granites facies are impoverished in these elements, which is explained by contemporaneous crystallization of cassiterite and columbite. Lithium enters the crystal lattice of trioctahedral micas via the exchange vector $Li_3\Box Si_3Fe_{-6}Al_{-1}$ up to concentrations of ~2.5 wt.% Li_2O (1.5 apfu Li). At higher Li concentrations, Li is incorporated through the exchange vector $Li_3Si_1\Box_{-1}Fe_{-2}Al_{-1}$.

KEYWORDS: trioctahedral micas, Li-mica, rare-metal granite, Bohemian Massif, laser ablation inductively coupled plasma mass spectrometry.

Introduction

TRIOCTAHEDRAL micas are the most common hydrous Fe- and Mg-bearing silicates in granites, granodiorites and granitic pegmatites. Due to their flexible crystal lattice, trioctahedral micas are also important carriers

of many minor and trace elements, including F, Li, Rb, Cs, Sn, Nb, Ta, etc. Therefore, unsurprisingly, the literature on mica is extensive and focuses on different aspects of the chemical and physical properties of micas and their geological interpretations. The following section discusses the most important publications addressing Li-enriched micas.

The first modern classification of Li-bearing micas was compiled by Foster (1960). The current valid classification of micas resulted from a

*E-mail: breiter@gli.cas.cz

<https://doi.org/10.1180/minmag.2016.080.137>

long-lasting discussion (Rieder *et al.*, 1999), although slightly different opinions were published by Tischendorf *et al.* (1997, 1999, 2004) and Rieder (2001). The physical properties and crystal structure of micas have been studied by Rieder (1970), Černý *et al.* (1995), Shihua and Jie (1999) and Brigatti *et al.* (2000, 2003). Speer (1984) and Förster and Tischendorf (1989) used micas to estimate the volatile contents in magmas. The compositions of micas from granites, including minor and trace elements, were studied by Stone *et al.* (1988), Henderson *et al.* (1989), du Bray (1994), Van Lichtenvelde *et al.* (2008), Li *et al.* (2015) and Xie *et al.* (2015). A comprehensive overview of this topic was compiled by Tischendorf *et al.* (2001). The compositions of micas from pegmatites (in this case, primarily the muscovite–lepidolite series) were published by Černý and Burt (1984), Černý *et al.* (1995, 2003), Wise (1995), Ford *et al.* (1995), Roda *et al.* (1995) and Roda-Robles *et al.* (2012). The partition coefficients for F, Cl, Rb, Cs and high-field-strength elements between biotite and leucocratic melt were studied by Bea *et al.* (1994) and by Icenhower and London (1995, 1997). The effects of alteration and ore-bearing processes on mica composition has been studied mainly by Charoy *et al.* (1995), Johan *et al.* (2012), Petřík *et al.* (2014), Li *et al.* (2015) and Xie *et al.* (2015). Tindle and Webb (1990) and Tischendorf *et al.* (1997) proposed equations to estimate Li concentrations in mica, which cannot be determined via electron microprobe analysis (EMPA), on the basis of measured concentrations of Si or F. An overview of the current understanding of micas was published in two volumes of *Reviews in Mineralogy & Geochemistry*, edited by Bailey (1984) and Mottana *et al.* (2002).

Contrary to the huge amounts of mica-related literature, papers with large data sets of analyses of granitic and/or pegmatitic micas (i.e. major elements, Li and trace elements) measured using *in situ* analytical methods with sufficient sensitivity and accuracy are surprisingly sparse: These papers are effectively limited to Van Lichtenvelde *et al.* (2008), Roda-Robles *et al.* (2012) and Xie *et al.* (2015). Other authors have published analyses of major and some trace elements but did not measure Li, which was only computed (Johan *et al.*, 2012; Li *et al.*, 2015).

Currently, no synoptic studies on the Li and trace-element compositions of trioctahedral micas from granites of different geochemical types and grades of differentiation have been performed. Thus, we decided to use a combination of electron microprobe

and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) methods to analyse representative samples of trioctahedral micas from different plutons within the Bohemian Massif in Central Europe. The major goals of this study are to: (1) compile a representative data set of compositions of trioctahedral micas from different types of granitoids; (2) determine if chemical differences occur between micas from I-, S- and A-type magmas; and (3) describe the evolutionary trends in mica composition during magma differentiation.

Geological setting and samples investigated

Several contrasting types of granitoid plutons of Variscan age (c. 370–310 Ma, Cháb *et al.*, 2010) occur within the Bohemian Massif. The selected complexes of granitic rocks (plutons) include the major types of magmas that intruded during the Variscan orogeny throughout Europe. Certain plutons comprise suites of intrusions that differ in their degree of differentiation, e.g. in their concentrations of major and trace elements. Therefore, the samples studied herein combine differences resulting from the parental magma compositions and the variations caused by melt fractionation, mixing and other processes. Trioctahedral micas from the following representative Variscan granitoid plutons in the Bohemian Massif were collected for this study (Fig. 1, Supplementary file 1 which has been deposited with the Principal Editor of Mineralogical Magazine and is available from http://www.minersoc.org/pages/e_journals/dep_mat_mm.html)

Central Bohemian Pluton

The Central Bohemian Pluton, situated in the south-central part of the Czech Republic, is a composite pluton, comprising intrusive suites of different geochemical types (354–336 Ma, Holub *et al.*, 1997; Janoušek *et al.*, 2000; Janoušek and Skála, 2011). The most important suites are as follows: (1) the calc-alkaline Sázava suite – mostly metaluminous amphibole-biotite tonalites and quartz diorites to biotite trondhjemites and granodiorites with associated basic rocks; (2) the high-K calc-alkaline Blatná suite – biotite ± amphibole granodiorites and granites and associated shoshonitic basic rocks; (3) a highly K- and Mg-enriched Čertovo Břemeno suite containing porphyritic amphibole-biotite melasyenites and melagranites (durbachites), biotite-two-pyroxene melasyenites, and associated K- and Mg-rich

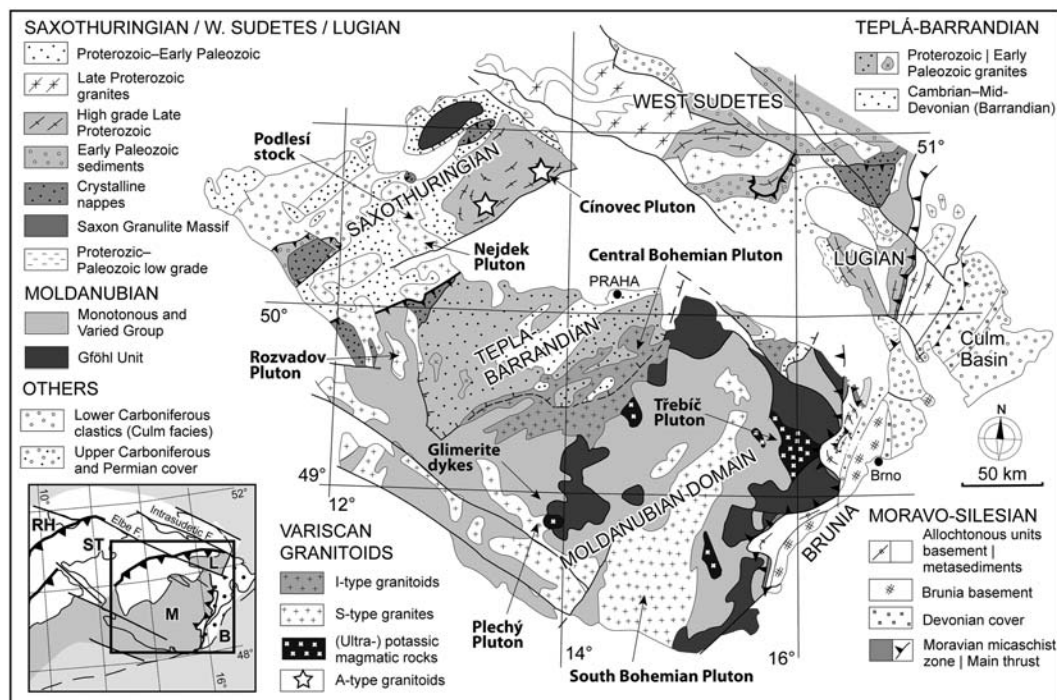


FIG. 1. Schematic map of the Bohemian Massif and the studied Variscan granitoids (modified after Lexa *et al.* (2011)). CBP, Central Bohemian Pluton; CMP, Central Moldanubian Pluton. Inset bottom left shows the position of the Bohemian Massif in the European Variscides. RH, Rhenohercynian Unit; ST, Saxothuringian Unit; M, Moldanubian Unit; B, Brunia Continent; L, Lugian domain.

(amphibole)-biotite granites; and (4) the peraluminous Říčany suite – biotite ($\pm$ muscovite) granites. The Sázava suite is presumed to represent the mixing of CHUR-like [chondrite uniform reservoir] mantle (subduction-modified) magmas with melts of local metabasic crust (Janoušek *et al.*, 2000). In contrast, the crustal sources for the magmas associated with the Blatná suite were probably immature greywackes rich in Neoproterozoic or Upper Cambrian–Lower Ordovician volcanogenic detritus. The high-K and -Mg melagranitoids (durbachites) are suggested to be the products of the melting of metasomatized upper mantle and their interaction with the crustally derived leucogranitic melts, while the Říčany suite was formed by partial melting of mature Moldanubian metasedimentary rocks (Janoušek and Skála, 2011). Five samples (Nos. 4849, 4845, 4846, 4847 and 4850; Supplementary file 1 deposited at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html) were selected for analysis and represent the four individual suites mentioned above.

South Bohemian Pluton

The South Bohemian Pluton is a complex of Variscan peraluminous granites in southern Bohemia and northern Austria (330–315 Ma). The pluton is composed of several composite bodies, the largest of which are the Central Massif in the SE (Breiter and Koller, 1999) and the Plechý Massif in the SW (Breiter *et al.*, 2007). Petrographically, the pluton comprises slightly deformed biotite > muscovite granites of Lipnice type, slightly deformed two-mica granites of Lásenice type, undeformed two-mica granites (Mrákotín, Čiměř and Aalfang types), younger fractionated two-mica granites (Eisgarn type s.s. according to Waldmann, 1950) and topaz-muscovite granites enriched in Na, P, F, Rb, Sn and Nb. All these rocks are products of voluminous melting of the surrounding Moldanubian basement during and shortly after the thermal peak of the Variscan orogeny (Gerdes *et al.*, 1998). Muscovite is interpreted in all the investigated granites as a primary magmatic mineral (Breiter and Koller, 1999), in the deformed facies slightly replaced by sillimanite.

Four selected samples from two-mica granites of Aalfang and Eisgarn s.s. types (#2777, 2949, 2954 and 2962) represent the evolution of comagmatic intrusions in the main body of the pluton in northernmost Austria and adjacent southern Bohemia (328–327 Ma, Gerdes *et al.*, 2003). Additional samples (#4362, 4363 and 4365) represent the two-mica granites from the Plechý Pluton on the Austrian-Bavarian-Czech border (328–321 Ma, Siebel *et al.*, 2008).

Třebíč Pluton

Melanocratic K- and Mg-enriched granitoids (durbachites) represent one of the most typical features of the European Variscan orogeny. The Třebíč Pluton is the largest (160 km², Holub, 1997) of the several durbachitic intrusions in the Moldanubian unit of the Bohemian Massif. Two samples (#4588 and 4592) represent the amphibole-biotite melasyenite (342 Ma, Kusiak *et al.*, 2010), the most typical rock of the whole durbachitic series.

Rozvadov Pluton

The Rozvadov Pluton, situated on the Czech-Bavarian border, consists of four types of strongly peraluminous S-type granitoids (302–312 Ma, Siebel *et al.*, 1999): (1) coarse-grained cordierite-biotite tonalite; (2) fine-grained two-mica granite of the Rozvadov type; (3) coarse-grained two-mica granite of the Barnau type; and (4) highly fractionated F-, Li-, Rb- and Sn-enriched fine-grained albite-zinnwaldite topaz granite of the Křížový Kámen/Kreuzstein type. These rock types resulted from the anatexis of the surrounding Moldanubian paragneisses and metapelites (Siebel *et al.*, 1999). Four samples from the different granite types were selected (#4851, 4852, 4853 and 4854). The sampled pluton represents the geographical and lithological transition between plutons of common two-mica granites in Moldanubicum and plutons of rare-metal granites in the Erzgebirge.

Nejdek Pluton

The Nejdek Pluton, including the late highly fractionated Podlesí stock, is the most typical example of a strongly peraluminous rare-metal granite pluton in the western Krušné Hory/Erzgebirge area (329–320 Ma, Breiter *et al.*, 1999; Förster *et al.*, 1999; Tichomirowa and Leonhardt, 2010). This pluton is composed of an

older intrusive suite represented by biotite granites and a younger intrusive suite of albite-annite granites with topaz. The most fractionated, extremely F- and P-rich batches of residual magma crystallized at Podlesí as albite-zinnwaldite-topaz granite in the form of layered rock with comb-quartz layers (Breiter *et al.*, 2005). Two samples (#4742 and 4743) represent the biotite granites of the older complex, four samples (#4744, 4745, 3475 and 3490) represent the younger albite-annite granites and five samples (#3458, 3740, 4012, 4706 and 4746) represent different facies of the Podlesí stock.

Anorogenic granites from the eastern Erzgebirge

The late Variscan A-type volcano-plutonic complex of the eastern Erzgebirge (Altenberg-Teplička caldera) consists of the comagmatic slightly peraluminous 'Teplička rhyolite' (309 Ma, Hoffmann *et al.*, 2013) and the slightly younger rare metal granites of the Činovec/Zinnwald pluton (Breiter, 2012). The 1596-m-deep borehole CS-1 drilled in 1960–1963 (Štemprok and Šulcek, 1969) provides a unique opportunity to study the vertical differentiation of a rare-metal granite intrusion. Nineteen samples were collected from this borehole; they represent, from top to bottom, the greisenized granite and greisen (#4685, 4930, 4931 and 4975), albite-zinnwaldite granite (#4677, 4683, 4687, 4688, 4689, 4690, 4691, 4936, 4937 and 4938) and Li-annite granite (#4692, 4693, 4940, 4941 and 4942).

Glimerite

Several dykes of extremely Mg-rich rock composed of plagioclase and phlogopite with only subordinate K-feldspar and quartz crosscut the Moldanubian crystalline rocks near the town of Prachatic, southern Bohemia (Breiter and Koller, 2009). Two samples (#4340 and 4343) were analysed as examples of mica crystallized from ultramafic magma.

Methods

The trace elements in the micas were analysed at the Laboratory of Atomic Spectrochemistry (LAS), Department of Chemistry, Faculty of Science, Masaryk University. A pulsed Nd:YAG-based laser ablation system UP 213 (New Wave Research, Inc., Fremont, CA, USA) operating at 213 nm and

equipped with a SuperCell was used for sampling. The ablation-generated aerosol was transported using helium carrier gas (1 L min^{-1} He) via 1-m-long polyurethane tubing with an internal diameter of 4 mm into the ICP source of the quadrupole-based mass spectrometer Agilent 7500ce (Agilent Technologies, Santa Clara, CA, USA). The He carrier gas was mixed with argon make-up gas via a Y-connector prior to the ICP. To minimize potential polyatomic interferences, a collision-reaction cell in He mode (1 mL min^{-1}) was used.

Time-resolved signals for the following isotopes were recorded: $^7\text{Li}^+$, $^{27}\text{Al}^+$ and $^{28}\text{Si}^+$ as matrix elements, and $^{45}\text{Sc}^+$, $^{69}\text{Ga}^+$, $^{72}\text{Ge}^+$, $^{93}\text{Nb}^+$, $^{115}\text{In}^+$, $^{118}\text{Sn}^+$, $^{133}\text{Cs}^+$, $^{181}\text{Ta}^+$, $^{182}\text{W}^+$ and $^{205}\text{Tl}^+$ as trace elements. An integration time of 0.1 s was used except for Ge (0.5 s) and In (0.7 s). Both the laser beam spot diameter (from 30 to 100 μm) and fluence (in the range of 3–15 J cm^{-2}) were optimized. The mineral grain size and signal stability were crucial parameters for selection of fluence and spot diameter. A fluence of 13 J cm^{-2} was found to be optimal, and a spot diameter of 80 μm and a repetition rate of 10 Hz were fixed. Each spot analysis incorporates ~ 30 s of background (Ar-He gas blank) followed by 30 s of data acquisition from the sample.

The elemental compositions of the mica samples studied were calibrated using three artificial reference materials: NIST SRM 612, NIST SRM 610 and BCR 2G. The calibration results were compared to determine the optimum calibration standard. Concentrations were calculated from the background-corrected peak areas. Differences in the ablation rates between the reference materials and the samples were compensated for by using Si as the internal reference element (IS). The Si concentrations were determined using an electron microprobe prior to the LA-ICP-MS analysis. Finally, the analyses were calibrated using NIST SRM 612 and NIST SRM 610. The operating conditions were optimized to achieve acceptable detection limits. The detection limits were calculated as three times the standard deviation of the background divided by the sensitivity (defined as the isotope intensity to elemental content ratio). The average detection limits under the operating conditions were as follows: 1.8 ppm Li; 1.5 ppm Al; 170 ppm Si; 0.70 ppm Sc; 0.18 ppm Ga; 1.0 ppm Ge; 0.08 ppm Nb; 0.04 ppm In; 2.1 ppm Sn; 0.15 ppm Cs; 0.08 ppm Ta; 0.21 ppm W and 0.41 ppm Tl.

The major elements in the micas were analysed using a CAMECA SX100 electron microprobe housed in the Institute of Geology of the Czech

Academy of Science, Prague. We used an accelerating voltage of 15 kV, a beam current of 10 nA and a beam diameter of 2 μm . The following standards were used: Na, Al – jadeite; Mg, Si, Ca – diopside; K – leucite; Ti – rutile; P – apatite; Mn – MnCr_2O_4 ; Fe – magnetite; F – fluorite, Rb – RbCl.

The whole-rock (WR) major element oxide analyses (wet technique) were performed at the Czech Geological Survey, Prague. Replicate analyses of international reference material (JG-3 granodiorite; Geological Survey of Japan) yielded an average error (1σ) of $\pm 1\%$ with respect to the recommended values (Govindaraju, 1994). The precision and accuracy of the Li_2O determinations (detection limit: 0.001 wt.%) via flame spectrophotometer were $\pm 1\%$ and $\pm 2\%$, respectively. The trace elements (Rb, Cs, Nb, Ta, Sn, W and Sc) were determined by ICP mass spectrometry following a lithium metaborate/tetraborate fusion and nitric acid digestion of a 0.2 g sample in the laboratory of ACME, Vancouver, Canada. (Details can be found at <http://acmelab.com/>)

The compositions of the micas were recalculated to the proposed structural formulae on the basis of 44 negative charges. The water content (OH^-) and trivalent iron content were not calculated due to the large uncertainties of such calculations for Li-rich micas.

Terminological remark: According to the IMA rules, only so-called ‘end member’ mineral names are valid. The actual nomenclature of micas (Rieder *et al.*, 1999) is based on this rule. Nevertheless, in the case of rock-forming minerals important for igneous rock classification, such as feldspars, amphiboles and micas, practical petrology typically uses more detailed mineral classifications. Therefore, in this article, we use the traditional name biotite for dark micas with $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios of 0.15–0.60 and the name zinnwaldite (Haidinger, 1845; Rieder *et al.*, 1996) for Li-rich micas that are close to the intersection of the siderophyllite–polyolithionite and the annite–trilithionite join with preferred formula $\text{K}_2\text{Li}_2\text{Fe}_2\text{Al}_2(\text{Al}_2\text{Si}_6\text{O}_{20})\text{F}_4$ (Fig. 2). Micas close to this composition are common not only in the rare-metal granites and greisens in the Erzgebirge but also in Sn- and W-bearing granites worldwide (Stone *et al.*, 1988; du Bray, 1994). This approach allows us to use only one mineral name for mica in a particular granite type (pluton). (Note that German authors (Tischendorf *et al.*, 1997, 1999, 2001; Förster *et al.*, 1999) commonly use the name siderophyllite for the most common type of mica in the Nejdek Pluton. According to IMA rules, this mica should be termed annite or Li-annite.) To

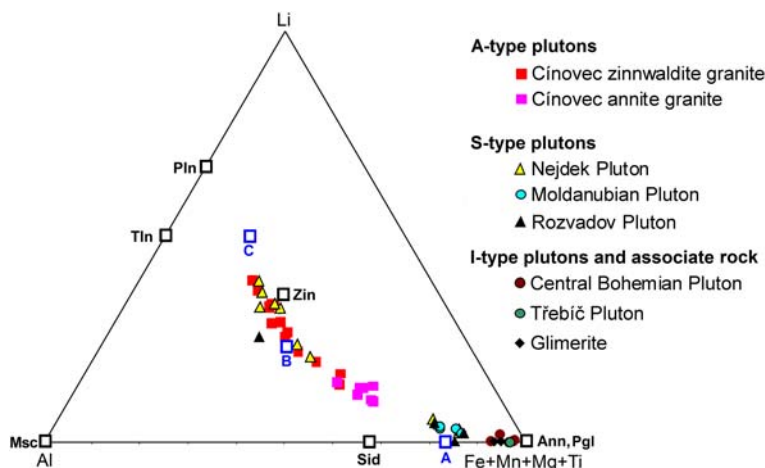


FIG. 2. Classification diagram of Li-bearing micas according to the occupation of the octahedral layer (according to Foster (1960), modified). The mica names used in this article and ideal positions of end-members according to the IMA rules (Rieder *et al.*, 1999) are shown: Pgl, phlogopite; Ann, annite; Sid, siderophyllite; Msc, muscovite; Tln, trilithionite; Pln, polyolithionite; Zin, zinnwaldite. Blue symbols A, B, C indicates the positions of apparent end-members from Fig. 8.

simplify description of the results and further discussion, the strongly differentiated granite types, e.g. the granites of the younger intrusive complex of the Nejdek Pluton, the albite-zinnwaldite granites of the Rozvadov Pluton and the A-type granites from the eastern Erzgebirge, are termed ‘rare-metal granites’ and all the other less differentiated granitoids are termed ‘common granites’.

Results

We studied the composition of trioctahedral micas in thin sections (150 µm thick) from 51 granite samples. From these samples, analysis of four to six mica grains was performed using two EMPA spots (core and rim) and a minimum of five ICP spots on each grain, e.g. 10 EMPA and 25 ICP spots on each sample on average. The primary database contains data from ~500 EMPA and 1250 ICP spot analyses. Data presented in the tables (Table 1, Supplementary files 2 and 3 deposited at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html) and figures represent average values of the samples after elimination of <10% of incidental errors (e.g. hits on mineral inclusions).

The silica content (Fig. 3a) varies between 34.3 and 47.9 wt.% SiO₂ (5.4–6.8 apfu Si). The lowest Si content was found in the biotites from the peraluminous South Bohemian Pluton (5.4–5.6 apfu Si), and biotites from the I-type granitoids of the

Central Bohemian Pluton, Třebíč Pluton and ultramafic dykes were found to contain 5.4–5.8 apfu Si. The highest contents of Si (up to 6.8 apfu) were found in the Li-rich micas (zinnwaldites) from the most fractionated facies of the Nejdek and Cínovec rare-metal granites.

The alumina content in the trioctahedral mica (Fig. 3a) varies from 13.4 to 20.8 wt.% Al₂O₃ (2.4–3.7 apfu Al). The lowest values were found in biotites from I-type granites in the Central Bohemian Pluton and Třebíč Pluton, and the highest values were found in zinnwaldites from rare-metal granites from the Nejdek and Cínovec plutons. The fundamental difference in mica composition between the rare-metal granites and the common granites is expressed in the partitioning of alumina into tetrahedral and octahedral sites (Fig. 3b): The Li-poor biotites from the common granites contain ~2.2–2.6 apfu Al in tetrahedral and <1 apfu Al in octahedral sites, whereas the Li-enriched micas (Li-annite, zinnwaldite) contain <2.2 apfu tetrahedral Al but >1.3 apfu octahedral Al. Furthermore, the correlation between ^{IV}Al and ^{VI}Al in common granites is positive and the total content of Al increases with increases in the alumina saturation index (ASI = molar Al₂O₃/(CaO + K₂O + Na₂O)) of the rock (Fig. 4), whereas this correlation is negative in the case of the rare-metal granites, regardless of their geochemical type (S or A).

The lithium content (Fig. 3c) increases from <0.01 wt.% Li₂O in phlogopites from ultramafic

LITHIUM AND TRACE ELEMENTS IN TRIOCTAHEDRAL MICAS

TABLE 1. Representative compositions of micas (major elements (wt.%) via microprobe, Li₂O (wt.%) and trace elements (ppm) via LA-ICP-MS) and structural formula (apfu) on the basis of 44 negative charges.

No.	4343 phlogopite Chroboly	4592 phlogopite Třebíč	4845 biotite Kozárovce	4363 biotite Plechý	4745 Li-annite Nejdek	4706 zinnwaldite Podlesí	4683 zinnwaldite Cínovec
SiO ₂	39.02	38.84	37.21	35.05	42.04	47.92	47.88
TiO ₂	2.50	2.76	3.53	2.22	0.66	0.24	0.01
Al ₂ O ₃	15.00	13.97	13.40	16.97	20.74	19.78	19.31
FeO	9.22	13.97	19.95	27.32	16.77	10.22	10.05
MnO	0.07	0.23	0.27	0.31	0.32	0.40	1.26
MgO	18.66	15.91	10.99	3.44	1.04	0.32	0.02
CaO	0.01	udl	udl	udl	udl	udl	udl
BaO	0.36	0.06	udl	udl	udl	udl	udl
Rb ₂ O	udl	udl	0.05	udl	0.65	1.23	1.23
Li ₂ O	0.01	0.02	0.04	0.34	2.22	4.80	4.35
Na ₂ O	0.19	0.11	0.09	0.08	0.21	0.30	0.17
K ₂ O	9.46	9.89	9.80	9.88	9.95	9.88	10.04
F	udl	0.22	udl	0.05	4.35	8.51	8.10
O = F	0.00	-0.09	0.00	-0.02	-1.84	-3.59	-3.42
Total	94.49	95.90	95.32	95.65	97.11	100.01	99.02
Si	5.71	5.75	5.72	5.56	6.22	6.71	6.79
Al(IV)	2.29	2.25	2.28	2.44	1.78	1.29	1.21
Z	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al(VI)	0.30	0.19	0.15	0.73	1.83	1.97	2.02
Ti	0.28	0.31	0.41	0.26	0.07	0.03	0.00
Fe	1.13	1.73	2.56	3.62	2.07	1.20	1.19
Mn	0.01	0.03	0.04	0.04	0.04	0.05	0.15
Mg	4.07	3.51	2.52	0.81	0.23	0.07	0.00
Li	0.01	0.01	0.02	0.22	1.32	2.71	2.48
Y	5.79	5.78	5.70	5.69	5.57	6.03	5.85
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Rb	0.00	0.00	0.00	0.00	0.06	0.11	0.11
Na	0.05	0.03	0.03	0.03	0.06	0.08	0.05
K	1.77	1.87	1.92	2.00	1.88	1.76	1.82
X	1.84	1.90	1.95	2.03	2.00	1.95	1.98
F	0.00	0.10	0.00	0.03	2.04	3.77	3.63
Mg/(Mg + Fe)	0.78	0.67	0.50	0.18	0.10	0.05	0.00
Sc	15.9	18.8	15.3	7.1	39	10	49
Ga	59	47	69	70	128	94	75
Ge	3.0	4.6	6.0	5.9	3.3	3.8	2.8
Nb	48	85	77	168	320	108	47
In	0.12	0.16	0.04	0.20	1.06	0.68	1.28
Sn	44	44	52	65	346	81	132
Cs	52	56	40	125	1645	1210	358
Ta	3.6	5.7	6.1	10.0	102	24	8.0
W	2.2	1.3	1.4	2.4	73	168	32
Tl	7.4	11.7	8.8	16.3	28	32	36

udl, under detection limit.

dykes and the Třebíč Pluton to 0.3–0.4 wt.% Li₂O (0.15–0.25 apfu Li) in biotites from the two-mica granites of the South Bohemian Pluton to 5.3 wt.%

Li₂O (3.0 apfu Li) in zinnwaldites from the albite-zinnwaldite-topaz granite from the Podlesí stock, Nejdek Pluton.

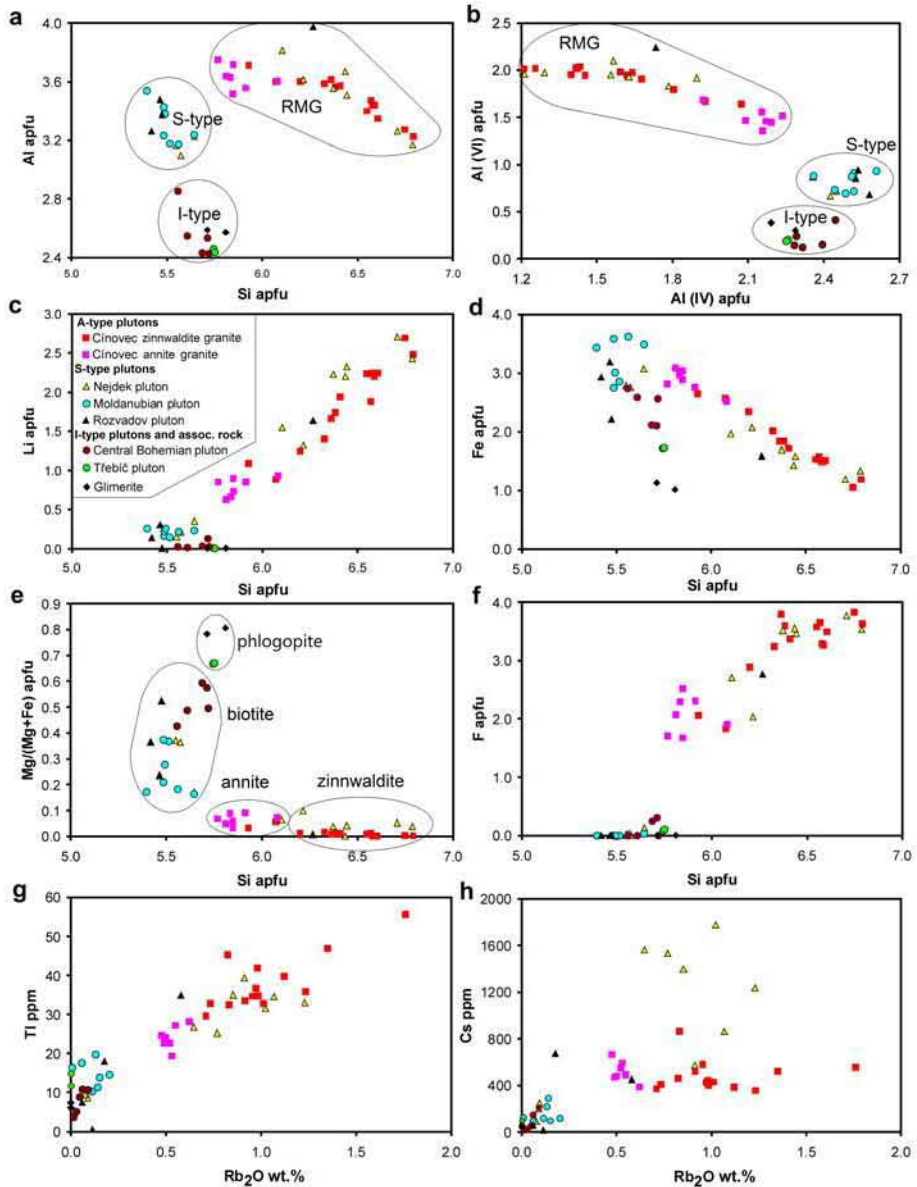


FIG. 3. Concentrations of selected major and trace elements in the trioctahedral micas investigated: (a) Si vs. Al; (b) ^{IV}Al vs. ^{VI}Al; (c) Si vs. Li; (d) Si vs. Fe; (e) Si vs. Mg/(Mg + Fe). (f) Si vs. F; (g) Rb₂O vs. Tl; (h) Rb₂O vs. Cs.

The iron content varies from 8.4 to 27.5 wt.% FeO (1.0–3.6 apfu Fe). The highest values occur in biotites from the two-mica granites of the South Bohemian Pluton, and the lowest values occur in the phlogopites from ultramafic dykes and the zinnwaldites from the rare-metal granites (Fig. 3d).

The magnesium content decreases from ~19 wt.% MgO (4.1 apfu Mg) in the phlogopite from ultramafic dykes to 16 wt.% MgO (3.5 apfu Mg) in the phlogopite from melasyenites of the Třebíč Pluton to 13.8–9.0 wt.% MgO (3.1–2.1 apfu Mg) in the biotite from I-type granitoids of the Central Bohemian Pluton and biotite

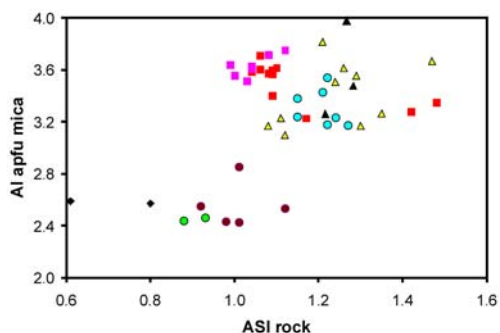


FIG. 4. Correlation between the alumina saturation index (ASI) of parental granites and contents of Al in mica. Symbols as in Fig. 3.

from the biotite-cordierite tonalite of the Rozvadov pluton to 3–7 wt.% MgO (1.6–0.7 apfu Mg) in the biotite from the peraluminous granites from the South Bohemian Pluton and the older biotite granites of the Nejdek Pluton. Micas from the rare-metal granites contain a maximum 1.3 wt.% MgO (0.3 apfu Mg) but usually <0.3 wt.% MgO (0.07 apfu Mg). The Mg/(Mg + Fe) ratio (Fig. 3e) decreased from ~0.8 in phlogopites from ultramafic dykes to <0.1 in Li-micas from the rare-metal granites. This ratio shows a good negative correlation with the Li content (Fig. 5a).

The manganese content in biotites from granites from the Třebíč, Central Bohemian, South Bohemian and Nejdek plutons varies in a narrow range of 0.2–0.4 wt.% MnO (0.03–0.05 apfu Mn). The lowest values occur in the phlogopite from ultramafic dykes (0.07 wt.% MnO), whereas strong enrichment has been found in all samples from the Činovec Pluton. In Činovec, the content of Mn increases from ~0.6 wt.% MnO in the Li-annite from the lower part of the pluton to ~1.3 wt.% MnO (0.15 apfu Mn) in zinnwaldite from its uppermost portion.

The titanium content increases from <0.1 to 0.5 wt.% TiO₂ in zinnwaldite from the rare-metal granites through 1.5–2.5 wt.% TiO₂ in biotite from the two-mica granites of the South Bohemian Pluton and phlogopite from the Třebíč Pluton and ultramafic dykes to 3.2–3.8 wt.% TiO₂ (up to 0.44 apfu Ti) in biotite from amphibole-biotite granitoids of the Central Bohemian Pluton and from the older biotite granites of the Nejdek Pluton.

High fluorine concentrations (Fig. 3f) are characteristic of micas from rare-metal granites, with values in the studied samples reaching 8.5 wt.% F (3.8 apfu F). The F content in common granites only rarely exceeds 0.3 wt.% F (0.15 apfu F).

The rubidium content of mica depends significantly on the differentiation grade of the parent

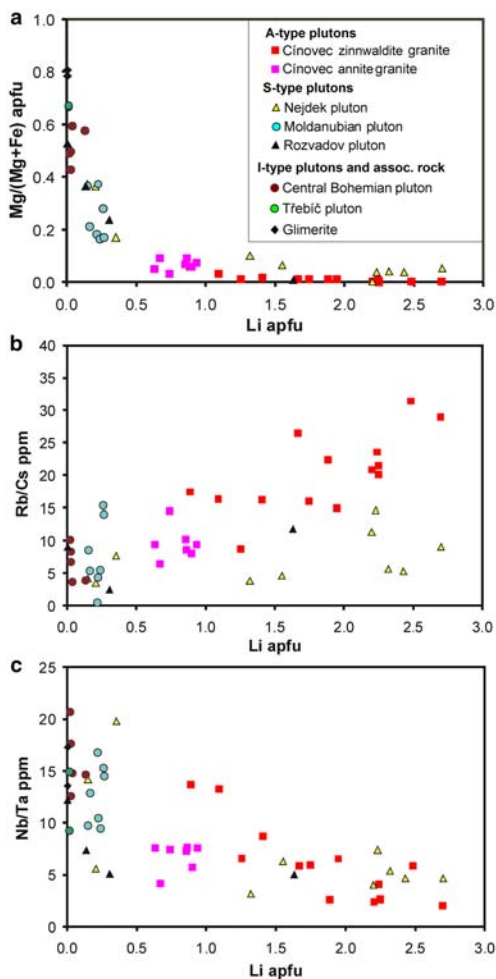


FIG. 5. Correlation between some elemental ratios monitoring differentiation of granic melt and content of lithium in micas: (a) Mg/(Mg + Fe) vs. Li; (b) Rb/Cs vs. Li; (c) Nb/Ta vs. Li.

rock: Rb increases from <0.1 wt.% Rb₂O in the phlogopites from the Třebíč Pluton and ultramafic dykes and biotites from the Central Bohemian Pluton to 0.05–0.2 wt.% Rb₂O in the biotites from the South Bohemian Pluton and older granites of the Nejdek Pluton to 0.5–1.7 wt.% Rb₂O (up to 0.16 apfu Rb) in the zinnwaldite from the rare-metal granites (Fig. 3g). The enrichment in Rb is positively correlated with enrichment in Li and F.

The behaviour of thallium is similar to that of Rb (Fig. 3g): The content of Tl increases from 6 to 16 ppm in the phlogopites and biotites from the I-type granitoids to 20–56 ppm in the zinnwaldites from the rare-metal granites.

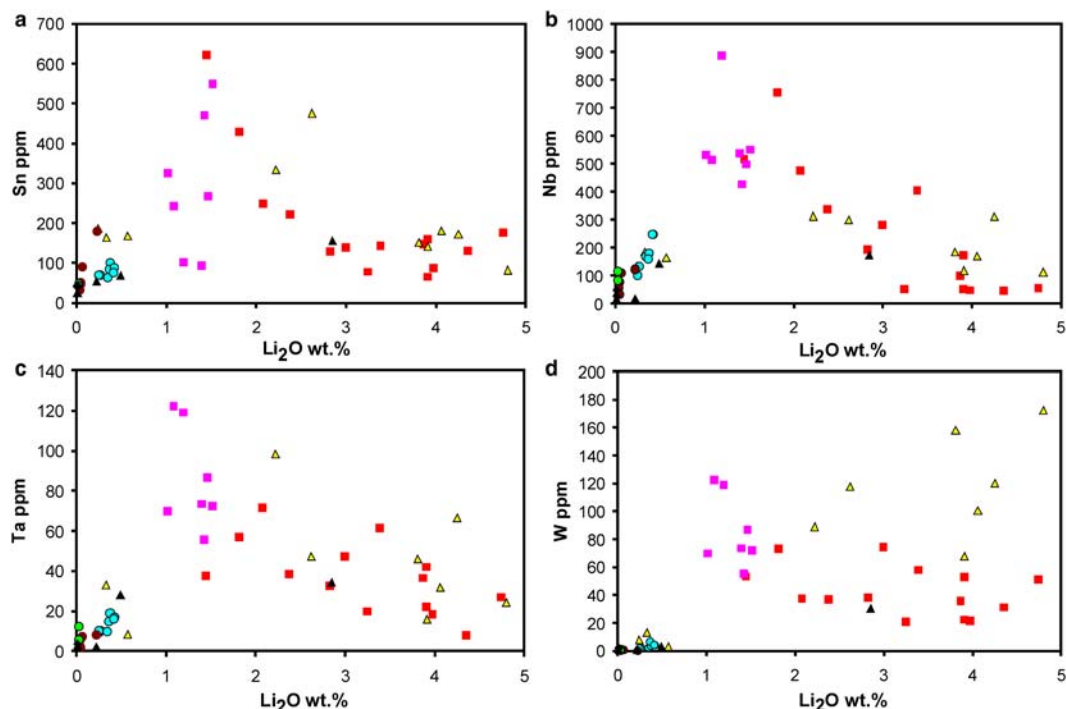


FIG. 6. Concentrations of Li and ore elements in the studied trioctahedral micas: (a) Li_2O vs. Sn; (b) Li_2O vs. Nb; (c) Li_2O vs. Ta; (d) Li_2O vs. W. Symbols as in Figs 3 and 5.

The caesium content in micas from common granites only rarely exceeds 200 ppm. The Li-rich micas from the Cínovec Pluton usually contain 400–700 ppm Cs, whereas zinnwaldites from the Podlesí stock (Nejdek Pluton) contain 1200–1770 ppm Cs (Fig. 3h).

The Rb/Cs ratio is highly scattered and only increases slightly with increasing content of Li up to 30 in the A-type rare-metal granite (Fig. 5b).

The tin content in the phlogopites and biotites from the amphibole-biotite and two-mica granites usually does not exceed 100 ppm (Fig. 6a). A slight enrichment in the range of 150–200 ppm was found in the biotites from the older biotite granites of the Nejdek Pluton. In both rare-metal granite plutons (Nejdek and Cínovec), remarkably high Sn concentrations of 350–600 ppm were found in the Li-annites from the relatively less-evolved rock facies. During differentiation, Sn decreases to ~100–200 ppm in the zinnwaldites from the late facies.

The distributions of niobium and tantalum (Fig. 6b,c) are similar to those of tin, with values of 30–200 ppm Nb and 2–17 ppm Ta in the micas from common granites, 300–600 ppm Nb and 60–120 ppm Ta in the annites from the older facies

of the rare metal granites and 40–350 ppm Nb and 10–70 ppm Ta in the zinnwaldites from the late facies of the rare-metal granites. The Nb/Ta ratio in micas from common granites (10–20) agrees well with the crustal Nb/Ta values of ~10–12 (Rudnick and Fountain, 1995). In contrast, the zinnwaldites from rare-metal granites feature a value of 2–8. The Nb/Ta ratio is negatively correlated with the Li content (Fig. 5c).

The tungsten content (Fig. 6d) is in the range of 0.5–172 ppm. The micas from the common granites contain less than 10 ppm W, whereas the Li-enriched micas from the rare-metal granites contain 20–172 ppm W. A decreasing trend in W from 250–600 ppm to 50–200 ppm during differentiation was found in the Cínovec Pluton.

The indium content in the micas from the common granites does not exceed 0.5 ppm. An enrichment to 1–2 ppm (with a maximum of 3 ppm) occurs in the Li-rich micas from the rare-metal granites.

The scandium content in the phlogopites and biotites from the common granites is in the range of 5–30 ppm. A remarkable difference has been found within the South Bohemian Pluton: Although biotites in the western part contain only 6–7 ppm

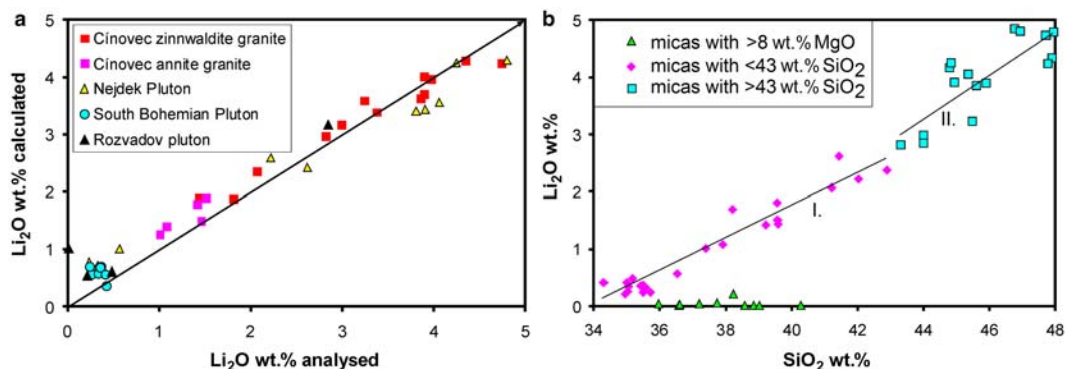


FIG. 7. Computation of the Li-content of mica analysed using microprobe: (a) comparison of Li₂O concentrations obtained by LA-ICP-MS and those computed according to Tischendorf *et al.* (1997, 1999); (b) correlation between SiO₂ and Li₂O in micas from Bohemian massif: I. – proposed equation for micas containing 34–43 wt.% SiO₂ and <8 wt.% MgO is $\text{Li}_2\text{O} = 0.2902 \cdot \text{SiO}_2 - 9.8651$ ($R^2 = 0.9366$); II. – apparent correlation for mica with SiO₂ > 43 wt.% Li₂O = $0.384 \cdot \text{SiO}_2 - 13.635$ ($R^2 = 0.6787$) is not recommended due to the large scatter of analysed values.

Sc, biotites from the eastern part contain 21–30 ppm Sc. The micas from the Nejdek and Cínovec plutons are enriched in Sc to >80 ppm with a clear decreasing trend during differentiation.

The germanium content in the micas studied is uniform at ~10 ppm. Individual samples with enrichments of >15 ppm were found in the South Bohemian, Nejdek and Cínovec plutons.

The gallium content varies in the range of 50–150 ppm, with a minimum (50–60 ppm) in the phlogopites from the Třebíč Pluton and ultramafic dykes and a maximum (90–150 ppm) in the annites and zinnwaldites from the Nejdek Pluton.

Discussion

Comparison of computed and analysed Li concentrations in trioctahedral micas

The chemical analyses of Li-micas before 1975 were performed using classical wet chemistry including Li (Foster, 1960; Rieder, 1970). The most common method of mineral analysis, the electron microprobe, cannot be used to analyse lithium. Many authors addressed this deficiency using additional methods. For example Stone *et al.* (1988, 1997), du Bray (1994), Ford *et al.* (1995), Černý *et al.* (1995), Breiter (2002) and Brigatti *et al.* (2003) prepared mono-mineralic separates of mica *via* crushing, sieving, magnetic separation, separation in heavy liquids and handpicking. Separates with 95%–99% purity were analysed for Li using classical wet chemistry methods, e.g. atomic absorption, flame photometry

or emission spectroscopy. From the late 1980s, the secondary ion mass spectrometry (SIMS) has also been used (Henderson *et al.*, 1989; Charoy *et al.*, 1995). The financial and time demands of aforementioned methods instigated the creation of several computing methods on the basis of supposed crystallo-chemical relationships between Li and other major elements in mica. Tindle and Webb (1990), using a data set of 250 chemical analyses, proposed the equation $\text{Li}_2\text{O} = (0.287 \cdot \text{SiO}_2) - 9.552$, which should be valid for trioctahedral micas with MgO < 8 wt.%. Later, Tischendorf *et al.* (1997, 1999) evaluated more than 500 published mica analyses and proposed the equation $\text{Li}_2\text{O} = (0.289 \cdot \text{SiO}_2) - 9.658$ for micas with SiO₂ > 34 wt.% and MgO < 3 wt.%. Both the proposed equations are very similar and statistically acceptable and are widely used by many authors (e.g. Colombo *et al.*, 2010; Johan *et al.*, 2012; Petřík *et al.* 2014; Li *et al.*, 2015). The first author who questioned the proposed equations and the computational methods was Thiergärtner (2010), who stressed that the difference between averaged and individual data sets results from different substitution mechanisms of Li incorporation in the mica crystal lattice. To evaluate the usability of proposed computational methods, we compared the real Li concentrations in micas with those computed according to Tischendorf *et al.* (1997) (Fig. 7a). The accordance of measured and computed values in studied micas through the whole interval of Li-concentrations from 0 to 5 wt.% is acceptable. The computed values seem to be slightly overestimated for Li₂O < 2 wt.% and slightly underestimated for Li₂O

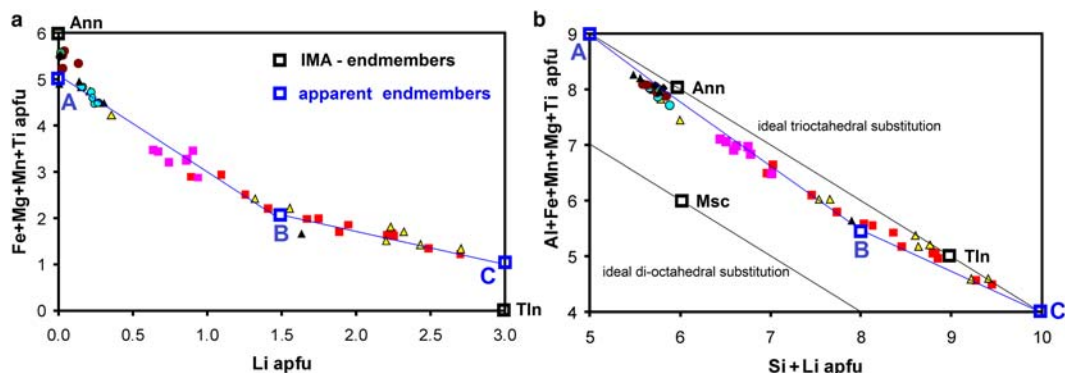


FIG. 8. Substitution in studied LiFe micas: (a) Fe + Mg + Mn + Ti vs. Li; (b) Al + Fe + Mg + Mn + Ti vs. Si + Li. Blue symbols A, B and C indicate position of apparent end members: A – $K_2(Fe_5Al)(Al_3Si_5O_{20})F_4$ (=annite-siderophyllite join); B – $K_2(\square_{0.5}Li_{1.5}Fe_2Al_2)(Al_{1.5}Si_{6.5}O_{20})F_4$ (Li-poor zinnwaldite); C – $K_2(Li_3FeAl_2)(AlSi_7O_{20})F_4$ (Fe-bearing trilithionite). Sample symbols as in Figs 3 and 5.

> 4 wt.%. On the basis of our analyses, we propose the equation $Li_2O = 0.2902 * SiO_2 - 9.8651$ ($R^2 = 0.9366$) for micas containing 34–43 wt.% SiO_2 and <8 wt.% MgO (Fig. 7b). For micas with >43 wt.% SiO_2 , the data is much more scattered; the apparent equation $Li_2O = 0.384 * SiO_2 - 13.635$ ($R^2 = 0.6787$) cannot be recommended.

the end-members represent ideal trioctahedral mica positioned on the siderophyllite–polyolithionite join (Fig. 2). The exchange vector is $\square Li_3Si_3Fe_6Al_{-1}$ in the first case and $Li_3Si_1\square Fe_2Al_{-1}$ in the other. This change in the exchange vectors at ~1.5 apfu Li (~2.5 wt.% Li_2O) is one of the reasons for the inaccuracy in the computational methods.

Accommodation of Li in the mica crystal lattice

Lithium enters the mica crystal lattice via complex substitutions that induce changes in both the tetrahedral and octahedral layers. Trioctahedral micas ideally contain 6 apfu in the octahedral layer, with the entry of Li following the substitution $6Fe^{2+} \leftrightarrow 4Li + 2Al$. The charge deficiency created by this substitution is balanced by the replacement of Al cations by Si cations in the tetrahedral layer ($2Al + 6Si \leftrightarrow 8Si$, annite $\leftrightarrow$ polyolithionite) (Rieder *et al.*, 1999). Our analysed micas contain less Fe (and other divalent elements) and are somewhat enriched in Al in comparison with the ideal composition (Fig. 8). In the broad category of studied Li-bearing micas with $Li = 0.2$ –1.5 apfu, the complex substitutions can be expressed as $K_2(Fe_5Al)(Al_3Si_5O_{20})(OH > F)_4 \leftrightarrow K_2(\square_{0.5}Li_{1.5}Fe_2Al_2)(Al_{1.5}Si_{6.5}O_{20})(F > OH)_4$ (Fig. 8, line AB), where the former end-member corresponds to annite–siderophyllite join according to the IMA nomenclature; and the later end-member should be termed as Fe-poor-zinnwaldite. The Li-micas with $Li > 1.5$ apfu evolved along different substitution pathways, which can be generalized as $K_2(\square_{0.5}Li_{1.5}Fe_2Al_2)(Al_{1.5}Si_{6.5}O_{20})(F > OH)_4 \leftrightarrow K_2(Li_3FeAl_2)(AlSi_7O_{20})F_4$ (Fig. 8, line BC), where

Correlation between chemical composition of micas and their parental granites

Trioctahedral micas in magmatic rocks are important carriers of many trace elements, including Rb, Cs, F, Sn, W, Nb, Ta, Sc etc. (Stone *et al.*, 1988; du Bray, 1994; Wise, 1995; Tischendorf *et al.*, 2001; Van Lichtervelde *et al.*, 2008; Li *et al.*, 2015; Xie *et al.*, 2015). In the case of Li, micas are the dominant carriers in granitoids because appearance of other potentially Li-rich silicate and phosphate minerals, such as spodumene and amblygonite, is restricted to extremely fractionated facies of certain rare-metal granites and pegmatites.

The concentration of Li in mica correlates well with that in the whole rock (Fig. 9a). This pattern is in good agreement with unique position of trioctahedral micas as the Li carriers in the rocks investigated. The ratio of $Li(mica)/Li(WR)$ (by weight) increases from ~10 in F-poor common granites to ~20 in the F-rich rare-metal granites, again in perfect correlation with the decrease in the modal abundances of mica from ~10% to ~5% in these granite types.

In contrast to Li, rubidium has two principal carriers in granitoids – micas and K-feldspar.

LITHIUM AND TRACE ELEMENTS IN TRIOCTAHEDRAL MICAS

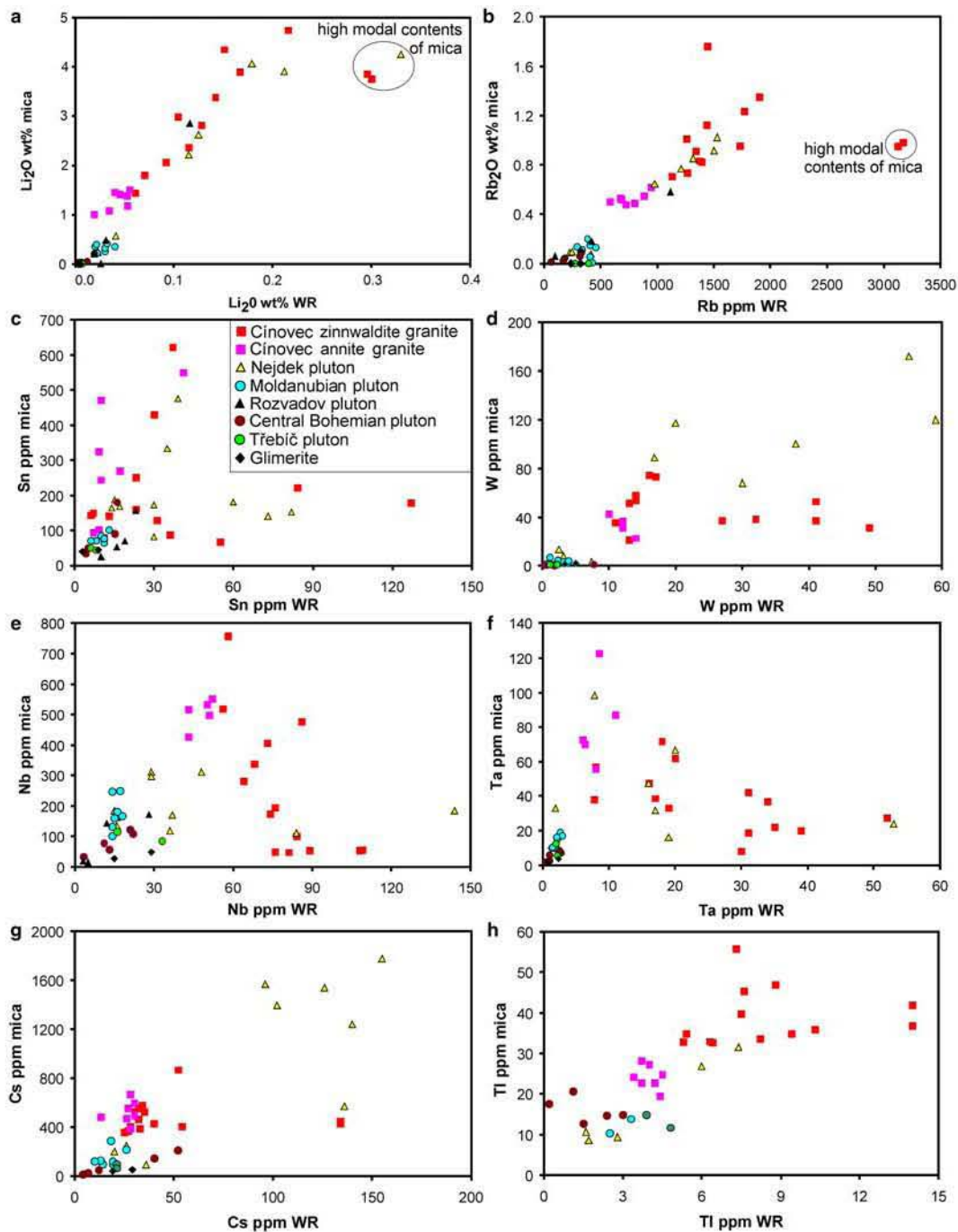


FIG. 9. Comparison of certain compositional parameters of mica with the composition of the parent granite: (a) Li_2O (rock) vs. Li_2O (mica); (b) Rb (rock) vs. Rb (mica); (c) Sn (rock) vs. Sn (mica); (d) W (rock) vs. W (mica); (e) Nb (rock) vs. Nb (mica); (f) Ta (rock) vs. Ta (mica); (g) Cs (rock) vs. Cs (mica); (h) Tl (rock) vs. Tl (mica).

Nevertheless, the correlation between Rb(mica) and Rb(WR) by weight is good, especially in rare-metal granites (Fig. 9b). The ratio of Rb(mica)/Rb(WR) is ≈ 5 . Together with ~ 5 modal% of mica in the rock, this ratio means that $\sim 25\%$ of the Rb is hosted in the mica and the rest in the K-feldspar.

In contrast to common granites, which feature a slight positive correlation between the concentrations of Nb, Ta, Sn and W in mica and in the whole rock due to the primary magmatic dissemination of these metals in crystallized micas, the concentrations of these metals in micas from rare-metal granites vary broadly, and any interpretation is rather speculative (Fig. 9c–f). Tin is hosted dominantly in micas in common granites and less-differentiated rare-metal granites. We found the ratio Sn(mica)/Sn(WR) to be ~ 10 in granites with 10 modal% mica and ~ 20 – 30 in granites with 5 modal% mica. In strongly evolved rare-metal granites, tin forms disseminated cassiterite and its content in mica is much lower. For tungsten, the ratio of W(mica)/W(WR) (by weight) is only occasionally >1 . The major portion of W is hosted in other minerals, probably in Ti- and Fe-oxides.

The ratios of Nb(mica)/Nb(WR) and Ta(mica)/Ta(WR) in the common granites are the same: ≈ 3 . Therefore, at 10 modal% of mica in the rock, $\sim 1/3$ of the Nb and Ta is disseminated in mica and the remaining $2/3$ are probably hosted in Ti-oxides (Zack *et al.*, 2002). In less-differentiated facies of rare-metal granites, the ratios of Nb(mica)/Nb(WR) and Ta(mica)/Ta(WR) are as high as 20–30. Therefore, in these cases, all the Nb and Ta are hosted in micas (~ 5 modal%). In more differentiated facies, the concentrations of Nb and Ta in mica decrease significantly, and Nb and Ta form oxide minerals – a Nb- and Ta-rich rutile and namely columbite.

The ratios of Cs(mica)/Cs(WR) and Tl(mica)/Tl(WR) (Fig. 9g,h) are ≈ 10 and ≈ 5 , respectively. This is in good agreement with the fact that nearly all Cs is hosted in mica, while a substantial part of Tl is hosted in K-feldspar (Breiter *et al.*, 2015).

Composition of micas from rare-metal granites, pegmatites and greisen

Comprehensive overviews of published analyses (major, minor and trace elements) of Li-enriched micas from different magmatic lithologies were published by Černý and Burt (1984) and by Tischendorf *et al.* (2001). The vast majority of the Li and trace-element analyses in these compilations were performed using mineral concentrates.

However, the use of this method implies the concentrations of elements such as Ti, Sn, W, Nb and Ta might be overestimated because the method analyses not only the mica but also inclusions of Ti-oxides, cassiterite, columbite and other accessory minerals. For comparison with the micas from rare-metal granites from the Erzgebirge, we searched (major and trace elements) LA-ICP-MS analyses of micas from rare-metal granites and pegmatites. Unfortunately, such data are surprisingly rare and are limited to the Tanco pegmatite (Van Lichtervelde *et al.*, 2008), Zamora pegmatite in Spain (Roda-Robles *et al.*, 2012) and the Qitianling granite in China (Xie *et al.*, 2015). Therefore, for comparison, we were forced to use analyses of trace elements obtained from mineral concentrates, including data from the peraluminous Cornwall batholith (Stone *et al.*, 1988), A-type rare-metal granites from eastern Arabian Shield (du Bray, 1994), the classical zoned LIF-pegmatite Dobrá Voda in the Czech Republic (Černý *et al.*, 1995) and anorogenic miarolitic pegmatites at Pikes Peak in Colorado (Ford *et al.*, 1995). In all cases, we used only data with directly analysed Li. The results of the comparison of these micas are presented in Fig. 10. In the Si vs. Al plot (Fig. 10a), the discussed micas form three well-separated patterns: (1) the Li-poor biotites from less evolved parts of the rare-metal granite plutons form a homogeneous group with 5.5–5.8 apfu Si and 2.5–3.5 apfu Al; (2) a major differentiation trend in the trioctahedral micas from rare-metal granites evolves from ~ 5.2 apfu Si and 4.0 apfu Al to ~ 7.2 apfu Si and 3.0–3.5 apfu Al (the majority of micas from the miarolitic Pikes Peak pegmatites follow this trend); and (3) the trend in the dominantly dioctahedral Li-micas from the classical zoned pegmatites Tanco and Dobrá Voda. The most evolved parts of the trends (2) and (3) meet in the lepidolite composition field.

The Si vs. Li and Li vs. F diagrams (Fig. 10b,c) demonstrate good positive correlations between these elements regardless of lithology or the tri- or di-octahedral character of the particular mica. The micas from Tanco contain somewhat less F but are rich in Rb (up to 0.3 apfu Rb, Fig. 10d) relative to micas from other localities. The distributions of Sn (Fig. 10e) in micas from all the rare-metal granites from the Arabian Shield are similar to the Erzgebirge patterns, decreasing from 200 to 1000 ppm in biotites to ~ 200 ppm in zinnwaldites. In the Cornwall batholith, all micas are poor in Sn, with a maximum of 100 ppm. (No data on the Sn concentrations in micas from the discussed

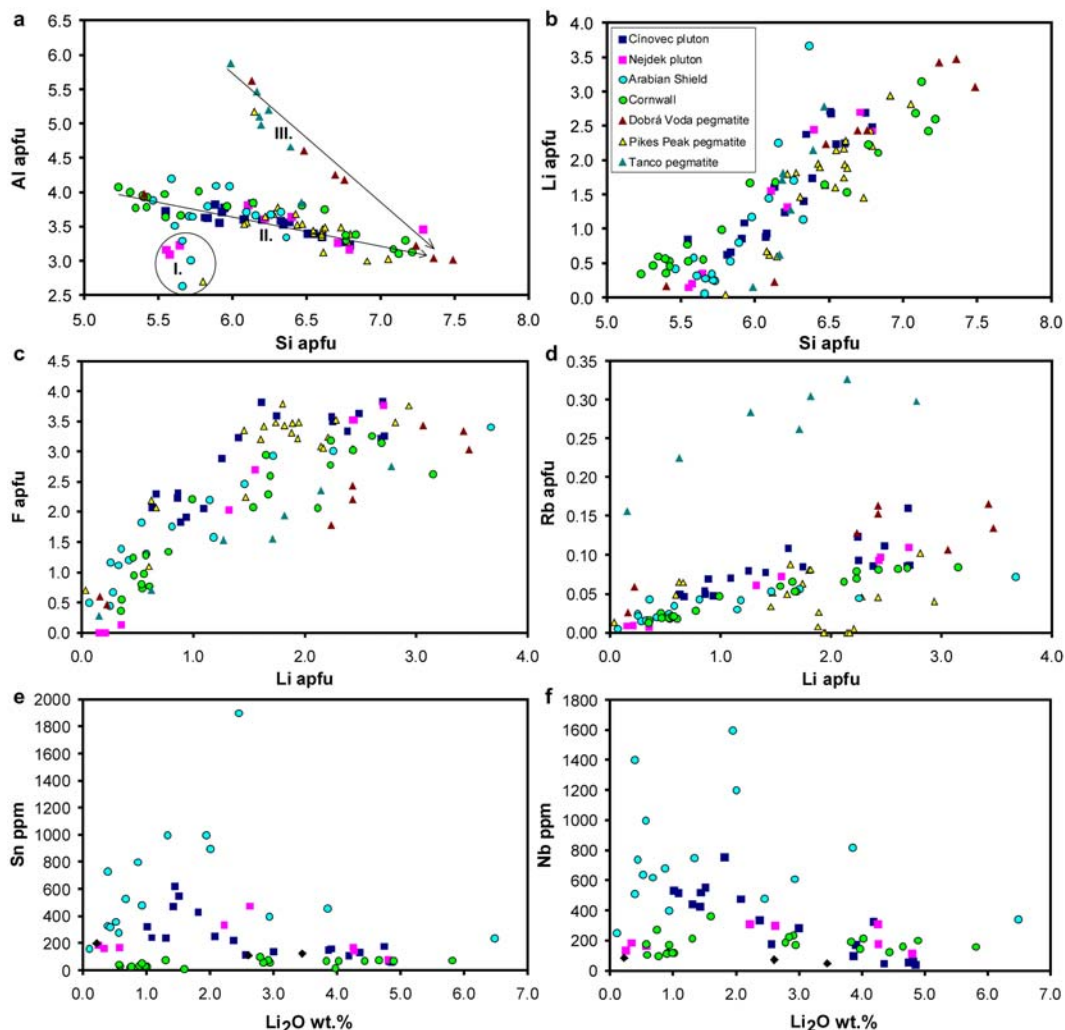


FIG. 10. Comparison of compositions of the trioctahedral micas from rare-metal granites from the Bohemian Massif with trioctahedral Li-micas from rare-metal granites and tri- and dioctahedral Li-micas from pegmatites worldwide: (a) Si vs. Al (I. – less fractionated granites; II. – rare-metal granites; III. – rare-metal pegmatites); (b) Si vs. Li; (c) Li vs. F; (d) Li vs. Rb; (e) Li_2O vs. Sn; (f) Li_2O vs. Nb. Data source: granites from the Arabian Shield (du Bray, 1994), granites from Cornwall (Stone *et al.*, 1988), Tanco pegmatite (close to dioctahedral micas, Van Lichtervelde *et al.*, 2008), Dobrá Voda pegmatite (close to dioctahedral micas, Černý *et al.*, 1995), Pikes Peak pegmatite (Ford *et al.*, 1995).

pegmatites are available.) The highest Nb values are reported from micas from the Arabian Shield (up to 1600 ppm, Fig. 10f). Similar to Sn, Nb also decreases from biotites to zinnwaldites. The concentration of Nb in micas from the Tanco pegmatite is relatively low (<200 ppm). Nevertheless, the high Sn and Nb values in micas from the Arabian Shield (du Bray, 1994), should be taken with caution as data were taken from mineral concentrates.

The elements Rb, Cs and Tl are geochemically similar to potassium and the decrease of ratios K/Rb, K/Cs and K/Tl may be used as indicator of the grade of magmatic fractionation. In the studied micas, the K/Rb ratio decreases from >800 to ~5, the K/Cs ratio from 5500 to 50 and K/Tl ratio from 14,000 to 1500. Černý and Burt (1984) reported even smaller values (K/Rb → 2, K/Cs → 10, K/Tl → 400) from pegmatitic Li-micas of the

muscovite–lepidolite series. It is worth mentioning, that the Cs-dominant analogue of polyolithionite ($K/Cs \approx 0.04$) was found in the Koktokay#3 pegmatite China (Wang *et al.*, 2007) as result of metasomatic processes. In pegmatites in Manitoba, Canada, magmatic zoned micas with rims near to theoretical Rb and Cs end-members have been found by Černý *et al.* (2003). Moreover, nanpingite, the Cs-analogue of muscovite, was reported from pegmatite in China (Yang *et al.*, 1988). All occurrences of the Rb- and Cs-dominant micas are restricted to highly fractionated LCT-type pegmatites. Similar newer micas were found in granites. For the plutons not displayed on Fig. 10, the concentrations of Rb, Cs and Sn compiled by Tischendorf *et al.* (2001) fully meet the range of rare-metal granites from the Erzgebirge. Li *et al.* (2015) reported from the Yashan granite Li-Fe mica featured values of up to 5 wt.% Rb_2O , 200 ppm W and 235 ppm Ta. Wise (1995), compiling data from worldwide Li-enriched pegmatites, reported micas with up to 8000 ppm Cs, 675 ppm Sn, 295 ppm W, 413 ppm Nb and 348 ppm Tl. Taken together, the concentrations of the rare alkalis Rb and Cs in micas from rare-metal granites can reach ~1.5 wt.% and 500 ppm, respectively.

The concentrations of the rare elements Sn, Nb and Ta increase from zero or tens of ppm in biotites from common granites to hundreds of ppm in Li-Fe micas from certain rare-metal granites and pegmatites. In mineralized rare-metal granites, clear decreases in Sn, Nb and Ta have been found in micas that formed during the final stage of pluton crystallization. These decreases can be explained by contemporaneous crystallization of disseminated cassiterite and columbite and/or admixture of ore-bearing fluids.

Among the 19 mica samples from the Činovec pluton, we also analysed four samples of zinnwaldite from high-temperature quartz–zinnwaldite ($\pm$ topaz, fluorite) greisen bodies. The composition of all these samples fit well with the trend of Li–annite–zinnwaldite samples from the ‘fresh’ surrounding granites, i.e. low concentrations of the ore elements Sn, W, Nb and Ta. No apparent differences exist between zinnwaldite of magmatic origin (from granites) and hydrothermal origin (from greisen).

Conclusions

This study analysed the compositions of trioctahedral micas in 51 samples from granitoids of different geochemical affiliations and grades of

differentiation. The principal results of this study are summarized as follows:

(1) Mica from less differentiated I- and S-type granites (common granites) differ primarily in the proportions of the major elements: Biotites from S-type granites contain more Al (^{VI}Al) and Fe and less Mg than biotites and phlogopites from I-type granitoids. The $Mg/(Mg + Fe)$ ratio decreases from 0.4–0.6 in the I-type granites through 0.2–0.4 in the common S-type granites to <0.1 in the rare-metal granite. Micas from the common S-type rocks are also slightly enriched in Li in comparison with the I-type rocks, whereas the differences in contents of F, Tl, Sn, Nb, Ta and W and in Nb/Ta- and Rb/Cs-ratios are negligible.

(2) The composition of Li-Fe micas and the style of their evolution during the differentiation of rare-metal granite plutons are independent of the compositional type of the parent rare-metal granite magma. The S-type plutons (Nejdek and Cornwall) and A-type plutons (Činovec and the Arabian Shield) contain identical micas that evolved from Li–annite (0.2–0.5 apfu Li) to zinnwaldite (lepidolite IMA, 2.5–3 apfu Li). Similarly the more leucocratic Beauvoir granite from France contains dioctahedral micas of the Li–muscovite–lepidolite series. Among pegmatites, the majority of classically zoned LCT pegmatites contain dioctahedral micas; only the anorogenic miarolitic Pikes Peak pegmatite, which represents the residual melt of the surrounding biotite granite, contains trioctahedral micas similar to the rare-metal granites in the Erzgebirge. The only compositional difference between micas from the S- and A-type rare-metal granites is the higher concentrations of Cs in the former.

(3) The concentrations of Li, Rb and F in trioctahedral micas increase during differentiation of the plutons proportionally to their concentrations in the whole rock. Micas contain ~1/4 of the Rb and all the Li in the rocks studied.

(4) Micas are important carriers of Sn, Nb and Ta. The highest concentrations – 600 ppm Sn, 600 ppm Nb and 120 ppm Ta – were found in Li–annites from the less fractionated facies of the rare-metal granites. In these granites, micas contain nearly all the Sn and ~1/3 of the Nb and Ta. The concentrations of these elements in zinnwaldites from the most differentiated facies of rare-metal granite are substantially lower. Furthermore, micas host only subordinate amounts of W.

(5) The composition of the zinnwaldite from the greisen in Činovec does not differ from the zinnwaldite from the surrounding rare-metal granite.

(6) Li enters the crystal lattice of trioctahedral micas through the exchange vector $\square\text{Li}_3\text{Si}_3\text{Fe}_{-6}\text{Al}_{-1}$ up to concentrations of ~2.5 wt.% Li_2O (1.5 apfu Li). At higher Li concentrations, Li is incorporated via the exchange vector $\text{Li}_3\text{Si}_1\square_1\text{Fe}_{-2}\text{Al}_{-1}$.

(7) For calculation of the Li-content in micas as addition to the EMPA, we may propose the equation $\text{Li}_2\text{O} = 0.2902 \cdot \text{SiO}_2 - 9.8651$ ($R^2 = 0.9366$) for micas containing 34–43 wt.% SiO_2 and <8 wt.% MgO. In micas with $\text{SiO}_2 > 43$ wt.%, the Si/Li-ratio is more scattered.

Acknowledgements

This work was supported by the Czech Science Foundation, project No. P210/14/13600S and RVO 67985831 in the Institute of Geology of the CAS. The results of this research have been acquired within CEITEC 2020 (LQ1601) project with financial contribution made by the Ministry of Education, Youths and Sports of the Czech Republic within special support paid from the National Programme for Sustainability II funds. I. Petrik, M. Van Lichtervelde and Xiao-Long Huang and the Editorial Board Member L. Campbell are thanked for numerous remarks which helped improve the manuscript.

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