




## Article

# Can lithium contents in mica be correctly calculated? Tischendorf's proposal (*Mineralogical Magazine* 61/1997) 25 years after

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### Abstract

Micas are the most common hosts of lithium in granitoid igneous rocks. Unfortunately, their Li contents cannot be determined by electron-probe microanalysis (EPMA) which is the most common method of mineral analysis. In an effort to avoid the use of other, technically more complex and expensive methods, several empirical schemes for the estimation of Li-contents from EPMA data have been developed. The methods proposed by Tischendorf (*Mineralogical Magazine*, 1997) have found the widest application. After 25 years of common usage, we have evaluated these methods by direct Li determination using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Approximately 3000 spot analyses of Li in micas from eight areas worldwide obtained by LA-ICP-MS were compared with the values yielded by the methods of Tischendorf. We conclude that none of the lithium estimation methods can compensate fully for a real local analysis by LA-ICP-MS or secondary-ion mass spectrometry (SIMS). Generally, SiO<sub>2</sub>-based estimation for trioctahedral micas provides a better match to the analysed values than F-based estimation for dioctahedral micas. The Rb-based estimation for dioctahedral micas does not provide acceptable results. The usage of averaged Si- and F-based estimations can be accepted in common petrological studies for a general characterisation of mica species. Large errors of individual spot estimations preclude their usage in detailed mineralogical studies.

**Keywords:** lithium mica; lithium analyses; lithium estimation

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### Introduction

Micas are one of the most widespread and probably the most compositionally diverse group of the common rock-forming minerals. As such, they are commonly the subject of petrological and mineralogical studies (see reviews in Bailey 1984 and Mottana *et al.*, 2002). The crystal structure of mica is favourable for incorporation of a broad spectrum of minor and trace elements including lithium. Contents of Li vary from dozens of ppm in phlogopite from melanocratic rocks (Breiter *et al.*, 2017a) up to ca. 6.5 wt.% Li<sub>2</sub>O in polyolithionite from fractionated granites and pegmatites (Černý *et al.*, 1995). In addition, the Li-rich micas, zinnwaldite and lepidolite, are objects of economic interest as potential sources of Li metal for battery technologies (e.g. the Cínovec/Zinnwald Li deposit, <https://www.europeanmet.com>). The principles of the classification of Li-bearing micas were defined by Foster (1960), and an updated classification approved by the International Mineralogical Association (IMA) was published by Rieder *et al.* (1999).

The correct study of the composition of Li-bearing micas is not trivial. Before the end of the 1980s (Rieder 1970; Monier

*et al.*, 1987; Stone *et al.*, 1988, etc.) and rarely later (Du Bray 1994; Foord *et al.*, 1995; Černý *et al.*, 1995; Roda *et al.*, 1995; Brigatti *et al.*, 2000), in common with other minerals, micas were analysed using classical methods of wet chemistry applied to monomineralic concentrates of the best achievable purity. This method permitted the determination of major and trace element concentrations, including Li, although only as average values of the entire mica sample.

Since the 1980s, electron-probe microanalysis (EPMA) has become a standard method of mineral analysis enabling the study of compositional zoning and heterogeneity of individual mineral grains. Unfortunately, Li cannot be analysed by this method. As a consequence, several researchers have attempted to evaluate the Li contents by a calculated estimation based on EPMA data.

Initially, based on experiments, Monier and Robert (1986) proposed that Li=F in atomic values. Subsequently, on the basis of analyses of Li-mica concentrates from Cornubian granites, Stone *et al.* (1988) proposed the equation  $\text{Li}_2\text{O} = 0.236 \times \text{SiO}_2 - 7.56$  (wt.%) for trioctahedral micas. Tindle and Webb (1990) modified this equation to  $\text{Li}_2\text{O} = (0.287 \times \text{SiO}_2) - 9.552$  (in wt.%). Tischendorf *et al.* (1997), on the basis of their evaluation of more than 1200 published mica compositions worldwide, proposed a very similar equation  $\text{Li}_2\text{O} = (0.289 \times \text{SiO}_2) - 9.658$  for trioctahedral Mg-poor micas, and equations  $\text{Li}_2\text{O} = 0.3935 \times \text{F}^{1.326}$  and  $\text{Li}_2\text{O} = 1.579 \times \text{Rb}_2\text{O}^{1.45}$  (in wt.%) for

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dioctahedral micas. The equation, valid for Mg-rich (>6 wt.% MgO) trioctahedral micas  $\text{Li}_2\text{O} = [2.7/(0.35+\text{MgO})] - 0.13$  (in wt.%) (Tischendorf *et al.*, 1997), was subsequently revised to  $\text{Li}_2\text{O} = [2.1/(0.356+\text{MgO})] - 0.088$  (in wt.%) (Tischendorf *et al.*, 1999). These Tischendorf equations quickly became generally accepted and have been applied to major element data obtained by EPMA in most mica-related papers in the past decades (Roda-Robles *et al.*, 2006, Wang *et al.*, 2007, Legros *et al.*, 2016, Zhu *et al.*, 2018, Bouguebrine *et al.*, 2023, etc.).

Neiva (1987) combined arithmetic means of several electron microprobe spot analyses with chemical analyses of mica concentrates for trace elements (Li analysed by atomic absorption spectroscopy) to obtain average mica compositions. A rather specific approach by Roda *et al.* (2007) was the application of EPMA + chemical analyses to monomineral concentrates, using Li estimation by another, slightly modified Tischendorf's equation  $\text{Li}_2\text{O} = 0.72 \times \text{F} - 0.612$  (wt.%) for the construction of structural formulae, although Li was analysed by AAS. In similar settings, Vieira *et al.* (2011) applied the equation  $\text{Li}_2\text{O} = 0.5387 \times \text{F} - 0.1205$  (wt.%), and similarly Marignac *et al.* (2020) used another of the Tischendorf-proposed equations:  $\text{Li}_2\text{O} = 0.697 \times \text{F} + 1.026$ , for micas from the Panasqueira W deposit.

Several authors have combined major element EPMA compositions with LA-ICP-MS data for trace elements. However, the apparent contents of Li were calculated according to Tischendorf *et al.* (1997) or by similar equations from Si or F values (Martins *et al.*, 2012, Xie *et al.*, 2015, Li *et al.*, 2015, Legros *et al.*, 2018, Launay *et al.*, 2021). This approach was probably justified by the difficulty in achieving identical analysis locations for the two analytical methods. For example, Van Lichtervelde *et al.* (2008) applied EPMA (major elements) and LA-ICP-MS (minor elements including Li) to Tanco micas but used the equation  $\text{Li}_2\text{O} = 0.782 \times \text{F} + 0.013$  (wt.%, F from EPMA) for structural formulae.

Grew *et al.* (2018) using EMPA interpreted the Li-Al micas from the Sinceni pegmatite as a solid solution of muscovite, polyolithionite and trillithionite components, resulting in the equation  $\text{Li}_2\text{O} = \text{F}/9.34 \times 5.92$  (wt.%) which was considered as valid for two di- and trioctahedral mica species. Nevertheless, the existence of the muscovite–lepidolite solid solution was questioned recently by Sulcek *et al.* (2023) who interpret the transitional compositions as a mechanical mixture of muscovite with a polyolithionite–trillithionite solid solution.

Michaud and Pichavant (2020) and Monnier *et al.* (2022) have published extensive EPMA and LA-ICP-MS data for micas from Argemela, Portugal and Beauvoir, France, respectively, but provided no correlation of the two analytical methods.

Published analyses of micas with comprehensively analysed and evaluated Li contents are still surprisingly scarce. A combination of EPMA with ion microprobe Li analyses was used by Henderson *et al.* (1989), Černý *et al.* (1995) and Charoy *et al.* (1995). A combination of EPMA with LA-ICP-MS has gradually become the standard operating procedure for *in situ* complex Li-mica analyses (Roda-Robles *et al.*, 2012, Petřík *et al.*, 2014, Breiter *et al.*, 2017a, 2019, 2022, 2023a, 2023b).

Most of the aforementioned methods of Li estimation are based on a statistical treatment of datasets, i.e. on the correlation between the contents of Li and other elements, mostly  $\text{SiO}_2$ , F, and  $\text{Rb}_2\text{O}$ , and are only valid for the tri- or dioctahedral micas. Although the general error of estimation can be minimised by processing large data sets, the error of the estimates for individual samples/spots remains large (Thiergärtner, 2010). Methods based

on structural considerations (Monier and Robert, 1986, Grew *et al.*, 2018) have been treated as independent of octahedral site occupancy; their use in petrological practice are evaluated below in the Discussion.

This paper is based on an extensive set of complex local analyses obtained in our labs in the past years (Breiter *et al.*, 2017a, 2019, 2022, 2023a, 2023b). The objectives are to show (1) the bias in Li content estimations according to the Tischendorf's proposals; and (2) the limits of using estimated values in petrological practice.

## Samples

The datasets evaluated comprise micas from: representative granitoids of the Bohemian Massif, Czech Republic, ranging from phlogopites from ultramafic dykes to zinnwaldites from stanniferous rare-metal granites (RMG) of the Nejdek and Cínovec plutons (Breiter 2017a, 2019); muscovites to lepidolites from the Argemela rare-metal granite, Portugal (Breiter *et al.*, 2022); muscovites from the Panasqueira tungsten deposit, Portugal (Breiter *et al.*, 2023a); zinnwaldites to lepidolites from the Beauvoir rare-metal granite, France; biotite, muscovite, phengite, zinnwaldite and lepidolite from the Orlovka Ta deposit, Siberia; biotite to zinnwaldite from the Wiborg batholith, Finland; and biotite to lepidolite from the Madeira pluton, Brazil (all in Breiter *et al.*, 2023b). Though the Nejdek, Argemela, Panasqueira and Beauvoir plutons represent strongly peraluminous P-rich granites, the Cínovec, Wiborg and Orlovka plutons represent only slightly peraluminous P-poor post-orogenic granites. The Madeira pluton is an example of a transition from meta-aluminous to peralkaline anorogenic granites.

For additional geological information on the plutons investigated see Badanina *et al.* (2004) for Orlovka, Costi *et al.* (2009) and Bastos Neto *et al.* (2009) for Madeira, Raimbault *et al.* (1995) and Monnier *et al.* (2022) for Beauvoir, Marignac *et al.* (2020) and Launay *et al.* (2021) for Panasqueira, Michaud and Pichavant (2020) for Argemela, Lukkari *et al.* (2009) for Wiborg, and Breiter *et al.* (2017b) for Cínovec.

Data from our laboratory are supplemented with EPMA + SIMS data from Cornwall, UK (Henderson *et al.*, 1989) in order to: (1) show data obtained using methods other than LA-ICP-MS; and (2) to discuss Cornwall as one of the classical provinces of rare-metal granites. In addition, a limited published dataset from the Tanco pegmatite (Van Lichtervelde *et al.*, 2008) allows comparison with analysed (LA-ICP-MS) and estimated (by the authors on the basis of F contents) Li contents in micas from a rather different environment of extremely fractionated Li–Cs–Ta-enriched (LCT) pegmatite.

In the following text we used the IMA terminology (Rieder *et al.*, 1999) supplemented with group-names biotite (solid solution of annite, phlogopite and siderophyllite), lepidolite (solid solution of polyolithionite and trillithionite), phengite (dioctahedral mica close to muscovite–celadonite join) and zinnwaldite (trioctahedral mica close to the siderophyllite–polyolithionite join).

## Methods

The contents of major elements in micas were analysed using a CAMECA SX100 electron microprobe housed at the Institute of Geology of the Czech Academy of Sciences, Praha. An accelerating voltage of 15 kV, a beam current of 10 nA and a beam diameter of 2  $\mu\text{m}$  were applied. The following standards were used: Na,

Al – jadeite; Mg, Si, Ca – diopside; K – leucite; Ti – rutile; Mn – MnCr<sub>2</sub>O<sub>4</sub>; Fe – magnetite; F – fluorite; Rb – RbCl; Cs – pollucite; and Zn – willemite. Counting times on each peak were optimised for individual elements according to their expected concentrations (10–60 s), and half that time was used to obtain background counts. X-ray lines and background offsets were selected to minimise interference. The X-Phi correction procedure (Merlet, 1994) was applied. An in-house standard of Li–Fe–mica was analysed in every analytical session to monitor stability of results, namely F and Rb. Analytical data of micas were recalculated to the proposed structural formulae based on 44 negative charges. The average detection limits (3σ) under the operating conditions were as follows: 0.01 wt.% for Mg; 0.02 wt.% for Ca and Na; 0.05 wt.% for Al, Mn, Rb, Cs and K; 0.06 wt.% for Si and Ti; 0.07 wt.% for Zn; 0.08 wt.% for F; and 0.19 wt.% for Fe.

The contents of trace elements in mica samples were analysed using two different LA–ICP–MS instrumentation configurations. The solid-state Nd:YAG laser (UP 213) working at a wavelength of 213 nm (New Wave Research, Inc., Fremont, California, USA) coupled to quadrupole-based ICP mass spectrometer Agilent 7500ce and installed at the Department of Chemistry, Masaryk University Brno, with an average detection limit of 1.8 ppm Li was used to analyse all the samples from the Bohemian Massif (Breiter *et al.*, 2017, 2019). The second LA–ICP–MS instrumentation, housed at Faculty of Chemistry, Brno University of Technology and BIC Brno, consists of the ArF\* excimer laser ablation system Analyte Excite+ (Teledyne CETAC Technologies, Omaha, Nebraska, USA), which emitted the laser beam at a wavelength of 193 nm, connected to quadrupole ICP mass spectrometer Agilent 7900. The average detection limit was 1.7 ppm Li. This instrumentation was used to analyse all other samples (Breiter *et al.*, 2022, 2023a, 2023b). In all cases, Li contents were quantified using standards SRM NIST 610 and 612, and Si and Al as internal reference elements. An in-house mica standard was included in each analytical session to monitor the stability of results. For details on all analytical settings see the referred papers.

This contribution is based on 3000 individual spot analyses for which lithium contents were obtained using LA–ICP–MS and combined with ca. 2000 individual spots where EPMA contents of major elements were obtained. The purpose of the older studies from the Bohemian Massif was to evaluate Li contents in micas to assess the potential of micas as Li resources (Breiter *et al.*, 2017a, 2017b). In such cases, 15–20 EPMA spots were combined with 20–25 laser-ablation spots spread over one thin section and resulting means were presented as one sample. Later, with the intention to express better local compositional variability, typically five mica grains within each thin section were evaluated (Breiter *et al.*, 2023a, 2023b); i.e. 3–5 laser ablation spots were combined with 2–3 EPMA spots in each mica grain according to their size. The means of both methods were coupled and are presented here as one analysis, i.e. usually 5 analyses per one sample. In petrological studies from Argemela (Breiter *et al.*, 2022) and the Bohemian Massif (unpublished), one EPMA and one laser ablation spot, successively in exactly the same place were realised, and coupled data from each spot are presented here, in total giving 560 analyses plotted in the figures.

Compositions of the micas were recalculated to the proposed structural formulae on the basis of 44 negative charges. The water content (OH<sup>−</sup>) and trivalent iron content were not calculated due to the large uncertainties of such calculations for Li-rich micas. All results are available in the Supplementary Tables with an indication of how many LA-analyses of Li were

coupled to obtain the value presented. In addition, the totals of octahedral occupation, crucial for choosing the correct equation, are shown. The same data are presented in Figs 1–3.

## Results

In the text below, estimations of Li contents according to Tischendorf *et al.* (1997, 1999) are compared with the real Li contents analysed by LA–ICP–MS. Equation  $\text{Li}_2\text{O} = (0.289 \times \text{SiO}_2) - 9.658$  was used for trioctahedral Mg-poor micas, equation  $\text{Li}_2\text{O} = [2.1 / (0.356 + \text{MgO})] - 0.088$  for Mg-rich trioctahedral micas, and equations  $\text{Li}_2\text{O} = 0.3935 \times \text{F}^{1.326}$  and  $\text{Li}_2\text{O} = 1.579 \times \text{Rb}_2\text{O}^{1.45}$  were applied to dioctahedral micas.

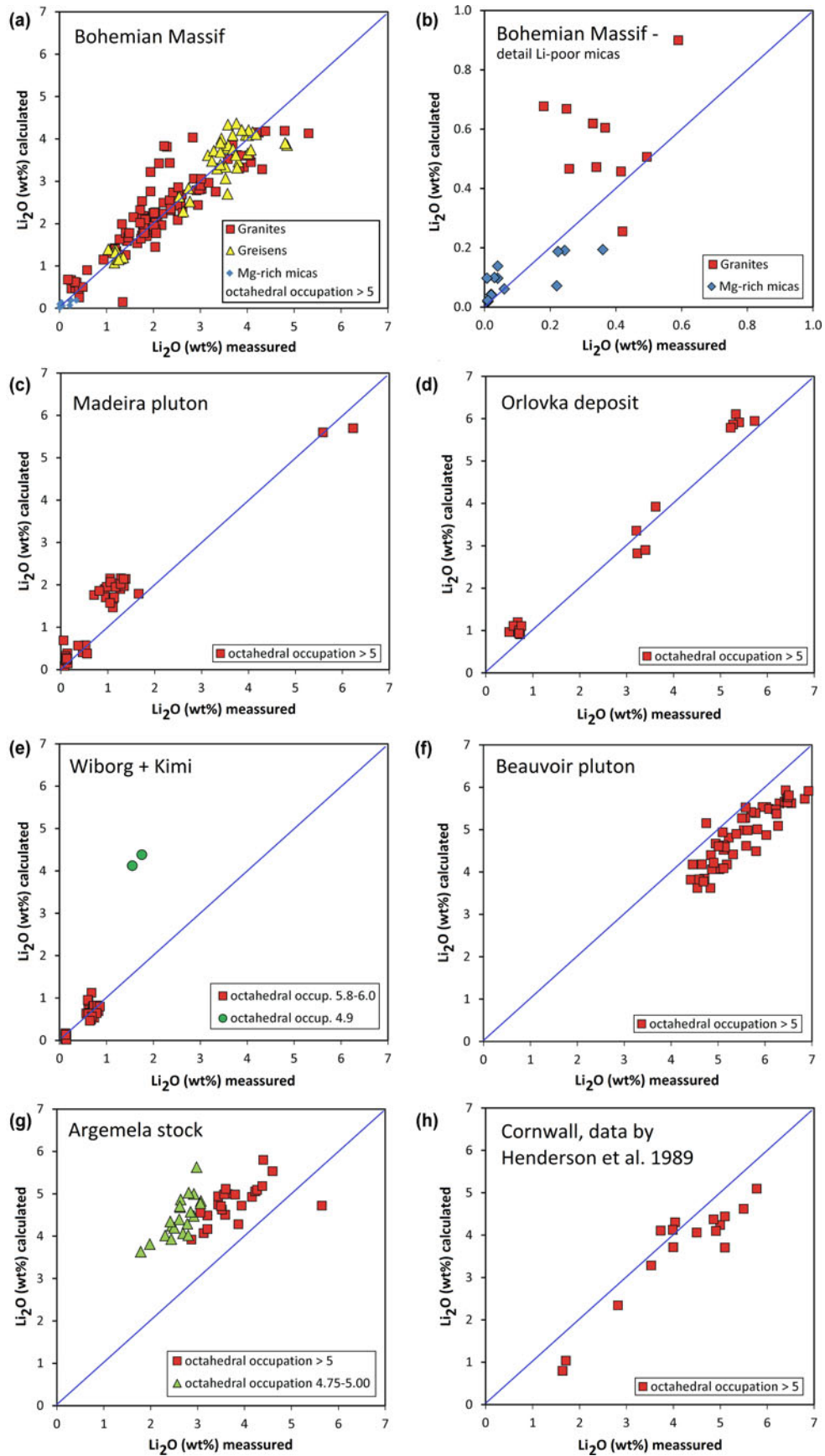
Data for trioctahedral micas are illustrated in Fig. 1. The Li-enriched Mg-poor micas from the Bohemian Massif, (Nejdek and Cínovec plutons from the Erzgebirge) show a good correlation between the measured and estimated values, namely in the interval between 1–3 wt.% Li<sub>2</sub>O (Fig. 1a). In the case of Li-poor biotite from the Central Bohemian Pluton and South Bohemian Pluton (Li<sub>2</sub>O < 0.5 wt.%, Fig. 1b) and Li-rich zinnwaldite (Li<sub>2</sub>O > 3 wt.%, Fig. 3a), the dispersion is rather larger. It is worth mentioning that no difference was found in reproducibility of estimated values between magmatic and hydrothermal (greisen) micas.

Data for Mg-rich trioctahedral micas, phlogopite to Mg-rich annite (Fe/(Fe+Mg) = 0.19–0.57) from the Bohemian Massif are shown on Fig. 1b. All samples represent ultramafic dykes, durbachitic rocks and geochemically less evolved granitoids of the Central Bohemian Pluton (details in Breiter *et al.*, 2017a). As is evident from the figure, the estimations give a generally valid assumption for low Li contents, but the dispersion of individual analysed vs. estimated values is rather wide, giving both over- and underestimated values.

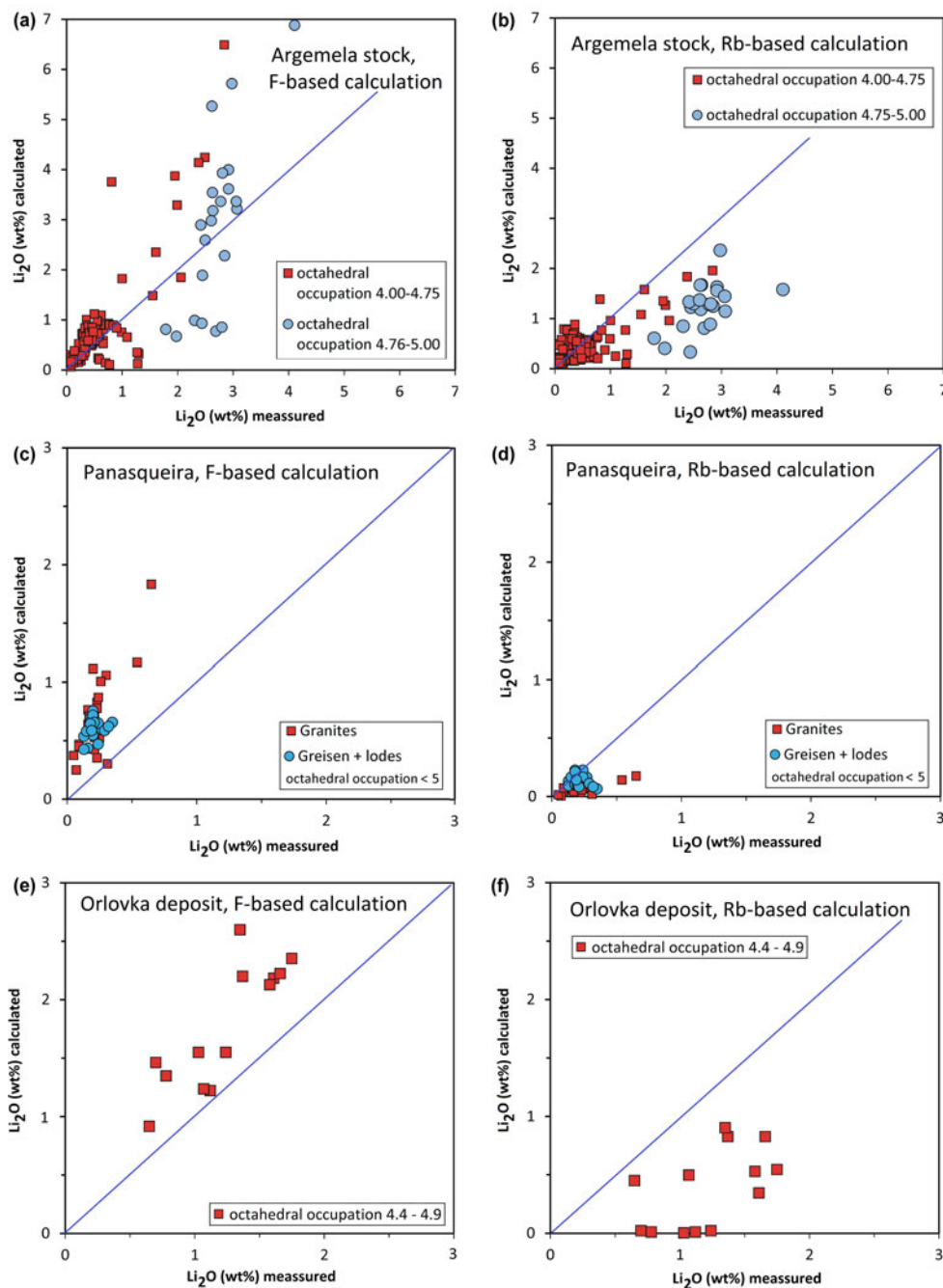
The Madeira pluton in central Brazil comprises three mica-bearing rock types. Although the estimations of Li in Li-poor biotite (< 0.5 wt.% Li<sub>2</sub>O) from the amphibole–biotite granite and slightly Li-enriched biotite from the biotite granite give acceptable results, Li contents in all samples of Li-enriched annite (0.5–1.5 wt.% Li<sub>2</sub>O) from the peralkaline granites are strongly overestimated (Fig. 1c). The explanation is simple: micas from Al-deficient peralkaline granites contain unusually low <sup>IV</sup>Al, i.e. they are relatively Si-enriched compared to micas from peraluminous rocks. Higher than ideal Si occupation in the tetrahedra is compensated by vacancies in the octahedral layer. As a consequence, calculations based on SiO<sub>2</sub> contents give unrealistically high Li values. Lepidolite from the cryolite granite (5.6–6.2 wt.% Li<sub>2</sub>O) gives a good correlation.

The Orlovka layered granite pluton comprises several facies bearing dioctahedral micas and three facies with trioctahedral mica species: biotite; zinnwaldite; and lepidolite. Whereas Li estimations for zinnwaldite and lepidolite give very acceptable results, all biotite values are slightly overestimated due to high <sup>IV</sup>Si occupancy (Fig. 1d).

The rather monotonous Wiborg batholith contains Li-poor biotite while the adjacent Kimi stock contains Li-rich biotite in the matrix and large flakes of macroscopically black mica in the border pegmatite facies. The Li estimations are generally acceptable for Li-poor micas, although a closer look at Wiborg biotite reveals a relative large error for grains, probably affected by mild alteration (Fig. 3b). The values for pegmatitic Li–Fe–mica are strongly overestimated (Fig. 1e): the unusually high



**Figure 1.** A comparison of the analysed and estimated contents of  $\text{Li}_2\text{O}$  in trioctahedral Mg-poor micas using equation  $\text{Li}_2\text{O} = (0.289 \times \text{SiO}_2) - 9.658$  and Mg-rich micas using equation  $\text{Li}_2\text{O} = [2.1 / (0.356 + \text{MgO})] - 0.088$  (in the Bohemian Massif only): (a) Bohemian Massif; (b) Bohemian Massif, detail of Li-poor micas; (c) Madeira pluton; (d) Orlovka pluton; (e), Wiborg batholith incl. Kimi stock; (f) Beauvoir granite stock; (g) Argemela stock (lepidolites in rims of zoned mica grains); (h) Cornwall (Henderson *et al.*, 1989).



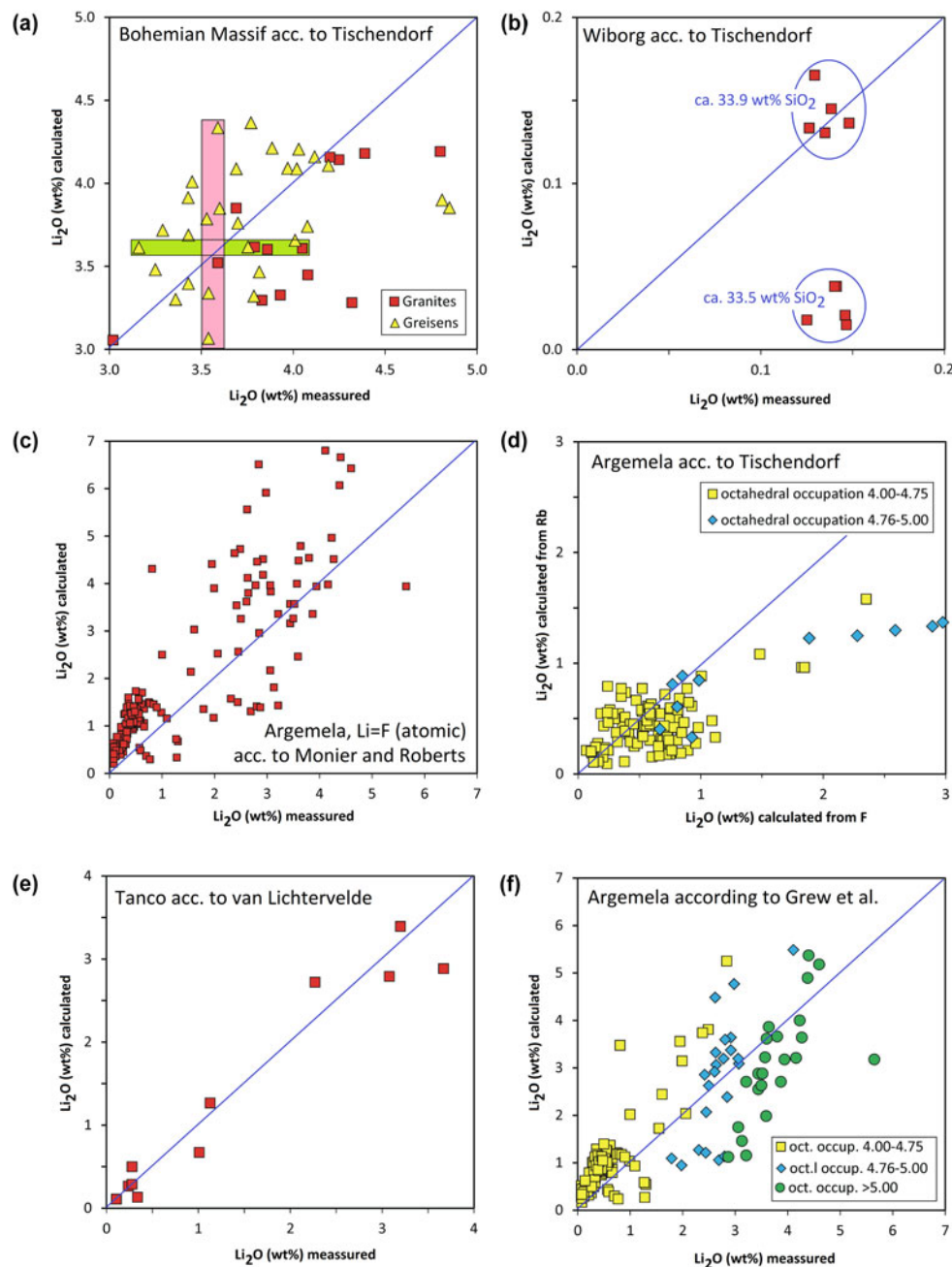
**Figure 2.** A comparison of the analysed and estimated contents of  $\text{Li}_2\text{O}$  in dioctahedral micas using equations  $\text{Li}_2\text{O} = 0.3935 \times \text{F}^{1.326}$  and  $\text{Li}_2\text{O} = 1.579 \times \text{Rb}_2\text{O}^{1.45}$ : (a) Argemela, estimation based on F contents; (b) Argemela, estimation based on  $\text{Rb}_2\text{O}$  contents; (c) Panasqueira, estimation based on F contents; (d) Panasqueira, estimation based on  $\text{Rb}_2\text{O}$  contents; (e) Orlovka, estimation based on F contents; (f) Orlovka, estimation based on  $\text{Rb}_2\text{O}$  contents.

$^{\text{IV}}\text{Si}$ -occupation here decreases the hexahedral occupation to ca. 4.9, i.e. this mica, regardless of its biotite appearance, is already dioctahedral and the use of this calculation method is not entirely correct. (Note that all equations proposed for dioctahedral micas in this case give similarly overrated values.)

Micas in the vertically zoned Beauvoir granite stock evolved upwards from zinnwaldite to lepidolite. Analysed and calculated values correlate well, albeit the majority of the estimated values are underestimated by ca. 0.5–1 wt.%  $\text{Li}_2\text{O}$  (Fig. 1f). This reflects the strongly peraluminous character of Beauvoir rocks as is evident in the high  $^{\text{IV}}\text{Al}$  and low Si contents (siderophyllite

component) of the micas. The equation best fitting this set of Li-rich trioctahedral micas from Beauvoir is  $\text{Li}_2\text{O} = 0.257 \times \text{SiO}_2 - 7.388$  (wt.%).

Leucogranites from Argemela contain mica species of the muscovite–lepidolite series, i.e. micas crossing the di/tri-octahedral occupation border; the trioctahedral mica (lepidolite) data are presented in Fig. 1g. Because the exact Li content is not known one cannot reliably calculate the layer occupation and choose the appropriate equation for Li estimation, in addition compositionally named dioctahedral micas with occupation approaching the di/tri-octahedral border are shown here. Hence the general



**Figure 3.** (a) Detail from the Bohemian Massif showing the dispersion of analysed and estimated values in Li-rich trioctahedral micas. Pink rectangles show the dispersion of estimated values (3.0–4.35 wt.%  $\text{Li}_2\text{O}$ ) from spots with nearly identical analyses (3.5–3.6 wt.%  $\text{Li}_2\text{O}$ ), while green ones show the dispersion of real Li contents (3.1–4.1 wt.%  $\text{Li}_2\text{O}$ ) at spots giving apparently identical estimated values of 3.55–3.65 wt.%  $\text{Li}_2\text{O}$ ; (b) a detail of the Wiborg batholith showing the dispersion of analysed and estimated values in Li-poor trioctahedral micas. The two groups of mica analyses differ by only  $\sim 0.4$  wt.%  $\text{SiO}_2$ , but for Li-poor micas the difference in Li-estimation is surprisingly high. A possible explanation is the presence of the initial stages alteration; (c) Argemela, an estimation based on Li=F (atomic values, Monier and Robert, 1986); (d) a comparison of Li estimations based on F and Rb contents in muscovite from Argemela; (e) Tanco, a comparison of the measured (LA-ICP-MS) and calculated Li values ( $\text{Li}_2\text{O} = 0.782 \times \text{F} + 0.013$  (wt.%), Van Lichtenvelde *et al.*, 2008); (f) micas from Argemela, comparison of analysed values and values calculated according to Grew *et al.* (2018):  $\text{Li}_2\text{O} = 0.644 \times \text{F}$  (wt.%). Micas with different octahedral occupation are distinguished with different colours.

overestimation of lithium is noticeable, still increasing with decreasing value of octahedral occupation. The reason is the low Fe-content combined with the high content of Si in this specific mica.

Mica varieties from Li-rich biotite to lepidolite from Cornwall (Henderson *et al.*, 1989) are shown in Fig. 1h. With the exception of one relatively Li-poor sample, the estimated values are generally valid. However, on closer inspection nearly identical estimated

values of 4.0–4.5 wt.% were obtained for samples with real contents between 3.5 and 5.2 wt.%  $\text{Li}_2\text{O}$ . This implies relatively significant differences between the real and estimated values in many situations.

Data for dioctahedral micas of the muscovite–Li-muscovite and muscovite–Li-phengite series are presented in Fig. 2, with values estimated using F and  $\text{Rb}_2\text{O}$  according to Tischendorf *et al.* (1997) shown for comparison (Fig. 2c,d).

Samples from all presented RMG plutons show large differences between Li values estimated from the F and Rb contents. Values calculated from F contents are generally better correlated with the measured values, but strongly overestimated, whereas calculations based on Rb contents tend to be underestimated. Note however that the muscovites are generally Li-poor (mostly below 0.8 wt.% Li<sub>2</sub>O in Argemela, and 0.5 wt.% Li<sub>2</sub>O in Panasqueira), so relative errors of estimation for such low Li are inevitably higher.

A notable difference between magmatic and late hydrothermal muscovite was found at Argemela. The F-based Li contents are overestimated but show a good positive correlation for the magmatic muscovite cores, whereas an apparent negative correlation was found in late hydrothermal muscovite overgrowth samples. Values calculated from Rb show a rather poorer correlation with analytical data (Fig. 2b). Both of the F- and Rb-based estimations depend on the octahedral occupation and spots with higher occupation approaching the di/trioctahedral border tend to show extreme dispersion (F-based estimation, Fig. 2a), or to be underestimated (Rb-based estimation, Fig. 2b). Unacceptable dispersion in the case of F-based estimation of micas with octahedral occupation between 4.76–5.00 (Fig. 2a) is caused by a large variation in the F content of this population.

Muscovite from the Panasqueira pluton is poor in Li. The F-based estimation gives rather high values (Fig. 2c), whereas the Rb-based estimation is relatively better in this specific case (Fig. 2d). Muscovite and phengite from Orlovka show overestimated, but well correlated F-based Li values (Fig. 2e) and strongly underestimated values with large dispersion in the case of Rb-based estimation (Fig. 2f). Strong underestimation of Rb-based values at Orlovka and Argemela can be explained by preferential incorporation of Rb in coexisting K-feldspar.

## Discussion

The first attempt to estimate the Li contents of mica from microprobe data was made on the basis of results from an experimental study of the muscovite–biotite miscibility gap by Monier and Robert (1986) who suggested Li=F in atomic proportions. This proposal found only limited response (i.e. Černý *et al.*, 2003), although recent experiments with micas of the Li–muscovite–lepidolite series (Sulcek *et al.*, 2023) confirmed the strong Li–F affinity in this mica species. The application of the Monier and Robert (1986) equation to Argemela samples shows a good positive correlation but a strong overestimation for low Li contents combined with a wide data dispersion in the case of higher Li contents (Fig. 3c). We can only speculate that the promising experimental results were based on stable conditions during the experiments, whereas natural micas have crystallised under highly variable Si–Al–Li–F(+Fe) ratios.

The majority of published, and used in petrological practice, attempts of Li estimation (Stone *et al.*, 1988, Tindle and Webb 1990, Tischendorf *et al.*, 1997, 1999) are based on statistical processing of compositional data of various sizes. If the number of evaluated analyses exceeds 1000, as in the paper of Tischendorf *et al.* (1997), the calculated error of the proposed equation might appear to be acceptable. Nonetheless, even in these cases the difference between the estimated Li and measured contents in individual samples remains unacceptably wide, as shown in Fig. 3a,b. This is because lithium is incorporated in the crystal lattice of trioctahedral micas in two possible ways: (1) Fe+Fe ⇌ Al+Li and (2) Al+Fe ⇌ Si+Li. The first substitution operates only in the octahedral layer, whereas the second combines changes in the

composition of the octahedral layer and in the tetrahedra. In natural samples, the two types of reactions combine in different proportions depending on the actual activity of Si, Al, and Fe (Breiter *et al.*, 2017a). In dioctahedral micas of the muscovite–Li–muscovite–lepidolite series, theoretical exchange vectors: (1) <sup>VI</sup>Al+2□ ⇌ 3Li; and (2) <sup>IV</sup>Al+<sup>VI</sup>Al+□ ⇌ Si+2Li are combined, although actual miscibility between Li–muscovite and lepidolite has been recently questioned by Sulcek *et al.* (2023). Moreover, the sum of cations in the octahedral layer is not constant, changing continuously from 6 to 4 without any discontinuities between tri- and dioctahedral micas. Furthermore, part of the iron present in the samples is typically oxidised to Fe<sup>3+</sup> (up to 10% according to unpublished author's data from the Erzgebirge). This suggests that a correct calculation of Li contents from the contents of the major elements (EPMA) is not practical.

Another important fact to be stressed is that the Li–Si relationships in trioctahedral micas and the Li–F relationship in the muscovite–lepidolite series are at least partly structurally conditioned, albeit being disturbed by changes in local PTX conditions. No structural relationship exists between Li and Rb in dioctahedral micas. Consequently, equations Li<sub>2</sub>O = 1.579 × Rb<sub>2</sub>O<sup>1.45</sup> proposed for dioctahedral micas only express the general trend of enrichment of relatively incompatible elements during magma fractionation. In this process, the relative behaviour of Li *versus* Rb is controlled by several factors, such as the regional specialisation and timing of mica versus K-feldspar crystallisation and water saturation/separation (Fig. 3d). Thus, the Rb-based estimation of Li in dioctahedral micas is even less correct and a riskier procedure than using other proposed estimations.

All proposed equations are sensitive to octahedral site occupation, i.e. are valid for di- or trioctahedral species only, which complicates their correct application to mica of the muscovite–lepidolite series. Especially in LCT pegmatites, micas evolve from muscovite to lepidolite, crossing the formal di- and trioctahedral border. In such cases, some authors applied an estimation based on the F content for the whole series. Equation Li<sub>2</sub>O = 0.782 × F + 0.013 was inferred for the Tanco pegmatite by Van Lichtervelde *et al.* (2008) based on a limited number of samples analysed using LA–ICP–MS (Fig. 3e). This “locally adjusted” equation was then used for Li addition to EPMA data of other samples. Such a method of estimation seems to be the best possible option for Li estimation when actual local Li analysis is not possible. Grew *et al.* (2018) in study of Li–Al micas from LCT Sinceni pegmatite, Swaziland, concluded that these micas represent a fine-grained admixture of Li,F-free muscovite and fully Li,F-saturated masutomilite, polyolithionite and trilithionite components; this resulted in an empirical equation Li<sub>2</sub>O = F/9.34 × 5.92 wt.%, which can be simplified to Li<sub>2</sub>O = 0.644 × F (wt.%). Notice the relatively small difference to the equation by Van Lichtervelde *et al.* (2008). We applied this equation to Argemela samples (Fig. 3f) and also found in this case, a marked dependence on the octahedral occupation: a decrease in occupation (<4.75) causes a relative rise in estimated Li values. The reason is probably that the Sinceni micas originate at stable conditions, whereas Argemela samples represent several successive stages of magmatic/hydrothermal evolution.

Monier and Robert (1986) conclusions were that the gap between di- and trioctahedral Li-free micas is large, and its width decreases with increasing Li content and that for a sufficient Li content (Li > 0.6 apfu based on 11 oxygens) a single Li-mica crystallised. In contrast, Sulcek *et al.* (2023) interpreted

the Li–Al micas as mixture of dioctahedral Li,F-free muscovite with trioctahedral Li,F-saturated solid solution of trilithionite and polyolithionite, i.e. an immiscibility gap divides all di- and trioctahedral micas and not only Li-poor species. Although the gap between muscovite and biotite was intuitively expected (muscovite–biotite granites are common, mixed mica compositions are not known), the gap between muscovite and lepidolite is seemingly at odds with thousands of electron microprobe analyses, covering the entire range between muscovite and trilithionite. This observation undoubtedly calls for further research. We can only note that the Li/F ratios in ideal muscovite, trilithionite and polyolithionite are 0/0, 1.5/2 and 2/2, respectively (Rieder *et al.*, 1999). If Sulcek *et al.*, are correct, the Li/F ratio in mixed micas should be within the interval from 1.5/2 to 2/2, i.e. 0.75–1. In actual Li–Al micas we found the Li/F ratio to be ca. 1 at Beauvoir, 0.5 at Argemela and only 0.2 at Panasqueira. Thus, the Li/F ratio in magmatic/hydrothermal micas is influenced not only structurally, but also, and most importantly, by the composition of the parental magma/fluid.

### Conclusive recommendation

As demonstrated above none of the lithium estimation methods can fully compensate for the actual determination of Li by LA–ICP–MS or SIMS at the same analytical site as used to obtain EMPA data. Generally, SiO<sub>2</sub>-based estimations of Li contents for trioctahedral micas provide a better match to the analysed values than F-based estimations for dioctahedral micas. The Rb-based estimations for dioctahedral micas do not provide applicable results. The use of Si- and F-based estimations can be accepted for general petrological studies where arithmetic means of a significant number of analysed spots, at least in part eliminating the errors of individual estimations, give realistic values for particular mica species. In the case of zoned micas or a superposition of two or more mica populations, it has to be considered that the substitutional mechanisms and hence also the Li–Si(F) relations might differ markedly in the individual mica zones or populations. This has hampered the use of the estimation method for a detailed interpretation of mica chemistry.

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### References

- Badanina E.V., Veksler I.V., Thomas R., Syritso L.F. and Trumbull R.B. (2004) Magmatic evolution of Li–F rare-metal granites: a case study of melt inclusions in the Khangilay complex, Eastern Transbaikalia (Russia). *Chemical Geology*, **210**, 113–133.
- Bailey S.W. (editor) (1984) *Micas*. Reviews in Mineralogy, vol. **13**. Mineralogical Society of America, Washington DC.
- Bastos Neto A.C., Pereira V.P., Ronchi L.H., Lima E.F. and Frantz J.C. (2009) The world-class Sn, Nb, Ta, F (Y, REE, Li) deposit and the massive cryolite associated with the albite-enriched facies of the Madeira A-type granite, Pitinga mining district, Amazonas State, Brazil. *The Canadian Mineralogist*, **47**, 1329–1357.
- Bouguebrine J., Bouabssa L. and Marignac C. (2023) Greisen and pseudogreisen in the Tamanrasset area (Central Hoggar, Algeria): petrography, geochemistry and insight on the fluids origin from mica chemistry. *Journal of African Earth Sciences*, **202**, 104898.
- Breiter K., Vaňková M., Vašínová Galiová M., Korbelová Z. and Kanický V. (2017a) Lithium and trace element concentrations in trioctahedral micas from granites of different geochemical types measured via laser ablation ICP–MS. *Mineralogical Magazine*, **81**, 15–33.
- Breiter K., Ďurišová J., Hrstka T., Korbelová Z., Hložková Vaňková M., Vašínová Galiová M., Kanický V., Rambousek P., Kněsl I., Dobeš P. and Dosbaba M. (2017b) Assessment of magmatic vs. metasomatic processes in rare-metal granites: a case study of the Cínovec–Zinnwald Sn–W–Li deposit, Central Europe. *Lithos*, **292**, 198–217.
- Breiter K., Hložková M., Korbelová Z. and Vašínová Galiová M. (2019) Diversity of lithium mica compositions in mineralized granite–greisen system: Cínovec Li–Sn–W deposit, Erzgebirge. *Ore Geology Reviews*, **106**, 12–27.
- Breiter K., Ďurišová J., Korbelová Z., Lima A., Vašínová Galiová M., Hložková M. and Dosbaba M. (2022) Rock textures and mineral zoning – A clue to understanding rare-metal granite evolution: Argemela stock, Central-Eastern Portugal. *Lithos*, **410–411**, 106562.
- Breiter K., Ďurišová J., Korbelová Z., Vašínová Galiová M. and Hložková M. (2023a) Granite pluton at the Panasqueira tungsten deposit, Portugal: Genetic implications as revealed from new geochemical data. *Minerals*, **13**, 163.
- Breiter K., Vašínová Galiová M., Hložková M., Korbelová Z., Kynický J. and Costi H.T. (2023b) Trace element composition of micas from rare-metal granites of different geochemical affiliations. *Lithos*, **446–447**, 107135.
- Brigatti M.F., Lugli C., Poppi L., Ford E.F. and Kile D.E. (2000) Crystal chemical variations in Li- and Fe-rich micas from Pikes Peak batholith (central Colorado). *American Mineralogist*, **85**, 1275–1286.
- Černý P., Staněk J., Novák M., Baadsgaard H., Rieder M., Ottolini L., Kavalová M. and Chapman R. (1995) Geochemical and structural evolution of micas in the Rožná and Dobrá Voda pegmatites, Czech Republic. *Mineralogy and Petrology*, **55**, 177–201.
- Černý P., Chapman R., Teerstra K. and Novák M. (2003) Rubidium- and cesium-dominant micas in granitic pegmatites. *American Mineralogist*, **88**, 1832–1835.
- Charoy B., Chaussidon M., Noronha F. (1995) Lithium zonation in white micas from the Argemela microgranite (central Portugal): an in-situ ion-, electron-microprobe and spectroscopic investigation. *European Journal of Mineralogy*, **7**, 335–352.
- Costi H.T., Dall’Agnol R., Pichavant M. and Rämö O.T. (2009) The peralkaline tin-mineralized Madeira cryolite albite-rich granite of Pitinga, Amazonian craton, Brazil: petrography, mineralogy and crystallization processes. *The Canadian Mineralogist*, **47**, 1301–1327.
- Du Bray E.A. (1994) Compositions of micas in peraluminous granitoids of the eastern Arabian Shield. *Contribution to Mineralogy and Petrology*, **116**, 381–397.
- Foord E.E., Černý P., Jackson L.L., Sherman D.M. and Eby R.K. (1995) Mineralogical and chemical evolution of micas from miarolitic pegmatites of the anorogenic Pikes Peak batholith, Colorado. *Mineralogy and Petrology*, **55**, 1–26.
- Foster M.D. (1960) Interpretation of the composition of Li-micas. *U.S. Geological Survey Professional Paper*, **354E**, 113–147.
- Grew E.S., Bosi F., Ros L., Kristiansson P., Gunter M.E., Halenius U., Trumbull R.B. and Yates M.G. (2018) Fluor-elbaite, lepidolite and Ta–Nb oxides from a pegmatite of the 3000 Ma Sinceni Pluton, Swaziland: evidence for lithium–cesium–tantalum (LCT) pegmatites in the Mesoarchean. *European Journal of Mineralogy*, **30**, 205–218.
- Henderson C.M.B., Martin J.S. and Mason R.A. (1989) Compositional relations in Li-micas from S.W. England and France. An ion- and electron-microprobe study. *Mineralogical Magazine*, **53**, 427–449.
- Launay G., Sizaret S., Lach, P., Melleton J., Gloaguen E. and Poujol M. (2021) Genetic relationship between greisenization and Sn–W mineralizations in vein and greisen deposits: Insights from the Panasqueira deposit (Portugal). *BSGF—Earth Sciences Bulletin*, **192**, 2.



- Legros H., Marignac C., Mercadier J., Cuney M., Richard A., Wang R.C., Charles N. and Lespinasse M.Y. (2016) Detailed paragenesis and Li-mica compositions as recorders of the magmatic-hydrothermal evolution of the Maoping W-Sn deposit (Jiangxi, China). *Lithos*, **264**, 108–124.
- Legros H., Marignac C., Tabary T., Mercadier J., Richar A., Cuney M., Wang R.C., Charles N. and Lespinasse M.Y. (2018) The ore-forming magmatic-hydrothermal system of the Piaontang W-Sn deposit (Jiangxi, China) as seen from Li-mica geochemistry. *American Mineralogist*, **103**, 39–54.
- Li J., Huang X-L., He P-L., Li W-X., Yu Y. and Chen L-l. (2015) In situ analyses of micas in the Yashan granite, South China: constraints on magmatic and hydrothermal evolutions of W and Ta-Nb bearing granites. *Ore Geology Reviews*, **65**, 793–810.
- Lukkari S., Thomas R. and Haapala I. (2009) Crystallization of the Kymi topaz granite stock within the Wiborg rapakivi batholith, Finland: Evidence from melt inclusions. *The Canadian Mineralogist*, **47**, 1359–1374.
- Marignac C., Cuney M., Cathelineau M., Lecomte A., Carocci E. and Pinto F. (2020) The Panasqueira rare metal granite suites and their involvement in the genesis of the world-class Panasqueira W-Sn-Cu deposit: a petrographic, mineralogical, and geochemical study. *Minerals*, **10**, 562.
- Martins T., Roda-Robles E., Lima A. and De Parseval P. (2012) Geochemistry and evolution of micas in the Barroso-Alvao pegmatite field, Northern Portugal. *The Canadian Mineralogist*, **50**, 1117–1129.
- Merlet C. (1994) An accurate computer correction program for quantitative electron probe microanalysis. *Microchimica Acta*, **114**, 363–376.
- Michaud J.A-S. and Pichavant M. (2020) Magmatic fractionation and the magmatic-hydrothermal transition in rare metal granites: evidence from Argemela (Central Portugal). *Geochimica et Cosmochimica Acta*, **289**, 130–157.
- Monier G. and Robert J-L. (1986) Evolution of the miscibility gap between muscovite and biotite solid solutions with increasing lithium content: an experimental study in the system  $K_2O-Li_2O-MgO-FeO-Al_2O_3-SiO_2-H_2O-HF$  at 600°C, 2 kbar  $P_{H_2O}$ : comparison with natural lithium micas. *Mineralogical Magazine*, **50**, 641–651.
- Monier G., Charoy B., Cuney M., Ohnenstetter D. and Robert J.L. (1987) Evolution spatiale et temporelle de la composition des micas du granite albitique a topaze-l'epidolite de Beauvoir. *Geologie de la France*, **2-3**, 179–188.
- Monnier L., Salvi S., Melleton J., Lach P., Pochon A., Baily L., Beziat D. and De Parseval P. (2022) Mica trace-element signatures: highlighting superimposed W-Sn mineralizations and fluid sources. *Chemical Geology*, **600**, 120866.
- Mottana A., Sassi F.P., Thompson Jr. J.B. and Guggenheim S. (editors)(2002) *Micas: Crystal Chemistry & Metamorphic Petrology*. Reviews in Mineralogy and Geochemistry, Volume 46. Mineralogical Society of America and the Geochemical Society, Washington DC.
- Neiva A.M.R. (1987) Geochemistry of white micas from Portuguese tin and tungsten deposits. *Chemical Geology*, **63**, 299–317.
- Petrík I., Čík Š., Miglierini M., Vaculovič T., Dianiška I. and Ozdín D. (2014) Alpine oxidation of lithium micas in Permian S-type granites (Gemic unit, Western Carpathians, Slovakia). *Mineralogical Magazine*, **78**, 507–533.
- Raimbault L., Cuney M., Azencott C., Duthou J.L. and Joron J.L. (1995) Geochemical evidence for a multistage magmatic genesis of Ta-Sn-Li mineralization in the granite at Beauvoir, French Massif Central. *Economic Geology*, **90**, 548–596.
- Rieder M. (1970) Chemical compositions and physical properties of lithium-iron micas from the Krušné hory Mts. (Erzgebirge). *Contributions to Mineralogy and Petrology*, **27**, 131–158.
- Rieder M., Cavazzini G., Dyakonov Y.S., Frank-Kamenetskii V.A., Gottardi G., Guggenheim S., Koval P.V., Muller G., Neiva A.M.R., Radoslovich E.W., Robert J.L., Sassi P.F., Takeda H., Weis Z. and Wones D.R. (1999) Nomenclature of micas. *Mineralogical Magazine*, **73**, 267–279.
- Roda-Robles E., Pesquera A., Gil-Grespo P.P., Torres-Ruiz J. and De Parseval P. (2006) Mineralogy and geochemistry of micas from the Pinilla de Fermoselle pegmatite (Zamora, Spain). *European Journal of Mineralogy*, **18**, 369–377.
- Roda-Robles E., Pesquera A., Gil-Grespo P. and Torres-Ruiz J. (2012) From granite to highly evolved pegmatite: a case study of the Pinilla de Fermoselle granite-pegmatite system (Zamora, Spain). *Lithos*, **153**, 192–207.
- Roda E., Pesquera A. and Velasco F. (1995) Micas of the muscovite-lepidolite series from the Fregeneda pegmatites (Salamanca, Spain). *Mineralogy and Petrology*, **55**, 145–157.
- Roda E., Keller P., Pesquera A. and Fontan F. (2007) Micas of the muscovite-lepidolite series from Karibib pegmatites, Namibia. *Mineralogical Magazine*, **71**, 41–62.
- Stone M., Exley C.S. and George M.C. (1988) Compositions of trioctahedral micas in the Cornubian batholith. *Mineralogical Magazine*, **52**, 175–192.
- Sulcek L., Marler B. and Fechtelkord M. (2023) Cation and anion ordering in synthetic lepidolites and lithian muscovites: influence of the OH/F and Li/Al ratios on the mica formation studied by NMR (nuclear magnetic resonance) spectroscopy and X-ray diffraction. *European Journal of Mineralogy*, **35**, 199–217.
- Thiergärtner H. (2010) Can the  $Li_2O$  content of mica really be calculated from its main chemical components? *Zeitschrift für geologische Wissenschaften*, **38**, 195–205.
- Tindle A.G. and Webb P.C. (1990) Estimation of lithium contents in trioctahedral micas using microprobe data: application to micas from granitic rocks. *European Journal of Mineralogy*, **2**, 595–610.
- Tischendorf G., Gottesmann B., Förster H-J. and Trumbull R.B. (1997) On Li-bearing micas: estimating Li from electron microprobe analyses and an improved diagram for graphical representation. *Mineralogical Magazine*, **61**, 809–834.
- Tischendorf G., Gottesmann B. and Förster H-J. (1999) The correlation between lithium and magnesium in trioctahedral micas: Improved equations for  $Li_2O$  estimation from MgO data. *Mineralogical Magazine*, **63**, 57–74.
- Van Lichterfelde M., Grégoire M., Linnen R.L., Béziat D. and Salvi S. (2008) Trace element geochemistry by laser ablation ICP-MS of micas associated with Ta mineralization in the Tanco pegmatite, Manitoba, Canada. *Contributions to Mineralogy and Petrology*, **155**, 791–806.
- Vieira R., Roda-Robles E., Pesquera A. and Lima A. (2011) Chemical variation and significance of micas from the Fregeneda-Almendra pegmatitic field (Central-Iberian Zone, Spain and Portugal). *American Mineralogist*, **96**, 637–645.
- Wang R.C., Hu H., Zhang A.C., Fontan F., De Parseval P. and Jiang S.Y. (2007) Cs-dominant polyolithionite in the Koptokay#3 pegmatite, Altai, NW China: in situ micro-characterization and implication for the storage of radioactive cesium. *Contributions to Mineralogy and Petrology*, **153**, 355–367.
- Xie L., Wang R-C., Groat L.A., Zhu J-C., Huang F-F. and Cempirek J. (2015) A combined EMPA and LA-ICP-MS study of Li-bearing mica and Sn-Ti oxide minerals from the Qiguling topaz rhyolite (Qitianling District, China): the role of fluorine in origin of tin mineralization. *Ore Geology Reviews*, **65**, 779–792.
- Zhu Z., Wang R., Marignac C., Cuney M., Mercadier J., Che X. and Lespinasse M-Y. (2018) A new style of rare metal granite with Nb-rich mica: the early Cretaceous Huangshan rare-metal granite suite, northeast Jiangxi Province, southeast China. *American Mineralogist*, **103**, 1530–1544.