

# A multiple regression method for estimating Li in tourmaline from electron microprobe analyses

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## ABSTRACT

Lithium cannot be determined by electron microprobe, but it may be an essential component in tourmaline-supergrupp minerals. Therefore, its estimation is important for structural formula calculation and nomenclature. In this paper, we present a method to estimate Li content in tourmaline from microprobe data based on a multiple linear-regression model, which is not reliant on a particular normalization scheme. The results derived from this model are reasonably accurate, particularly for low-Mg tourmalines (<2 wt.% MgO) with Li<sub>2</sub>O contents higher than ~0.3 wt.%. Furthermore, it provides a better fitness compared with estimations of Li assuming that Li fills any cation deficiency at the Y site.

**KEYWORDS:** tourmaline, lithium content, multiple regression method.

## Introduction

TOURMALINE is a complex borosilicate and is the main sink for boron in crustal rocks. The compositional variability, together with its refractory character, ubiquity, and a pronounced sensitivity to the bulk-rock composition, make tourmaline a useful tool as a marker of boron flux and crustal evolution, as well as a key player in the boron cycle (London *et al.*, 2002; Henry and Dutrow, 2002; Slack, 2002; Leeman and Sisson, 2002; van Hinsberg *et al.* 2011). The composition of tourmaline is expressed as  $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ , where X = Na, Ca, K, vacancies; Y = Li, Fe<sup>2+</sup>, Mg, Mn, Al, Fe<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, Ti<sup>4+</sup>; Z = Al, Cr<sup>3+</sup>, V<sup>3+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mg; V = O<sup>2-</sup>, OH<sup>-</sup>; and W = OH<sup>-</sup>, O<sup>2-</sup>, F (Henry *et al.*, 2011). Lithium can be an essential constituent of tourmaline but, together with H and Fe<sup>3+</sup>, cannot be analysed by electron microprobe. Although boron in tourmaline

has been determined by electron microprobe, it has not been done routinely because of the many analytical problems involved (see McGee and Anovitz, 2002 for an overview). In recent years, Li data for tourmaline have been obtained by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Secondary Ion Mass Spectrometry (SIMS), but the electron microprobe is still the most commonly used analytical technique for determining tourmaline composition. In this method, the Li content can be approximated on a stoichiometric basis using the expression Li (atoms per formula unit (apfu)) = 15 - (T + Y + Z) cations. This requires the structural formula either to be calculated on a 6 Si basis (Dutrow and Henry, 2000) or to calculate Li iteratively using a fixed number of oxygens and assuming OH + F = 4 (Clark, 2007). These approaches work relatively well in some cases, but tend to underestimate and overestimate the Li contents, respectively (see Henry *et al.*, 2011). Furthermore, they present serious limitations, particularly if there is a lack of stoichiometry in octahedral sites, (OH + F) ≠ 4 apfu, and the B content is not

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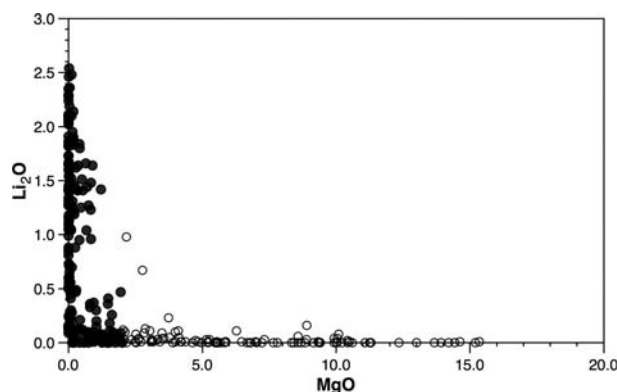


FIG. 1. MgO vs.  $\text{Li}_2\text{O}$  for 294 tourmaline samples using data from the literature. Open circles correspond to those tourmaline samples that have not been considered in this study ( $\text{MgO} > 2$  wt.%).

determined. In this paper, we present a method to estimate Li from microprobe data in tourmaline based on a multiple linear-regression model, which uses statistically significant wt.% oxide data and does not depend on the normalization procedure.

## Procedure and results

In order to estimate Li in tourmaline from microprobe data, 294 analyses have been taken from the literature in which Li is measured directly by other techniques such as SIMS, LA-ICP-MS and others. Data sources for  $\text{Li}_2\text{O}$  analyses of tourmalines derive from Deer *et al.* (1986), Jolliff *et al.* (1986), Dyar *et al.* (1998), Federico *et al.* (1998), Aurisicchio *et al.* (1999a,b), Bloodaxe *et al.* (1999), Dyar *et al.* (1999), Kalt *et al.* (2001), Ertl *et al.* (2003), Pieczka and Kraczka (2004); Bosi *et al.* (2005a, b) Ertl *et al.* (2005, 2006, 2010, 2012), Roda-Robles *et al.* (2012, 2015) and Zagorsky (2015). Overall, the relative reproducibility ( $< 1$  s

where  $s$  = standard deviation of the mean.) and accuracy for Li data from SIMS are estimated to be  $< 5\%$  and  $< 20\%$ , and those from LA-ICP-MS are  $< 3\text{--}7\%$  and  $< 15\%$ , respectively. Tourmalines with  $\text{MgO} > 2.0$  wt.% are presumed to have negligible Li content due to the antipathetic behaviour of Li and Mg (Henry *et al.*, 2002; Tindle *et al.*, 2002). In fact, tourmalines with  $\text{MgO} > 2.0$  wt.% seem not to have more than  $\sim 0.10$  wt.%  $\text{Li}_2\text{O}$  (Fig. 1), which represents  $< 0.07$  apfu Li in the structural formula. Accordingly, they have been discarded from the dataset, and 191 tourmalines are considered for the multiple linear-regression model.

In order to calculate the Li content, a multiple linear-regression model is used taking  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{FeO}_T$ , MnO, MgO, ZnO, CaO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and F as independent variables. First,

TABLE 1. Steps indicating which variable is entered in each step and the value of the adjusted  $R$ -squared.

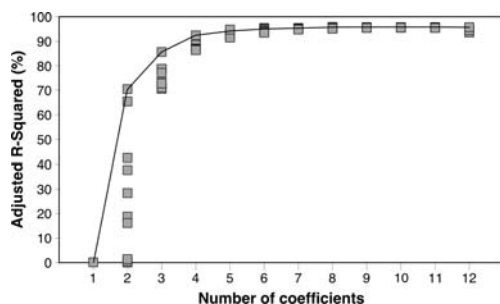


FIG. 2. Adjusted  $R$ -squared coefficient (%) vs. number of variables.

Step	Variable introduced	Variable deleted	Adjusted $R$ -squared
1	$\text{FeO}_{(\text{Total})}$		0.7021
2	$\text{SiO}_2$		0.8609
3	MnO		0.8988
4	$\text{Al}_2\text{O}_3$		0.9449
5	MgO		0.9501
6	ZnO		0.9521
7	$\text{Na}_2\text{O}$		0.9533
8	CaO		0.9552
9		ZnO	0.9546
10	$\text{Cr}_2\text{O}_3$		0.9559

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TABLE 2. Subset of variables with the standard error and limits.

Coefficient	Estimate	Standard error	Lower limit	Upper limit
Intercept	2.356	0.807	0.763	3.950
SiO <sub>2</sub>	0.124	0.013	0.098	0.151
Al <sub>2</sub> O <sub>3</sub>	-0.121	0.009	-0.141	-0.102
FeO <sub>(Total)</sub>	-0.178	0.007	-0.193	-0.163
MnO	-0.162	0.009	-0.181	-0.143

the optimal subset of predictive variables should be obtained. This must be combined with the principle of parsimony which should be considered in any statistical model, that is, to optimize the information with the fewest number of variables. Indeed, analysis of all possible subsets (4096) indicates that over 4 or 5 variables the increase in the adjusted R-squared coefficient is minimal. Supporting evidence for a reduced number of variables is sought on a plot of the R-squared coefficient (in %) vs. the number of variables included in the model (number of variables plus one as it is considered a model with constant term) (Fig. 2). In order to

obtain the optimal subset of predictors we used a stepwise regression procedure. This ensures we have the variables with higher partial correlation with Li after removal of the influence of the other variables. Accordingly, the stepwise method identifies the next subset of regressors: FeO<sub>p</sub>, SiO<sub>2</sub>, MnO, Al<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, CaO, Cr<sub>2</sub>O<sub>3</sub> (Table 1). It is noteworthy that the same result is obtained after using the Akaike information criterion (AIC). The AIC is a measure of the relative quality of statistical models for a given set of data. Given a set of models for the data, the AIC estimates the quality of each model relative to the other models. Hence, the AIC

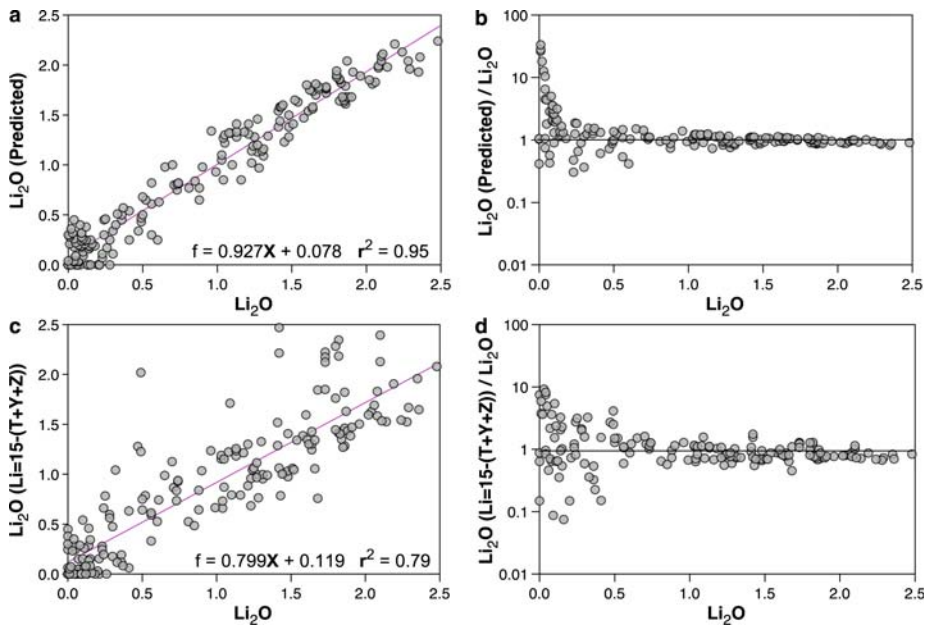


FIG. 3. (a) Observed Li<sub>2</sub>O vs. predicted Li<sub>2</sub>O content using a multiple regression model. (b) Predicted Li<sub>2</sub>O values with a multiple regression model normalized to observed data. (c) Observed Li<sub>2</sub>O vs. predicted Li<sub>2</sub>O content using the equation Li (apfu) = 15 – (T + Y + Z) cations. (d) Observed Li<sub>2</sub>O content vs. predicted Li<sub>2</sub>O values with the equation Li (apfu) = 15 – (T + Y + Z) cations normalized to observed data.

provides a means for model selection and, given a set of candidate models for the data, the preferred model is the one with the minimum AIC value. Accordingly, the AIC rewards goodness of fit (as assessed by the likelihood function), but it also includes a penalty that is an increasing function of the number of estimated parameters. The penalty discourages overfitting (increasing the number of parameters in the model usually improves goodness of fit). In fact, the AIC value for the full model is  $-694.52$ , and after removing sequentially the variable that produces a smaller increase in AIC, we arrive at the previous subset of predictors with  $\text{AIC} = -699.77$ ; no subsequent removal leading to an improved AIC. It should be noted that the last four parameters provide little information on the dependent variable ( $\sim 1.1\%$  of the variability of the dependent variable). For this reason, and taking into account the principle of parsimony, we consider the subset  $\{\text{FeO}_T, \text{SiO}_2, \text{MnO}, \text{Al}_2\text{O}_3\}$ . The results for this choice of predictor variables are reported in Table 2, with the estimated hyperplane

$$\text{Li}_2\text{O} = 2.356 + 0.124\text{SiO}_2 - 0.121\text{Al}_2\text{O}_3 \\ - 0.178\text{FeO}_T - 0.162\text{MnO}$$

which explains the behaviour of Li in a 94.49% (adjusted  $R$ -squared = 0.9449). The plots of observed vs. predicted values (Fig. 3a) and predicted values normalized to observed data vs.  $\text{Li}_2\text{O}$  content (Fig. 3b) reveal that the goodness of fit is reasonably accurate ( $r^2 = 0.95$ ), particularly for  $\text{Li}_2\text{O}$  contents higher than  $\sim 0.3$  wt.% (obviously, the predicted negative values should be considered as zero). The lower and upper limits in Table 2 determine intervals including the true value of the average increase of the Li, where the corresponding variable increases by one unit and the other variables remain constant. By comparison, the estimation of Li from the equation  $\text{Li}(\text{apfu}) = 15 - (\text{T} + \text{Y} + \text{Z})$  cations (Fig. 3c, d), assuming  $(\text{OH} + \text{F}) = 4$ , involves a lower correlation ( $r^2 = 0.79$ ) and variations significantly higher than those resulting from the regression model (Fig. 3a, b). In short, this model provides a method to calculate the Li content in tourmaline from microprobe data with a reasonable accuracy (whole uncertainty of 5%), particularly for low-Mg tourmaline ( $< 2$  wt.% MgO) and  $\text{Li}_2\text{O}$  contents higher than  $\sim 0.3$  wt.% (Fig. 1, 3b). Tourmaline with MgO contents  $> 2$  wt.% can be considered to have a negligible or very low Li content ( $< 0.3$  wt.%  $\text{Li}_2\text{O}$ ).

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